PROCEEDINGS
OF THE
18th ANNUAL MEETING
FERTILIZER INDUSTRY ROUND TABLE
1968

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Held at the
MAYFLOWER HOTEL
Washington, D. C.
November 13, 14, 15, 1968

Editors

Executive Committee

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Fertilizer Industry Round Table

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The 18th Annual Meeting of the Fertilizer Industry Round Table convened at one-thirty-five o'clock p.m. in the Grand Ballroom of the Mayflower Hotel, Washington, D.C., Dr. Vincent Sauchelli, Chairman, presiding.

CHAIRMAN SAUCHELLI: Gentlemen, let's come to order. It is a pleasure to welcome you to the 18th Meeting of the Round Table.

Judging by comments heard and exchanged in the lobby and by the eager look on your faces, I know that you anticipate a meeting worthwhile in all respects. I feel sure that the very large audience is a recognition of the importance of the program and of the eminence of our speakers.

We have a number of guests from foreign countries and from neighboring Canada. We have quite a nice delegation. I recommend that you give them a warm welcome. We want them to feel at home. Just for the heck of it, I'm going to ask the guests, our foreign guests, to stand so that we can see them. Please rise.

We really have a fine delegation from the European countries, from Mexico and, of course, always an excellent delegation from our neighbors North of the Border.

Recent progress in the technology of fertilizer production has inspired a great deal of interest in new processes and products. The technology concerned with the manufacture of acceptable kinds of nitric phosphates seems to dominate this development. This was evident during the year in the programs of various technical organizations devoted to chemical processing and engineering:

The American Institute of Chemical Engineers in July, the American Chemical Society in September, the TVA Seventh Demonstration at Muscle Shoals last month.

We have recognized this trend in our previous two Annual Meetings and in the current program. The economic status of sulfur spurs the growing interest in the use of nitric acid for making phosphate fertilizers.

Our program is designed to satisfy the diverse interests of our membership while concentrating on those closely related to the operating personnel of the industry. Let me reiterate that this Round Table has been and remains primarily the forum to provide the operation men a place where their problems receive priority status.

As I said, our program offers a variety of items. Technology and economics of nitrophosphates, a special panel on materials of construction for fertilizer plants, sulfuric acid from gypsum, elemental phosphorus as a raw material for fertilizer, bulk blend fertilizers, bulk blend mixers, bags and bagging systems, trace elements, fluid fertilizers, polyphosphates, ammonium phosphates and prevention of accidents in the plant.

There we have a great variety of items, all of particular interest to this group. So much for the introductory. Let me now get to the program speakers.

The Keynote Speaker is Dr. Raymond Ewell, Vice President of Research at the State University of New York at Buffalo. He is an amazing person, versatile, internationally known and recognized as a buff on the statistics, economics and technology of fertilizers from the world viewpoint.

He is an authority on foods and on wines. You will agree that the Round Table is very fortunate to be able to have Dr. Ewell on our Program. He has selected as his subject Appraisal of Nitrophosphates and Comparative Processes for Making NP and NPK Fertilizers. Ray.

DR. RAYMOND EWELL: Thank you, Vince. It's a real honor for me to appear before this highly professional body.

I have been reading the proceedings of the Fertilizer Round Table for several years now. This is the first opportunity I have had really to participate in your deliberations.

I want to tell two very short stories that have certain relationship to nitrophosphates. The first one is about the gentleman in a bar who, after several drinks, says to his companion, That bartender is getting pretty drunk; I can't see him clearly anymore. The second story concerns a lady who divorced her husband because none of their children looked like him.

These are both examples of *non sequiturs* and in the study of this nitrophosphate business you find lots of *non sequiturs.* Actually, since I had given Vince this title, I've got another slightly fancier title which I am going to use.

Economics of Nitrophosphate Fertilizers

Raymond Ewell*

Nitrophosphate fertilizer is a very complex subject—one surrounded by much mystery and many prejudices and mental fixations. I have studied this subject diligently for the past year, and what I have to say today is com-

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* Vice President for Research and Professor of Chemical Engineering, State University of New York at Buffalo, N.Y.

pletely objective and unbiased. I have no axes to grind, no positions to maintain, no products to sell.

First, as to nomenclature I have used the term "nitrophosphate" rather than "nitric phosphate." Both these terms are shorthand terms since there are no chemical compounds in the products which could be called nitrophosphate or nitric phosphate. The principal chemical compounds in the products are ammonium phosphates and ammonium nitrate. I have preferred the term "nitrophosphate" simply because it is one word instead of two words.

Nitrophosphate processes have been known and used since the 1920's. There are many nitrophosphate plants in Europe, five or six in the United States, and perhaps a few in other regions of the world. Most of the European plants are of the Odda type producing N-P fertilizers with water-solubility of phosphate (WSP) less than 50%, frequently around 30%. Other plants in Europe and all the plants in the U. S. use the sulfonitric or phosphonitric processes which use sulfuric acid or phosphoric acid as a supplement to nitric acid. These latter two processes therefore are still partially dependent on the use of sulfur.

New Nitrophosphate Processes

I will limit this paper to processes capable of producing N-P fertilizers with WSP greater than 75% and using nitric acid as the only acidulant. This leaves the sulfonitric and phosphonitric processes out of consideration. It also leaves out all nitrophosphate processes used prior to 1967 since all of them give products with WSP less than 75% (usually less than 50%) or they use sulfuric acid or phosphoric acid as a supplementary acidulant besides nitric acid.

The two types of processes which I will discuss are:

1. Calcium Nitrate Crystallization Process (CN Xlzn)
2. Ammonium Sulfate Recycle Process (AS Recycle)

There are many variations of each of these basic processes. I will not attempt to discuss all the variations since some of them will be discussed in later papers at this meeting and also since some of them are still in a development stage.

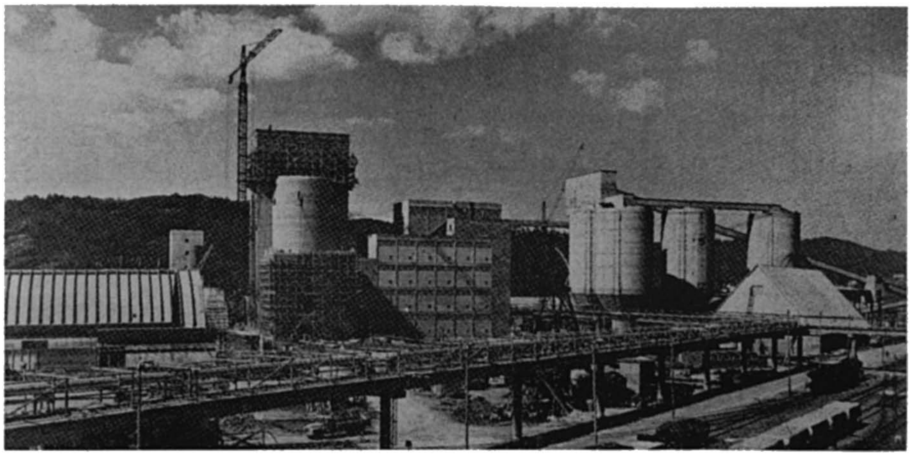


Figure 1

Norsk Hydro NPK plant at Eidanger, Norway (still under construction in summer 1967)

Only the CN Xlzn process has been put into actual practice. Two plants are now operating and one is under construction using the CN Xlzn process:

1. Norsk Hydro plant at Eidanger (Heroya), Norway which started operation in the fall of 1967 (Figure 1).
2. Severoceske Chemicke Zavody plant in Lovosice, Czechoslovakia which started operation in the spring of 1968 (Figure 2).
3. Farmers Chemical plant at Tunis, North Carolina which started construction in 1968.

The AS Recycle process, in several variants, is being offered by several engineering contractors, but so far no plant has been built.

Water Solubility of Phosphate

Next I want to comment on the WSP question. The new nitrophosphate processes, which have been discussed for the past five years and put into practice in 1967, can and do produce WSP greater than 75% using nitric acid as the only acidulant. These processes can in fact produce WSP up to 90% or more if that is desirable, although at somewhat higher cost. Moreover, agronomic tests on several crops have shown that there is no significant increase in fertilizer efficiency for WSP higher than 75%. This has been documented in several publications of the past few years, including papers given

Figure 2

Severoceske Chemicke Zavody NPK plant at Lovisice, Czechoslovakia

at previous meetings of the Fertilizer Industry Round Table. Therefore I believe that WSP should no longer be an issue. WSP as an anti-nitrophosphate argument is, in my opinion, a dead horse—or perhaps we should call it a dead red herring.

All NP's Contain Nitrates

A highly important fact concerning nitrophosphate fertilizers is that they all contain a lot of nitrate nitrogen—usually 40% to 45% of the nitrogen is in the nitrate form and 55% to 60% in the ammonium form. This is inescapable. When nitric acid is the sole or principal acidulant a lot of nitrate is inevitable. This is no handicap in most countries since nitrates are widely used fertilizers, but there is some evidence—not fully convincing—that nitrate nitrogen has a significantly lower fertilizer efficiency on paddy rice than ammonium forms of nitrogen, such as urea, ammonium sulfate, ammonium chloride or ammonium phosphate. This loss of efficiency is believed to be due to loss of nitrogen resulting from bacterial decomposition of nitrate ions in the anaerobic conditions existing in underwater culture as in paddy rice. This would tend to indicate against the use of nitrophosphate fertilizers in areas where rice is a major crop. However, it may be pointed out that two of the largest fertilizer plants in India—Nangal and Rourkela—produce only ammonium nitrate and that in the United Arab Republic calcium nitrate and ammonium nitrate are the only nitrogen fertilizers produced. It may also be pointed out that paddy rice is only one of many crops even in Southeast Asia. Nitrate fertilizers are quite suitable for wheat, corn, cotton, sugarcane, peanuts, beans, jute, tea, coffee, cocoa, rubber, tobacco, coconuts, potatoes, bananas and many other crops of the tropical zone.

However, the usefulness of a nitrate fertilizer even in a rice-growing area is purely a matter of economics. If a nitrate fertilizer is enough cheaper than a non-nitrate fertilizer, then it is economical to use it. For example, if a nitrophosphate fertilizer should have 90% of the fertilizer efficiency of an equivalent non-nitrate fertilizer, such as urea-DAP, and the nitrophosphate was priced at 90% of the price of the non-nitrate fertilizer, they would be then economically equivalent.

Effect of Phosphate Rock Composition

The product from a nitrophosphate process depends very heavily on the composition of the phosphate rock used—much more so than in the production of wet phosphoric acid and DAP. In particular, the nitrophosphate product depends on the P_2O_5 content and on the CaO/P_2O_5 ratio of the phosphate rock. Table I shows the wide range of CaO/P_2O_5 ratios and BPL values in 14 commercial phosphate rocks. Generally speaking, a high BPL and a low CaO/P_2O_5 ratio are desirable for making nitrophosphate fertilizers.

Table II shows the extreme ranges in the chemical analyses of the 14 commercial phosphate rocks listed in Table I. Table II also gives a "standard" phosphate rock analysis which I have selected for use in the calculations in this paper. This "standard" phosphate rock has a BPL of 75, a CaO/P_2O_5 ratio of 1.5, and it is generally similar to phosphate rocks from Morocco, Jordan, Togo, Tunisia and North Carolina, but rather unlike Florida rocks (see Table I).

The last column of Table II shows the CaO equivalences of MgO, Al_2O_3, Fe_2O_3, and Na_2O in the "standard" phosphate rock. It is important to consider these equivalences since these metal oxides all react with nitric acid and ultimately give rise to equivalent amounts of ammonium nitrate in the final product, in the same way that CaO does.

Elements of Nitrophosphate Processes

Figure 3 shows simplified flow sheets of the Calcium Nitrate Crystallization and Ammonium Sulfate Recycle Processes, and also

Table I

CaO/P_2O_5 Ratios and BPL Values of Phosphate Rocks
(listed in orderof CaO/P_2O_5 ratio)

	CaO/P_2O_5 wt. ratio	CaO/P_2O_5 mole ratio	% CaO	% P_2O_5	B.P.L.
Curacao	1.30	3.30	50.0	38.6	84
USSR - Kola	1.34	3.40	52.1	38.9	85
Senegal - Taiba	1.37	3.48	52.6	38.4	84
Makatea	1.38	3.50	52.9	38.4	84
South Africa - Phalaborwa	1.40	3.56	53.3	38.1	83
Togo	1.41	3.58	52.0	36.9	80
Florida (70 BPL)	1.44	3.66	46.1	32.1	70
Morocco - Khouribga	1.45	3.68	53.5	36.9	80
Peru - Sechura	1.49	3.78	46.3	31.0	68
Jordan - Ruseifa	1.53	3.88	51.0	33.4	73
Morocco - Safi	1.54	3.91	49.9	32.4	71
North Carolina	1.61	4.09	49.4	30.7	67
Tunisia - Gafsa	1.63	4.14	48.8	30.0	66
Israel	1.76	4.47	50.2	28.6	62
For comparison:					
$3\ CaO \cdot P_2O_5$	1.18	3.00	54.2	45.8	100
$4\ CaO \cdot P_2O_5$	1.58	4.00	61.2	38.8	85
$5\ CaO \cdot P_2O_5$	1.97	5.00	66.3	33.7	74

Table II

Definition of "Standard" Phosphate Rock

	Extreme range of 14 phosphate rocks	"Standard" phos. rock	Relative moles P_2O_5 = 1	CaO equivalent of metal oxides
CaO	46.1-53.5	51.6	3.81	3.81
P_2O_5	28.6-38.9	34.4	1.00	----
F	2.0- 4.3	4.0	0.87	----
MgO	0.3- 0.9	0.4	0.04	0.05
Al_2O_3	0.3- 1.4	0.8	0.03	0.05
Fe_2O_3	0.2- 1.4	0.8	0.02	0.02
Na_2O	0.1- 1.3	0.5	0.03	0.03
CO_2	0.2- 5.6	4.0	0.38	----
SO_3	0.1- 2.7	1.0	0.05	----
SiO_2	0.8- 8.7	2.5	0.17	----
		100.0		3.96

Note: This analysis neglects MnO, Cr_2O_3, UO_3, rare earth oxides, etc. which sometimes occur in phosphate rocks. K_2O is included with Na_2O.

for comparison the conventional Sulfur-Sulfuric Acid-Phosphoric Acid Process. The product chosen for comparing these processes is 28-14-0. Potash is omitted from the analysis since it would only make the comparison more complicated and since potash can be added at the last stage of any compound fertilizer process.

28-14-0 was selected as the product for comparison of these processes since this is approximately the product obtained by either the CN Xlzn process or the AS Recycle process (straight through version) using a phosphate rock of 75 BPL and CaO/P_2O_5 ratio of 1.5. 28-14-0 is also the approximate product which would be obtained from wet-process phosphoric acid produced from phosphate rock of this description with enough nitric acid added to give a N/P_2O_5 ratio of 2:1 and neutralized with ammonia. However, products with N/P_2O_5 ratios from 1.5 to 2.5 can be made using the processes as shown in the flow sheets, depending on analysis of the phosphate rock and on the degree of neutralization of the phosphoric acid. Table III shows the minimum N/P_2O_5 ratios obtainable from the two nitrophosphate processes using phosphate rocks with various CaO/P_2O_5 ratios and depending on whether neutralization is stopped at the MAP stage or carried on through to DAP. The figures in Table III are minimum N/P_2O_5 ratios since obviously the ratios could be made higher in all cases simply by adding more nitric acid and ammonia.

CN Xlzn Process

In the CN Xlzn Process, a coolant in the temperature range of 20°C down to as low as −15°C is used to crystallize out most of the CN in the digestion liquor and the CN is separated in a filter or centrifuge. The removed CN is then ammoniocarbonated to AN, which may be re-injected into the process stream or it may be concentrated and prilled as a co-product. The portion of CN not removed by the low-temperature crystallization is converted to dicalcium phosphate in the neutralizer. This portion of the P_2O_5 in the product is not water-soluble. Therefore the CN crystallization step must be carried out at a low enough temperature that at least 75% of the P_2O_5 in the final product will be in the form of ammonium phosphates. The following data indicate the temperatures required to do this:

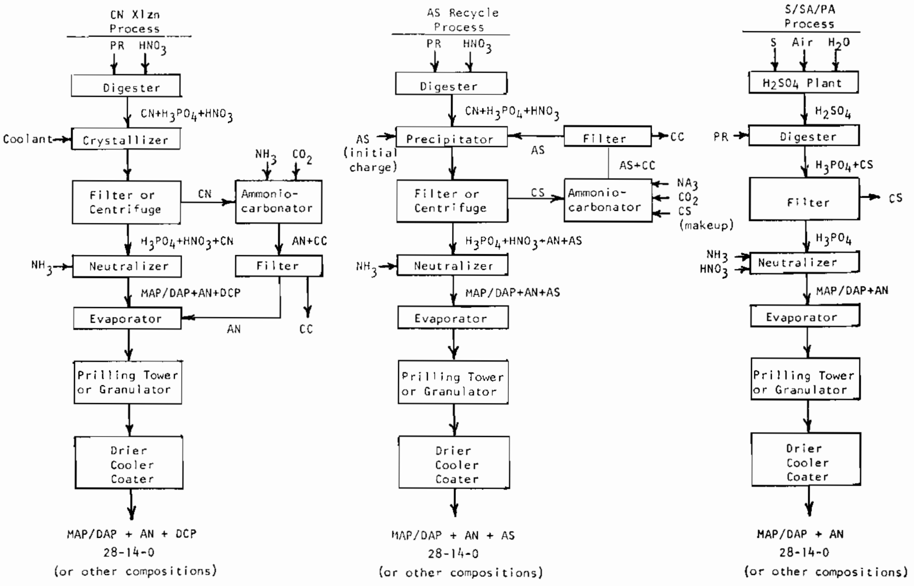
Crystallization temperature	WSP in final product
16°C	30%
13°C	40%
10°C	50%
6°C	60%
0°C	70%
−4°C	75%
−8°C	80%

The WSP for a given crystallization temperature depends to a considerable extent on the quantity of excess nitric acid, but unfortunately the reference from which these data came did not give the nitric acid concentration.

In the Norsk Hydro variant of this process, the CN crystallization

Figure 3

Flow Sheets of Three Processes for Making 28-14-0



is carried out in a conventional crystallization tank with cooling coils chilled with ammonia. A unique design of rotating drum filter is used to separate the CN crystals. The rest of the plant is of conventional design. The plant at Eidanger, Norway has a capacity of 1500 metric tons of product per day containing 400 MTN/D and 200 MTP_2O_5/D in a variety of NP and NPK products. This plant was engineered and built by Norsk Hydro, but the process is now being offered world-wide by Humphreys & Glasgow and by Wellman-Lord.

In the Czech/Kaltenbach variant of this process, the CN crystallization is carried out by using chilled naphtha in intimate two-phase contact with the digestion liquor. The crystallization is carried out in a uniquely designed crystallizer in which the chilled naphtha is introduced into the middle of the tank and rises to the top of the tank counter-current to the digestion liquor. The CN crystals are kept in suspension by a slowly turning agitator at the bottom of the tank until the crystals are large enough to fall through the gentle turbulence. The CN crystals are separated in a continuous centrifuge. The Czech plant at Lovosice, Czechoslovakia has a capacity of 700 metric tons per day containing 200 MTN/D and 100 MTP_2O_5/D in a variety of NP and NPK products. This process was developed by the Chemoprojekt organization in Prague and the plant was built by Czechoslovak government construction agencies. This process, with some improvements over the Lovosice plant, is now being offered world-wide by Kaltenbach et Cie., Paris, France.

AS Recycle Process

In the AS Recycle Process, ammonium sulfate is added to precipitate CN as CS, which is separated in a filter or centrifuge. The removed CS is then ammoniocarbonated to AS, which is re-cycled to the precipitator. Makeup CS is added to the ammonio-carbonator to make up for losses of AS in the product and in the CC filter cake. Since virtually all the CN is removed in this process the WSP of the product may be 90% or higher.

The version of the AS Recycle Process described above is the "straight through" version. No plant of this type has been built although the Dutch State Mines operates a plant using ammonium sulfate from a caprolactam plant but without converting the CS to AS and recycling the AS. Also, OSAG in Austria and FACT in India operate plants to convert CS into AS (Merseberg process). Therefore both sections of the process shown in the flow sheet are in operation somewhere in the world, but not in a complete integrated plant.

The straight through version of the AS Recycle Process and several process variants are offered by Chemico, Foster-Wheeler, Dorr-Oliver, Power Gas, Dutch State Mines and other engineering contractors.

Chemistry of Nitrophosphate Processes

Because the "standard" posphate rock selected for this paper has a CaO/P_2O_5 molar ratio of 3.96 (including CaO equivalent of MgO, Al_2O_3, Fe_2O_3 and Na_2O), the following chemistry is based on $4CaO{\cdot}P_2O_5$ instead of the conventional $3CaO{\cdot}P_2O_5$.

CN Xlzn Process

Primary chemical reactions:

$$4CaO{\cdot}P_2O_5 + 8HNO_3 \rightarrow 4Ca(NO_3)_2 + 2H_3PO_4 + H_2O$$

$$\times 2 \quad H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$$

$$\times 4 \quad Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O \rightarrow 2NH_4NO_3 + \mathit{CaCO_3}$$

$$4CaO{\cdot}P_2O_5 + 8HNO_3 + 10NH_3 + 4CO_2 + 3H_2O \rightarrow 2NH_4H_2PO_4 + 8NH_4NO_3 + 4\mathit{CaCO_3}$$

Secondary reactions in neutralizer:

$$Ca(NO_3)_2 + H_3PO_4 + 2NH_3 \rightarrow \mathit{CaHPO_4} + 2NH_4NO_3$$

$$Mg(NO_3)_2 + H_3PO_4 + 2NH_3 \rightarrow \mathit{MgHPO_4} + 2NH_4NO_3$$

$$Al(NO_3)_3 + H_3PO_4 + 3NH_3 \rightarrow \mathit{AlPO_4} + 3NH_4NO_3$$

$$Fe(NO_3)_3 + H_3PO_4 + 3NH_3 \rightarrow \mathit{FePO_4} + 3NH_4NO_3$$

$$Ca(NO_3)_2 + 2HF + 2NH_3 \rightarrow \mathit{CaF_2} + 2NH_4NO_3$$

AS Recycle Process

Primary chemical reactions:

$$4CaO{\cdot}P_2O_5 + 8HNO_3 \rightarrow 4Ca(NO_3)_2 + 2H_3PO_4 + H_2O$$

$$\times 4 \quad Ca(NO_3)_2 + (NH_4)_2SO_4 \rightarrow 2NH_4NO_3 + \mathit{CaSO_4}$$

$$\times 2 \quad H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$$

$$\times 4 \quad \mathit{CaSO_4} + 2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2SO_4 + \mathit{CaCO_3}$$

$$4CaO{\cdot}P_2O_5 + 8HNO_3 + 10NH_3 + 4CO_2 + 3H_2O \rightarrow 2NH_4H_2PO_4 + 8NH_4NO_3 + \mathit{4CaCO_3}$$

Secondary reactions in neutralizer:

$$Mg(NO_3)_2 + H_3PO_4 + 2NH_3 \rightarrow \mathit{MgHPO_4} + 2NH_4NO_3$$

$$Al(NO_3)_3 + H_3PO_4 + 3NH_3 \rightarrow \mathit{AlPO_4} + 3NH_4NO_3$$

$$Fe(NO_3)_3 + H_3PO_4 + 3NH_3 \rightarrow \mathit{FePO_4} + 3NH_4NO_3$$

$$HF + NH_3 \rightarrow NH_4F$$

Conventional S/SA/PA Process

Primary chemical reactions:

$$4CaO{\cdot}P_2O_5 + 4H_2SO_4 \rightarrow 2H_3PO_4 + \mathit{4CaSO_4} + H_2O$$

$$\times 2 \quad H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$$

$$\times 8 \quad HNO_3 + NH_3 \rightarrow NH_4NO_3$$

$$4CaO{\cdot}P_2O_5 + 4H_2SO_4 + 8HNO_3 + 10NH_3 \rightarrow 2NH_4H_2PO_4 + 8NH_4NO_3 + \mathit{4CaSO_4} + H_2O$$

Secondary reactions in neutralizer:

$$MgSO_4 + H_3PO_4 + 2NH_3 \rightarrow \mathit{MgHPO_4} + (NH_4)_2SO_4$$

$$Al_2(SO_4)_3 + 2H_3PO_4 + 6NH_3 \rightarrow \mathit{AlPO_4} + 3NH_4NO_2$$

$$Fe_2(SO_4)_3 + 2H_3PO_4 + 6NH_3 \rightarrow \mathit{FePO_4} + 3(NH_4)_2SO_4$$

$$HF + NH_3 \rightarrow NH_4F$$

Table III

Minimum N/P_2O_5 Ratios as Function of CaO/P_2O_5 Ratios in Phosphate Rocks

CaO^*/P_2O_5 weight ratio in phosphate rock	Calcium nitrate crystallization process neutralization of H_3PO_4		Ammonium sulfate recycle process neutralization of H_3PO_4	
	To MAP	To DAP	To MAP	To DAP
1.30	1.57	1.73	1.69	1.89
1.40	1.69	1.84	1.80	2.01
1.50	1.80	1.95	1.92	2.12
1.60	1.91	2.07	2.04	2.24
1.70	2.03	2.18	2.15	2.35
1.80	2.14	2.29	2.27	2.47

Notes:

1. CaO^*/P_2O_5 ratios include CaO equivalent of MgO, Al_2O_3, Fe_2O_3, Na_2O and other metal oxides present in phosphate rock.
2. In CN Xlzn Process, assumptions include 10% excess HNO_3, 75% of P_2O_5 in final product as MAP or DAP, 100% of AN re-injected into process stream.
3. In AS Recycle Process, assumptions include 10% excess HNO_3, 5% excess AS, 100% of P_2O_5 in final product nominally as MAP or DAP (but in actual practice some will be in Mg HPO_4, $AlPO_4$, $FePO_4$).

Two important facts to be noted is that all these processes (1) consume the same quantities of phosphate rock, nitric acid and ammonia, and (2) result in the same quantities of MAP and AN.

All of the above primary chemical reactions are based on neutralization of phosphoric acid to MAP. They could equally well have been written in terms of neutralization to DAP. In actual practice the ammonium phosphate product will usually be some mixture of MAP and DAP.

The quantities of MAP and AN indicated in the primary reactions, namely $NH_4H_2PO_4{:}4NH_4NO_3$, correspond to a composition 29-16-0. In actual practice 10% excess of nitric acid is used in the acidulation which would result in a 32-16-0 theoretical product, but the various impurities in the phosphate rock cut this down to a 28-14-0 product. This is the result when the phosphate rock has a CaO/P_2O_5 molar ratio of 4 or a weight ratio of 1.58 (including the CaO equivalents of MgO, Al_2O_3, Fe_2O_3, Na_2O). With other phosphate rocks a different product would result (see Table III).

The chemistry of nitrophosphate processes is so complex that it is impossible to predict the precise product composition on the basis of the phosphate rock analysis alone. It is necessary to conduct pilot experiments to determine what the product will be in actual practice from a particular phosphate rock under actual operating conditions.

Economic Comparison of Processes

The only unequivocal way to make an economic comparison of two or more processes is to compare their costs on the basis of identical or virtually identical products. If the product mixes are different then there is the sticky problem of byproduct or co-product credits. Therefore for a first comparison I will use the 28-14-0 product for all processes.

Plants for each of the three processes are assumed to be located adjacent to ammonia-nitric acid plants from which they would draw ammonia, nitric acid and carbon dioxide.

Table IV shows the material and energy inputs for the three processes concerned. Since the nitrophosphate plant is adjacent to an ammonia-nitric acid plant, no charge is shown for carbon dioxide. Also, no charges are shown for minor costs such as anti-foaming agents, coating materials, fillers, lubricants, miscellaneous chemicals, etc. These items might be a few cents per ton of product.

It should be noted that each

Table IV

Material and Energy Inputs per Metric Ton of 28-14-0

	CN Xlzn Process*	AS Recycle Process **	S/SA/PA Process	Prices of Inputs
Phosphate rock, tons ***	.427	.427	.427	\$10/MT
Nitric acid 100%, tons	.580	.580	.595	\$14/MT@
Ammonia, tons	.200	.200	.195	\$30/MT
Sulfur, tons	----	----	.135	\$30/MT
Gypsum, tons	----	.120	----	\$ 5/MT
Steam, tons	0.75	1.20	0	50¢/MT
Electric power, kwh.	80	70	60	1¢/kwh.
Fresh water, U.S. gallons	1,000	1,000	1,000	20¢/M gal.
Cooling water, U.S. gallons	8,000	8,000	8,000	5¢/M gal.

*CN Xlzn process operated with re-injection of all AN into process stream.

**Straight through versionof AS Recycle process with no offtake of AN or MAP.

***"Standard" phosphate rock as defined in Table II.

@Nitric acid produced in 800 MT/D plant with ammonia costed at \$30/MT.

Table V

Production Costs Based on Capital Investment

Operating labor + plant supervision	2% of investment per year
Maintenance labor + materials	5% " " " "
Plant overhead	2% " " " "
Taxes and insurance	3% " " " "
Interest on investment	8% " " " "
Depreciation	10% " " " "
Total	30%

of the three processes requires the same quantity of phosphate rock and virtually the same quantity of ammonia and nitric acid. Steam, electricity and water vary slightly but they are small cost items anyway.

In estimating the requirements of material inputs in Table IV it was assumed that there would be a 10% excess of HNO_3 above the stoichiometric quantity needed to combine with all the CaO, MgO, Al_2O_3, Fe_2O_3 and Na_2O. In the AS Recycle process it was assumed that there would be a 5% excess of AS above the stoichiometric amount needed to combine with all the CN in the precipitation step.

Also, in estimating the requirements of phosphate rock, nitric acid and ammonia in Table IV, it was assumed that there would be a 5% loss of N and a 5% loss of P_2O_5 in all processes. Therefore the inputs shown correspond to 0.294 MTN and 0.147 MTP_2O_5 per ton of 28-14-0 product.

Besides the material and energy inputs, labor, supervision, overhead, maintenance materials, taxes, insurance, interest and depreciation must be added to the cost picture. I have elected to put all these costs on a percent of investment basis, as shown in Table V. The figures in Table V are only examples. The reader may want to re-calculate these costs using other percentages of investment. The figures in Table V do not include any "return on investment" other than 8% interest on total invested capital. The reader may wish to add a further factor for "return on investment."

Table VI shows (1) capital costs for the plants for the three processes all at the same size—1430 MT/D of 28-14-0 containing 400 MTN/D and 200 MTP_2O_5/D, and (2) operating costs based on Tables IV and V. It should be emphasized again that these are the bare capital and operating costs for an N-P plant located adjacent to an ammonia-nitric acid plant. Also, these figures do not include either capital or operating costs for offsites, storage, bagging, shipping, research, sales and distribution. These costs will be about the same for all three processes so they would not affect the relative economics.

The capital investments for these plants were very difficult to arrive at and the figures given in Table VI must be regarded as very rough estimates. Here are some capital cost figures I received from some engineering contractor firms:

CN Xlzn Process (with total re-injection of AN)

Contractor A	$ 6.9 million
Contractor B	10.0 "
Contractor C	11.0 "

AS Recycle Process (straight through)

Contractor A	$ 5.7 million
Contractor B	7.0 "
Contractor C	7.8 "
Contractor D	8.0 "

Since I had no firm basis for any significant differential between the capital costs for these two processes, I selected $8 million for each of them.

For the S/SA/PA Process I selected a figure of $7.5 million, on the basis of limited data from contractors. This figure is intended to include the sulfuric acid plant, the phosphoric acid plant and the N-P plant.

The data in Table VI indicate a significantly lower production cost by either of the nitrophosphate processes as compared with

Table VI

Production Costs per Metric Ton of 28-14-0

	CN Xlzn Process	AS Recycle Process	S/SA/PA Process	Prices of Inputs
Capital investment*	$8,000,000	$8,000,000	$7,500,000	
Inputs:				
Phosphate rock	$4.27	$4.27	$4.27	$10/MT
Nitric acid	8.12	8.12	8.33	$14/MT
Ammonia	6.00	6.00	5.85	$30/MT
Sulfur	----	----	4.05	$30/MT
Gypsum	----	.60	----	$ 5/MT
Steam	.40	.60	----	50¢/MT
Electric power	.80	.70	.60	1¢/kwh.
Fresh water	.20	.20	.20	20¢/M gal.
Cooling water	.40	.40	.40	5¢/M gal.
Costs based on investment 30% of investment per year	5.10	5.10	4.80	
	$25.29	$25.99	$28.50	

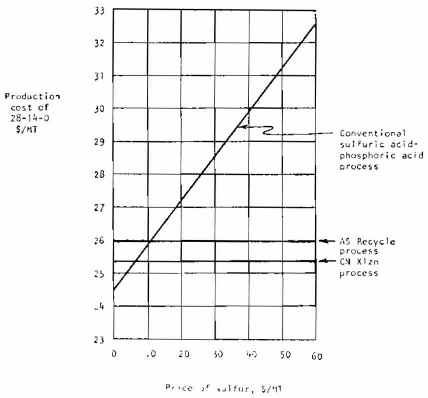
*Plant size is 1430 MT/D or 472,000 MT/Y of 28-14-0.

Capital investment for turnkey battery limits plant, not including land, raw material storage, product storage, bagging, shipping, offsites, or working capital.

Each $1 million in capital investment changes production costs per ton of 28-14-0 by $0.635 on basis of 30% of investment per year.

Figure 4

Cost of Production of 28-14-0
(as calculated in Table VI)



the S/SA/PA process. The difference is, of course, entirely accounted for by the cost of sulfur, reduced to some extent by lower steam cost and lower capital charges.

The costs of phosphate rock, nitric acid and ammonia are substantially the same for all three processes. *This leads to the important conclusion that the relative economics of these processes are independent of the prices of phosphate rock, nitric acid and ammonia.* This conclusion is especially significant for the developing countries. The principal factors determining the relative economics of these processes are, therefore, (1) the relative capital investment costs, (2) the way in which capital charges are calculated, and (3) the price of sulfur.

Figure 4 shows these production cost data plotted as a function of the price of sulfur. Figure 4 shows that the CN Xlzn Process is equivalent in cost to the S/SA/PA Process if sulfur is $6.00/MT, and that the AS Recycle Process is equivalent in cost to the S/SA/PA Process if sulfur is $11.00/MT. It must be emphasized again that these figures relate only to this particular product, namely, 28-14-0 comprised largely of MAP/DAP and AN plus lesser amounts of DCP in the CN Xlzn Process and AN in the AS Recycle Process.

Other Products Besides 28-14-0

There are variants of both the CN Xlzn Process and the AS Recycle Process which can be used to produce N-P products with N/P_2O_5 ratios of 1:1, 1:1.5 or 1:2. But in these cases there is a large co-product of AN (34-0-0) which would have to be disposed of. Also, the capital investment costs will be higher than the simple versions of these processes shown in Figure 3. In any event, the overall ratio of N/P_2O_5 in the two products produced will still be 2:1 in the case of our "standard" phosphate rock or in the range of 1.5 to 2.5 for other phosphate rocks.

In the CN Xlzn Process the AN produced in the ammonio-carbonation step can obviously be processed separately to pure AN and the remainder processed to products such as 24-24-0, 20-30-0 or 17-34-0, depending on the amount of CN removed in the crystallization step. For example, the process could be operated to produce:

840 MT/D of 24-24-0
590 MT/D of 34-0-0

For continuous operation this would require a second evaporation, prilling, drying, cooling, coating setup which might add $500,000 to the capital cost.

In the AS Recycle Process there are two principal variants available. Chemico offers a process in which MAP (+ some AN) is separated by cooling and crystallization immediately following the neutralization step. This variant might produce a product mix like:

480 MT/D of 14-42-0
950 MT/D of 34-0-0

Since this requires an additional crystallizer and filter plus another granulator-drier-cooler-coater setup, this might add $1.5 million to the capital cost.

Foster-Wheeler is offering the USS Agri-Chemicals process in which AN is separated by cooling and crystallization immediately after the CS filtration step, i.e. before neutralization. This variant of the AN Recycle process could give a product mix like:

840 MT/D of 24-24-0
590 MT/D of 34-0-0

This variant also requires an additional crystallizer and filter and might add $1.5 million to the capital cost.

Still another variant is the TAP Crystallization process being developed by TVA. In this process the ammonia neutralization is carried through to triammonium phosphate (TAP) under pressure, the TAP is separated, and one ammonia molecule removed and recycled, leaving DAP. It may be possible to get a fairly clean separation into DAP and AN by this process, but it is still in development.

Space precludes a more detailed discussion of these variants, but it may be noted that each $1 million of additional capital cost will add something like $0.635 per ton of product for capital charges at 30% per year.

However, it is clear that the production costs of products of the 1-1-0, 1-1.5-0 and 1-2-0 types, as well as the 2-1-0 type, made by nitrophosphate processes are significantly lower than for comparable products made by conventional processes using phosphoric acid.

The main problem in making a decision on a nitrophosphate project is whether there is a good market for the products that can be made, including a market for the rather large amount of co-product AN.

Nossen Nitric Acid Regeneration Process

An interesting variant of the CN Xlzn Process is the Nossen nitric acid regeneration process which is being offered by Power Gas Corporation. In this process the CN separated in the primary crystallizer is thermally cracked to nitrogen oxides which are re-oxidized to nitric acid which is then fed back to the initial digestion stage. By this process it is possible to produce a single product comprised of MAP/DAP + DCP which could have compositions in the range of 15-45-0 to 20-40-0 depending on the amount of CN removed in the primary crystallization and on the degree of neutralization of phosphoric acid in the neutralizer. This is a very attractive process, but it is still in a development stage and the capital costs are not yet well defined.

Comparison with Urea-DAP

One of the most popular and fastest-growing compound fertilizers in the world today is urea-DAP which can be formulated in a number of grades such as 34-17-0, 28-28-0 and 20-40-0. It is beyond the scope of this paper to make a detailed cost comparison between urea-DAP and nitrophosphates, but it seems certain that nitrophosphates will be much lower cost per unit of plant nutrient than urea-DAP, for the particular products which it is possible to make by nitrophosphate processes. The urea-DAP approach is, of course, much more flexible and it has the advantage in rice-growing areas of having entirely ammonium-type nitrogen.

Is There a Market for Nitrophosphate Fertilizers?

The foregoing analysis has indicated strongly — although possibly not yet conclusively — that nitrophosphate processes can make compound fertilizers of the 2-1-0 type cheaper than by any other method. These processes can also make fertilizers of the 1-1-0, 1-1.5-0 and 1-2-0 types (with large coproducts of ammonium nitrate) cheaper than by any other method. And these fertilizers can be made with WSP of 75% or even higher. But these fertilizers have 40-45% of the nitrogen in the nitrate form.

Now the question arises—Is there a market for these types of fertilizers? Let's look at the 2-1-0 type first since this is the cheapest one to make. This type of fertilizer could, of course, be modified by the addition of potash to give 2-1-1, 2-1-2, etc. types, but let's focus attention on the 2-1-0 type for simplicity.

There is not much market for 2-1-0 type fertilizers in the United States since so much nitrogen is applied in the form of anhydrous ammonia and nitrogen solutions. The biggest compound fertilizers used in the United States are the 1-1-1, 1-2-2, 1-3-3 and 1-4-4 types. Also, a good deal of nitrogen fertilizer is applied in the form of straight solid nitrogen materials, such as urea, ammonium sulfate and ammonium nitrate. Moreover, the overall consumption ratio of $N:P_2O_5$ is only 1.4.

The situation is somewhat different in Europe, Japan and the Soviet Union since these areas use very little anhydrous ammonia or nitrogen solutions, but they do use a good deal of nitrogen as straight solid materials. The overall consumption ratios of $N:P_2O_5$ are about 1.2 in Europe, 1.4 in Japan and 1.6 in the Soviet Union. Therefore there could be a fairly good market for nitrophosphate fertilizers in these areas unless the use of liquid forms of nitrogen develops further.

However, in the developing countries the situation is still more favorable for nitrophosphate fertilizers. The overall consumption ratios for $N:P_2O_5$ in the developing areas are:

Asia (except Japan)	3.6
Africa	1.4
Latin America	1.8

There is virtually no use of anhydrous ammonia or nitrogen solutions in these areas, but on the other hand they are accustomed to using largely straight materials—both nitrogen and phosphate—in many of the developing countries. Therefore even though the basic factors are favorable for a good market for nitrophosphate fertilizers, it may be necessary to develop the market.

Some countries (or areas) in which rice is not the major crop which should be good markets for nitrophosphate fertilizers include:

Northern India
West Pakistan
Northern China
Iran
Turkey
U.A.R. (Egypt)
South Africa
Brazil
Argentina
Peru
Mexico
Cuba

Some other countries (or areas) in which rice is the major crop, but which might be good markets for nitrophosphates anyway, if the price was low enough, include:

Southern India
East Pakistan
Southern China
Indonesia
North and South Korea
North and South Vietnam
Philippines
Taiwan

Making a Decision on a Nitrophosphate Project

In considering the economics and feasibility of competitive processes, the factors relating to a particular location must be considered. It is not possible to generalize. The analysis must be specific for a specific location.

The basic criteria for making a decision among competitive processes for a plant at a particular location are:

1. Is there a market for the particular types of fertilizers in the marketing area of the proposed plant? If not, is there a good possibility of developing a market?
2. What are the relative capital costs of the competitive processes?
3. What is the price of sulfur at the particular location (if a sulfur-using process is being considered)?

The price of phosphate rock is not relevant since all processes will use the same quantity of phosphate rock for a given amount of phosphate production.

The price of ammonia is, also, not relevant in making a decision among competitive processes since all processes will need the same quantity of nitrogen.

The existence (or not) of a domestic supply of sulfur, also, is not relevant, but the price of sulfur is relevant. I can conceive of a nitrophosphate plant being built in Mexico next door to a sulfur mine, if the economics was favorable. The fact that a country has a domestic supply of sulfur is no reason for not considering nitrophosphates. Sulfur has a certain value on the world market so why not sell it and make fertilizer the cheapest way.

Also, the existence (or not) of a domestic supply of phosphate rock is not relevant in deciding between two or more processes all of which use phosphate rock as a raw material. If a country has domestic phosphate rock or if it imports phosphate rock is irrelevant in deciding among competitive processes that use phosphate rock. However, every country that imports phosphate rock should consider importing solid phosphate fertilizers, phosphoric acid or elemental phosphorus as alternatives to phosphate rock, but this comparison is beyond the scope of this paper.

Conclusions

1. Nitrophosphate processes can produce certain types of N-P fertilizers at significantly lower cost than by conventional processes using phosphoric acid.
2. New nitrophosphate processes, recently put into operation in Norway and Czechoslovakia, can produce N-P fertilizers with 75% or higher water solubility of phosphate, without the use of sulfur.
3. However, the types of fertilizer that can be produced by nitrophosphate processes are limited to ones with $N:P_2O_5$ ratios of 1.5 to 2.5. The product might be a single product, such as 28-14-0, or two products, such as 24-24-0 plus ammonium nitrate as a co-product.
4. Nitrophosphate fertilizers have 40-45% of the nitrogen in nitrate form which may be an economic handicap in rice-growing areas.
5. The basic problem in making a decision on a nitrophosphate project is whether there is a market for the product.
6. Developing countries which should give serious consideration to using nitrophosphate processes include India, Pakistan, China, Indonesia, Korea, Vietnam, Philippines, Taiwan, Iran, Turkey, U.A.R., South Africa, Brazil, Argentina, Peru, Mexico and Cuba.

Chairman Sauchelli: Thank you, Ray. He calls himself an amateur. In my book the strict definition of an amateur is one who really loves the art and he is a man who just loves these discussions on fertilizer although he has been interested in so many other avenues. We have time for questions.

A Member: Where is the plant located in North Carolina?

Dr. Ewell: A small town called Tunis. It is on Albemarle Sound. We are going to get the phosphate rock by barge around from The Texas Gulf at the other end of the Sound. It is very cheap.

Abbreviations

PR = Phosphate rock
CN = Calcium nitrate
CS = Calcium sulfate
CC = Calcium carbonate
NA = Nitric acid
SA = Sulfuric acid
PA = Phosphoric acid
AN = Ammonium nitrate
AS = Ammonium sulfate
MAP = Monoammonium phosphate
DAP = Diammonium phosphate
TAP = Triammonium phosphate
DCP = Dicalcium phosphate
TCP = Tricalcium phosphate
NP = Nitrophosphate

Chairman Sauchelli: We have on our program a talk on a nitrophosphate plant that will refer to that Tunis plant. The talk will be given by Mr. William A. Lutz. We received his paper too late for it to get on our printed program, however, we are going to try to make time for Mr. Lutz's presentation.

Mr. Joseph Reynolds: Can you identify the $8 million and the $10 million investment as to the type of plants that are included in your estimates? Do you have a sulphuric or nitric acid plant included in this figure?

Dr. Ewell: Oh, no, no nitric acid. I made that clear. Every one of these processes takes the same amount of nitric acid.

Mr. Reynolds: I see.

Dr. Ewell: So you leave that out.

Mr. Reynolds: But if you are building a plant in Egypt or some other place, you are assuming they have certain facilities. What is in the $8 million?

Dr. Ewell: Everything that was on these flow sheets.

Mr. Reynolds: You've got a phosphoric acid plant.

Dr. Ewell: Yes. You see, I made the statement that each of these plants is assumed to be next door to an ammonia plant and a nitric acid plant because there are going to be three units: an ammonia plant, a nitric acid plant and this nitrophosphate product plant.

Mr. Reynolds: You are saying that you can build a phosphoric acid plant, a sulfuric acid plant and the storage and shipping facilities for 7½ to $8 million?

Dr. Ewell: No, this is a battery limits plant, no storage, no bagging, no storage of raw materials, no storage of end products, just the operating units, no storage and no bagging unit.

Mr. S. Strelzoff: I had better not ask any questions or I will be asked too many tomorrow. I would like to know the answer to one question. When you say battery limits, you include sulfuric acid?

Dr. Ewell: Oh, yes.

Mr. Strelzoff: Phosphoric acid and sulphuric acid but you didn't include nitric acid.

Dr. Ewell: (Nodding head.)

Mr. Strelzoff: Do you use phosphoric acid to produce the 35 per cent P_2O_5 or do you go to a concentrate of 54% before you go to DAP and so on?

Dr. Ewell: This is a technical detail I didn't get into, Sam.

Mr. Strelzoff: If you do need to concentrate phosphoric acid you have to use some steam or fuel.

Dr. Ewell: You've got the steam from your sulphuric acid operation.

Mr. Strelzoff: In other words, you have integration of the sulfuric acid, phosphoric acid and so on until you come to zero?

Dr. Ewell: You get the steam out of the sulfur burning.

E. N. Mortenson: Will your report to the United Nations come out before the report that is printed by the Round Table?

Dr. Ewell: Considering how long it takes the United Nations to review reports, I doubt if this will be coming out before April or May. I expect to turn it in to the United Nations in draft form only before Christmas and I am also going to send it to about 20 people who would like to comment on it and then probably around the first part of February I'll get out a final draft and that has to go through the committee approval procedure in the United Nations.

Vincent Sauchelli: About a year ago we asked Enrico to prepare a panel discussion on this subject for the Round Table. Although he is a very busy executive with C&I/Girdler, he accepted the assignment and found time to assemble for the purpose a remarkable group of talented persons.

Enrico has been a staunch friend and loyal supporter of our Round Table for many years. Rico, the floor is yours.

Materials of Construction For Fertilizer Plants

Dr. Enrico Pelitti, Panel Leader

E. A. Tice, W. E. Rushton, G. R. James, P. Moraillon, W. Berry and K. Harrison, Panel Members

MR. PELITTI: Thank you, Vince.

In periods of great construction activity, there is always considerable pressure to get new facilities completed as quickly as possible. Tight construction schedules in the critical early stages thus make it difficult for the design engineer to take the time to analyze and evaluate past experiences and to investigate alternate approaches.

In the mid sixties, the fertilizer industry has unquestionably witnessed a period of intense construction activity. On the other hand, I don't believe many will want to dispute the statement with which FORTUNE opened their article on fertilizers last June:

> "With startling and dramatic finality the big boom in chemical fertilizers is over."

This leaves many design engineers and operators with some spare time on their hands, and gives them an opportunity to use it to review the state of our knowledge and experience, and to develop the guide lines that can be used when the boom will resume. Which is bound to happen, as soon as the present wave of overcapacity is finally digested by the agricultural users.

In the letter sent to Round Table participants by the Executive Committee, I have been described as having "earned an enviable reputation" in the field of materials of construction. It all started, more or less accidentally, about 10 years ago while the fertilizer industry was undergoing another of its periodic recessions.

My assignment at the time included the assembling of design and process references on phosphate fertilizers, in preparation for a resumption of construction activities. While I found an abundance of process references, very little was available on materials of construction, and most of what I found could be considered obsolete. New references, therefore, had to be prepared, based on the direct experience of a number of material suppliers and plant operators, as well as my own.

After the job was completed, it was suggested that the results be made available to the industry. They were first presented at the 41st National Meeting of the A.I.Ch.E. in St. Paul, Minnesota in September 1959.

Two months later at the Round Table, here in Washington, Vince Sauchelli talked me into letting him use most of that material for the A.C.S. Monograph on "The Chemistry and Technology of Fertilizers," which he was in the process of assembling.

As a consequence of the rapid technological progress of the fertilizer industry, however, many changes have occurred, both in processes and materials, prompting a number of people to ask me to up-date my original notes. None of them was quite as convincing as my friend Archie Slack of TVA, as Editor in Chief of a new series on "Fertilizer Science and Technology." Even Archie had a bit of difficulty to get me to complete the chapter on materials of construction for the book on phosphoric acid, and I had the distinction of being the last of the various contributors to send in his material. Part I of the book has been available for several months. The chapter on "Materials of Construction" is included in Part II.

In assembling the panel, I have attempted to make it representative of different sectors of the fertilizer industry to provide different points of view. I have been extremely fortunate in securing the assistance of some of the best known experts in the respective areas:

Bill Rushton — representing the equipment industry.

Allen Tice — representing the metallurgical and alloy industry.

Bill Berry — representing the operating section of the fertilizer industry.

Russ James — a consultant and expert on ammonia and nitrogen fertilizers.

In line with the international character The Fertilizer Round Table has been noted for in recent years, we also have in the panel two foreign representatives:

Ken Harrison from Canada— an expert in the area of corrosion resisting coatings and linings.

Philippe Moraillon from France, well-known in the international field for his contributions in the area of fertilizer processes and materials.

We will first have the presentation of the respective topics by all panel members. Then the panel will be open to the audience and we will attempt to answer any of the questions which will be submitted.

We also have a movie about a new technique for field fabrication of large plastic vessels. It was provided by Mr. Moraillon of Pechiney-Saint-Gobain. It will be shown at the conclusion of today's session. For those in the audience who have an interest in this particular subject, this is something which I believe was never attempted in the United States and I urge Round Table members with an interest in plastic construction not to miss it.

We will now start our panel with Allen Tice.

Mr. Tice is a graduate of Rensselaer Polytechnic Institute, B.S. in chemical engineering. After 7 years of experience in the steel industry, primarily concerned with corrosion research, he joined in

1946 the International Nickel Company's corrosion engineering section, where he became closely associated with F. L. Le Que and W. Z. Friend. From 1960 to 1967, Mr. Tice was in charge of INCO's corrosion engineering section, and has just recently been transferred to the market development department, chemical industry section. Allen will talk to you about new corrosion resisting alloys on which the industry is working, in the Ni-Cr-Mo-Fe family, which appear to offer great promise for chemical fertilizer processes.

New Corrosion Resisting Alloys

E. A. Tice

Thank you, Enrico. For my part, I can only hope to touch on a few of the new alloys that have become available in recent years, and I will divide them in three groups.

The first group, as illustrated in Table I, covers some of the new cast corrosion-resistant materials that are available commercially. For comparison, the second line gives the composition of the "20" alloy, with which most of you are familiar. It is the old work-horse of the phosphoric acid industry for sulfuric acid handling. The three other alloys have come into play in the last few years.

The top one, Illium P, and the bottom one, CD-4MCU alloy, are somewhat similar, being high chromium alloys, with some nickel, and with molybdenum and copper additions. Both molybdenum and copper additions to the chrome nickel family improve acid corrosion resistance. Greater hardness is also available in both the Illium P and the CDM-4-CU alloy, for better erosion resistance.

Illium-98 has been especially designed for the handling of hot sulfuric acid solutions, particularly in the higher concentration ranges.

These new cast materials are finding their place in pumps, valves, and other components of this type.

The next family of alloys is shown in Table II. It includes some of the new wrought materials available today, and for comparison we have shown Incoloy 825, and Carpenter 20-CB-3. I'm sure you are familiar with both of these alloys, which have been on the market for at least 10 years.

TABLE I

COMPOSITION %

Alloy	Cr	Ni	Mo	Cu	Fe	Other
ILLIUM P	28	8	2.2	3.3	57	Low C
CN-7M ("20" ALLOY)	20	29	2.2	3.3	44	Low C
ILLIUM 98	28	55	8.5	5.5	1	Low C
CD-4M Cu	26	5	2	3	62	Low C

TABLE II

COMPOSITION %

Alloy	Cr	Ni	Mo	Cu	Fe	Other
INCONEL ALLOY 625	22	61	9	–	3	4 Cb
HASTELLOY ALLOY G	22	45	6.5	2	20	Low C
JESSOP JS-700	21	25	4.5	–	48	Low C
INCOLOY ALLOY 825	21	42	3	2	30	Ti *
CARPENTER 20 CB-3	20	34	2.5	3.3	39	Cb *

* Carbide Stabalizer

The three new alloys appear above these in the table. It will be noticed that the top two alloys, Inconel 625 and Hastelloy G, are nickel base with about 20 to 22 percent chromium and considerable molybdenum additions. Hastelloy G also has a 10 percent copper content, which should improve sulfuric acid resistance. These three new alloys are starting to come into play in phosphoric acid production, and should be of considerable interest to the fertilizer industry.

Jessop JS-700 will be recognized as very close to the European alloy HV-9, and somewhat similar to Uranus B 6. I believe Uranus B 6 has some copper in it, whereas the Jessop alloy made in this country does not.

Mechanical properties of these newer alloys are very similar to those of stainless steels. They have a little higher strength. For example, Inconel 625 and Hastelloy G have a yield strength of the order of 60,000 PSI, with tensile strength up around 100,000 in the annealed condition. Jessop JS-700 is not quite as strong, and more in line with the conventional stainless steels. So these new alloys offer somewhat higher strength levels as well as improved corrosion resistance.

They can be welded with companion electrodes designed for them, and have excellent ductility. For instance, a bar of Jessop JS-700 alloy can be bent 180° on a very small radius, without showing any crack. This is typical of this whole family of alloys.

Table III shows some recent corrosion data, accumulated by International Nickel for these alloys in phosphoric acid service, and how they compare with some of the older alloys. Three sets of corrosion data are shown. Those for Plants A and B represent digester equipment exposures at conventional temperatures, of the order of 175 to 180°F. Corrosion rates for Inconel 625 and Hastelloy G, and the 25 Ni-20 Cr-4½ Mo alloy, which could be either the HV-9 or the Jessop JS-700, are all quite low. By contrast, note how poorly Type 316 SS has done.

However, some of the newer processes might wish to use higher temperatures and higher acid concentrations, such as in Plant C. In this test at temperatures between 240 and and 260°F, corrosion rates for all materials were drastically increased.

So these new alloys would seem to be quite interesting in conventional phosphoric acid reaction equipment, but perhaps of questionable value for some of the newer processes operating at higher temperature.

We are planning to investigate the behaviour of both Hastelloy G and Inconel 625 as evaporator tubing. This we hope to do in a 22-tube unit heater, operated in

TABLE III

Corrosion Test Data – Wet Process Phosphoric Acid

Conditions	Plant A	Plant B	Plant C
% ACID, AS P_2O_5 % SULFURIC ACID	28 2	26 3	40 3
TEMP. °F	170–183	170–183	220–260
TEST PERIOD – DAYS	96	90	19
TEST LOCATION	PRIMARY DIGESTION TANK	FILTER FEED BOX, FROM REACTOR	IN REACTOR
Alloy	**CORROSION RATE, MPY**		
INCONEL 625	1	1	24
HASTELLOY G	1	1	33
25 Ni–20 Cr–4.5 Mo	–	1	–
ILLIUM 98	3	2	24
ILLIUM P	–	4	–
INCOLOY 825	7	3	68
CARP. 20 CB3	7	2	57
TYPE 317 SS	22	3	125
TYPE 316 SS	41–60	58	260

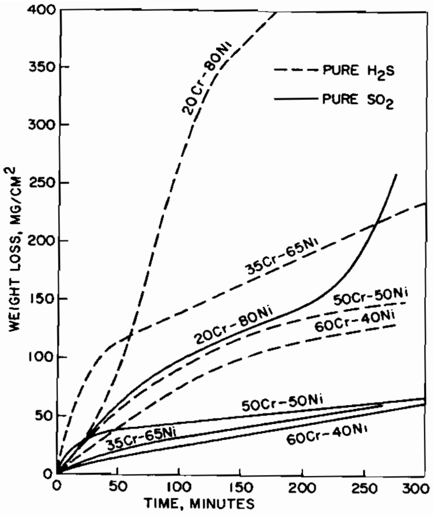


Fig. 1

Corrosion of Ni-Cr Alloys in Sulfur Containing Oxidizing and Reducing Media at 900°C

parallel with a first effect evaporator heater, at a typically corrosive phosphoric acid plant. The heater would have 10 tubes of each alloy, and a couple of reference alloy tubes of the 825 composition, to provide a comparison. If all goes well and we are successful, we would hope within a couple of years to prove whether or not either of these two alloys will really work as a heater tube. We cannot do this merely from laboratory data.

So, this is the state of some of the newer wrought materials that might be usable by the phosphoric acid industry.

Another interesting area is given by alloys with a composition of roughly 50 Cr and 50 Ni. It might seem rather surprising that an alloy system of this type could be made to work, but it is being done. There are two new alloys now available, one a wrought material of 50 Cr and 50 Ni, and one a cast material only of 60 Cr and 40 Ni. These two combinations of chromium-nickel provide unusually good corrosion resistance for extremely high temperature sulfur conditions, either sulfur dioxide or hydrogen sulfide. Figure 1 illustrates some corrosion data for this family of alloys. The solid lines indicate corrosion rates in a sulfur dioxide environment. The temperature here is 900°C, quite hot. None of the conventional chromium-nickel stainless steels are at all resistant to these environments. The chromium-nickel alloys are compared with a 20 Cr –80 Ni alloy, which is the composition of one of the better alloys available in the past. It can be seen that both the 50-50 and the 60-40 compositions have quite good corrosion resistance in this weight-change vs. time corrosion test.

Sulfur dioxide as an oxidizing enviroment, is not as corrosive as hydrogen sulfide, and the broken lines indicate the behaviour of these new alloys in an hydrogen sulfide atmosphere.

Just where these alloys are going to find application in the fertilizer industry I do not know, but in the power industry, for example, in superheater applications there have to be hangers or support brackets to support the superheater tubing, and some of the fuels being burned today have a sulfur content combined with a sodium problem also, and a very corrosive situation can exist with conventional hanger materials. Figure 2 shows the behaviour of one of these new chromium nickel alloys. This is the 60-40 cast material tube support, as compared with the conventional 25-20 Cr-Ni stainless that has been used in the past. The supports have been in service for over 9,000 hours in a superheater hanger application.

We have thus presented some brand new alloys which are now available, both as castings and as wrought materials. I hope that they will prove of interest to you, and that this presentation will inspire some of you to consider them for some of your new applications, where you have real rough corrosion problems.

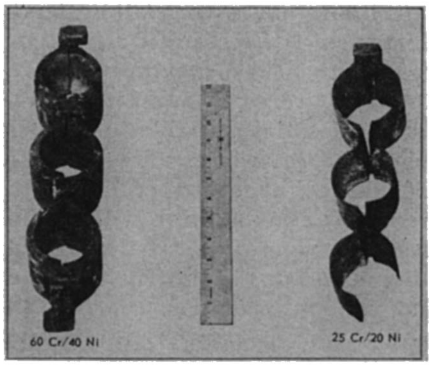


Fig. 2

Tube Supports — Consolidated Edison Company of New York—9429 Hours at 1500°F

Thank you very much.

MODERATOR PELITTI: Thank you, Allen.

Now that you have heard about a few promising new developments, a word of caution may be in order. Some serious and expensive disappointments have occurred in the past, when too much reliance was put on the results of static tests, and adoption of new materials was undertaken under conditions not exactly matching the ones of the tests.

Bill Rushton will talk to you about material requirements for phosphoric acid evaporators, and review the strange and fascinating story of Nionel, an experience to which probably a few of the participants of this Round Table have been exposed in the period between 1959 and 1961. Bill Rushton received his chemical engineering degree from The Missouri School of Mines in metallurgy in 1951. He joined the Swenson Division of the Whiting Corporation in 1956, and has been involved ever since in various phases of design, construction and sales of process equipment used in the fertilizer industry.

He is presently Manager of the Swenson phosphate department. Bill has presented numerous papers at technical meetings, especially on equipment, processes and materials for phosphoric acid and superphosphoric acid. Even though Bill insists he is not an expert on the subject of materials, his long exposure to problems related to materials used in these processes provides impressive credentials.

Materials of Construction for Phosphoric Acid Evaporator

W. E. Rushton

Most of the materials available for corrosive application have been used or tried in wet process phosphoric acid plants. Corrosion testing of new materials is continually going on, to find better solutions for specific jobs. One area of the plant that has seen very few changes in materials of construction over the years, however, is the concentration section.

At the present time, only few materials are normally used in the fabrication of the conventional phosphoric acid evaporator. They generally represent a compromise dictated by cost and service, and they are only acceptable for a narrow range of conditions. A change in any of a number of factors, can make them unacceptable and cause rapid failures. The only materials presently available as an alternate choice are much more costly, and result in very expensive solutions. I feel there is a need for new economical materials of construction which can resist corrosion under the special conditions found in the evaporator section of a wet acid plant, but they can only be developed through a clear understanding of how those conditions will affect any corrosion test.

Several attempts have been made to use metallic materials in evaporator equipment, but they have met only with very limited success, and in some cases with complete failure. I believe this poor showing is primarily due to improper testing of the materials, before their introduction on a commercial basis. Proper testing would have avoided some of the more prominent failures and left the industry less reluctant to investigate the new materials presently being developed.

A brief review of phosphoric acid concentration equipment from the point of view of materials of construction will show how we have arrived at a situation where everybody agrees that the existing materials should be improved, but virtually nobody is interested in being the first or even the second to put new materials into service.

Over the years, the design of phosphoric acid concentration equipment has changed considerably. The first units were hot gas evaporators, where the products of combustion were passed through a pool of phosphoric acid. This type of equipment operated at relatively high temperature, and corrosion was a very serious problem. In order to reduce temperatures and corrosion the industry turned to vacuum evaporators.

The first vacuum units were horizontal-tube cast lead evaporators. Later development allowed the use of the thermal syphon design, with natural circulation. Original construction was in lead-lined steel, followed later by rubber-lined steel. The heat exchangers generally had impervious graphite tubes, held in lead-lined tube sheets with rubber grommets.

About eight years ago, forced circulation replaced the natural circulation or thermal syphon design. As this type of evaporator is the one most commonly used at present, the remainder of this discussion will cover the materials of construction now in use and possible areas of improvement.

Rubber Lining

The major portion of the evaporator is of rubber-lined steel. This type of construction has been used almost exclusively since the mid 50's. Rubber lining today is considerably more reliable than when the first evaporators were built. Present lining techniques and cements make bond failures very rare. Rubber, however, does have limitations that make development of improved materials desirable. Present rubber linings are limited to temperatures below 200°F. Due to the high boiling point elevation of phosphoric acid, this limitation restricts all evaporators to single effect units, and vapor heads must be made very large to allow for very low pressure operation. Materials suitable for higher temperatures would allow the use of multiple effect evaporators, with resultant savings in steam and water consumption. If the cost of the material was no higher than for rubber-lined steel, the over-all cost of the evaporator installation could be reduced.

Another severe limitation of rubber is the difficulty of making repairs. At the present time new rubber used for patching must be vulcanized with steam for periods of 48 to 60 hours. This, of course, is very time consuming and costly. An additional disadvantage is that after several years of service, it is often very difficult to obtain a satisfactory bond between the old rubber and a new patch.

We are always interested in improvements and have investigated most of the new materials that have come to our attention. There are presently several coating materials that appear to be promising and deserve additional testing. So far, progress has been very slow, mostly due to the industry's reluctance to test new materials in process equipment.

Alloy 20

At present, Alloy 20 is generally used in the U.S. as the material of construction for evaporator circulating pumps and lump screens. While these alloys give a reasonably satisfactory service, they are a compromise material. To prevent or limit corrosion, a relatively low liquor velocity through the pump must be used. This results in many instances, in oversize pumps. In addition, potential suppliers of pump castings are limited, as only one foundry appears to have developed the techniques of heat treatment and annealing to impart maximum corosion resistance to the alloy.

Satisfactory experience with Alloy 20 is limited to acids produced from Florida and Western rocks. Any other rock source must be carefully reviewed, and in many cases may require more expensive alloys. For instance, acids produced from some African rocks may contain a fair amount of chlorides. With this condition, a French alloy, Uranus B6, or Hastelloy "C" must be used.

The wrought form of Alloy 20, used to fabricate the lump screen, seems to be less susceptible to corrosion than the castings in the pump. However, velocity across the screen is generally fairly low, and the erosive action of the $CaSO_4$ crystals tend to keep the screen clean so that conditions less likely to cause corrosion are maintained.

Evaporator Tubing

Traditionally, impervious graphite tubing has been used almost exclusively as the heat transfer source. The early horizontal tube and natural circulation evaporators used these tubes secured in lead-lined tube sheets with rubber grommets. The advent of the forced circulation evaporator, with reduced scaling and easier cleaning, made the change to cemented construction possible. Thus all recent forced circulation evaporators use impervious graphite tubes cemented into impervious graphite tube sheets. However, the graphite tubes are fragile, and are subject to mechanical damage during cleaning, or to failure by hydraulic shocks caused by process upsets. When tube breakage occurs, the resultant repairs are quite time consuming.

Because of the fragility of the graphite tubes and the frequency of repairs, this portion of the evaporator has probably received the most attention in the search for improved materials of construction. To date, no satisfactory replacement material has been found, and more than 90% of the tubes in service are of impervious graphite construction. A number of years ago, a new alloy, Nionel, was tested and installed commercially in phosphoric acid evaporators. Unfortunately, the commercial installations were made before the metal had been completely tested, and resulted in massive tube failures, which led to replacement of most of the alloy tubes with impervious graphite.

Because of this experience, subsequent testing of new alloys has been greatly reduced, and future commercial acceptance of any new alloy will be extremely slow. So that we can learn from the Nionel experience, I would like to review the testing procedures that preceded its adoptions and the eventual results.

The Story of Nionel

During the early 1950's Nionel, now known as Inconel 825, showed good corrosion resistance to phosphoric acid in laboratory tests. Subsequent field tests in reactors and pumps seemed to confirm that this alloy would withstand even wet process acid. As a result, some tubing was formed and supplied in quantities of 3 or 4 to several plants for installation in their evaporators. These test tubes were installed in existing heat exchangers of natural circulation evaporators, that contained up to 1,000 graphite tubes.

The natural circulation evaporators had to be cleaned every 3 to 4 days. Because the impervious graphite had a relatively rough interior surface compared to the Nionel, scale would adhere to it faster than in the metal tubes. Therefore, any clean-out schedule based on the scaling rate of the graphite tube found the metal tube only lightly scaled. A boilout that would remove the scale satisfactorily from the heavily scaled graphite tube would result in a completely clean metal tube. Under these conditions, the Nionel test tubes remained in service for up to 4 years with virtually no failures.

Before the advent of Nionel, it was felt that a forced circulation evaporator could not be designed in the sizes required, because of design limitations imposed by the graphite tubes. It could not be shown that tube breakage would be reduced by this approach, so it was thought that the cemented construction would not be acceptable, due to the time required to replace tubes. The ring gasket design could not be applied to tubes over 9 ft. long, which meant that extremely high and impractical circulation rates were required.

The promise of an acceptable alloy, which Nionel appeared to offer, meant that a long tube forced circulation evaporator could at last be designed. Forced circulation meant that longer operating cycles could be expected, and tube plugging reduced, resulting in better over-all performance. The metal tubes offered a mechanical strength that would eliminate tube breakage as a maintenance problem.

The Nionel test results became known in the late 50's, and coincided with the start of the phosphate industry expansion. About 7 different companies decided to install forced circulation evaporators with Nionel tubes between 1959 and 1962. The first of these units was started on the first of 1961. Within a few weeks, failures of the tubes began to occur. Inspection of the tubes revealed that both the inlet and exit ends were being severely eroded and corroded. The remainder of the tube showed signs of corrosion, but to a lesser degree. It was thought that the turbulence caused by the liquor entering and leaving the tubes was the cause of this condition and that tube inserts might solve the problem.

However, at about the same time, new tubes that had been installed in a natural circulation evaporator also began to fail. This precipitated an investigation into possible changes in the metallurgical structure of the alloy. Physical tests showed that the Nionel tubes supplied in 1960 were much harder than the original tubes previously tested, and had a much finer grain size. In addition, the chemical composition of the tubes had been slightly modified; the titanium content had been doubled from approximately 0.35% in the test tubes to 0.7% in the new tubes.

A number of metallurgists were consulted to determine what effect these changes might have on the corrosion resistance of the alloy. It was generally agreed that the changes in grain size and hardness should not have any major effect on the corrosion resistance of the alloy, but whatever effect they did have would tend to make the tube slightly less resistant to corrosion. It was also generally agreed that the increase in titanium content should not reduce the corrosion resistance of the alloy.

Based on these discussions it was decided to immediately modify the hardness and grain size of Nionel that had not already been produced. This meant a change in annealing procedures. As a result, all tubes produced after 1961 had the modified structure.

Later operation indicated that this modification seemed to solve the erosion problem at the ends of the tubes, but not the primary problem of tube failure. As additional evaporators started up, a pattern of tube failure began to emerge. Visual inspection indicated that all failures were the result of pit type corrosion. This corrosion always seemed to occur in scaled tubes, at points where the scale had cracked and acid got behind the scale. The amount of scale in the failed tubes further indicated that failures almost always occurred in tubes that had not been completely cleaned during the previous boil out. In most cases, the scale appeared to be an accumulation of several weeks. It was also noted that evaporators that produced only 54% P_2O_5 seemed to have very few tube failures.

As a result of these problems, most of the Nionel exchangers were eventually replaced with graphite exchangers. Only a few evaporators are still existing with metal tubes, and these are almost exclusively used on acid with 50% P_2O_5 or higher strengths. Even at this concentration, if scale is allowed to accumulate, corrosion will occur. However, the higher strength acid seems to be less agressive, and the degree of cleanliness is not as critical as in more dilute acid. Some exchangers have now been in operation for more than 5 years without any major tube failure. A review of all the facts after these many years of experience, appears to indicate that the Nionel tubes might have been satisfactory if the evaporators had been boiled out every 3 to 4 days. However, this limitation would do away with one of the primary advantages of the system.

Because of these experiences, there is now a tendency to avoid the use of new materials in any position where their failure would cause a prolonged shutdown. To prevent a recurrence of the above problems the next time a new material is suggested, the initial test program should be such as to insure that the material is tested under actual operating conditions. Preliminary tests can be conducted with corrosion test spools, but before final commercial application a test set-up should be made that conforms as closely as possible to actual conditions.

A new material for the vapor head, for instance, should be exposed to the same conditions of scaling, erosion, liquor and vapor as encountered in actual operation. A new tube material should be installed in a small heat exchanger, operating in parallel with the main exchanger. This small exchanger could then be operated on its own cycle, so that the conditions in the tubes would be similar to what would be expected in the proposed commercial operation. In addition, before a material is completely accepted, it should be tested on acids produced from a variety of sources, to determine exactly what limitations potential impurities and additives may put on its use.

MODERATOR PELITTI: Thank you, Bill.

We will now hear from Russ James, a chemical engineer, and consultant on fertilizer, ammonia and synthesis gas manufacture. He is well-known in the industry through numerous articles, papers and publications. I have known him since our association at Chemico, where he was Chief Engineer of the Industrial Projects Department and, later, Director of Development. He has been active in high pressure and naphtha reforming, carbonate processes, phosphoric and hydrofluoric acids. A Yale engineering graduate, he studied economics and government at Columbia. He will talk to you about problems of corrosion in urea reactors.

Urea Reactor Lining Materials

G. R. James

CO_2 and water are corrosive at low temperature. Materials in CO_2 removal systems, where temperatures are in the range of 100 to 250°F, have long been a problem in synthesis gas purification. Operators who have seen part of their CO_2 strippers disappear or whose copper liquor regenerator has acquired a moth-eaten appearance, can testify that CO_2 in water is corrosive.

Urea reactors have the prerequisites for CO_2 corrosion at 200°F. but temperature, one of the prime factors in corrosion, is not 200°F. It is as high as 400°F, in a mixture of CO_2, water, ammonia, carbonate, carbamate and urea. Even with a high excess of ammonia at these temperatures the urea reactor mass will dissolve many corrosion resistant materials.

Fortunately, the problem, which may have seemed difficult or impossible in the early stages, has now been resolved. There are several lining systems which do allow urea reactors to give satisfactory life. Many materials have been used. Lead, silver, titanium, zirconium and stainless steel each has it own story in urea reactor service. Each has its own problems in process application, fabrication and cost.

Early Test Data

Starting with some early work by J. G. Thompson, H. J. Krase and K. G. Clark in a six inch diameter tin-lined vessel 18" long, we see that corrosion in the reactor was of prime concern in 1930.

Table 1 shows the results of 4

Table I—Resistance of Metals to the System Urea-Water-Ammonium Carbamate at 142° C. under Pressure

SAMPLE	NON-FERROUS COMPOSITION					4-DAY TEST LOSS	7-DAY TEST		
	Carbon	Chromium	Nickel	Silicon	Other elements		Loss	Penetration per year	
						Mg./sq cm/day	Mg./sq cm./day	Inches	Mm
1 (Duriron)	.	..	.	14.5		0.024	0.012	0.00021	0.00533
2 (Silver)	.	.	.	.	Ag 99.9	.. .	0.026	0.00035	0.00889
3 (Illium G)	0.5	21.5	58.5	1.4	Cu, 8; Mo, 3; W, 2	0.069	0.066	0.0012	0.0305
4 (Chromium)		.	..	..		0.14 (gain)	0.084	0.0017	0.0432
5 (Lead)		..		..			0.11	0.0014	0.0356
6 (Nickel strip)		.	.	.		.	0.15	0.0025	0.0635
7 (Pioneer)	.	20	38	4	Mo, 3, some C, Cu, Mn	0.029	0.17	0.0031	0.0787
8 (Corrosiron)		.	.	12		0.68	0.175	0.0037	0.0940
9 (Rezistal 4)	0.23	18	22.5	2.9		0.90	0.95	0.017	0.432
10 (Stellite)	2 (approx.)	15 33	..	..	Co, 40–75; W, 10–17	.....	1.1	0.019	0.483
11 (Invar)		..	36	.		.....	1.49	0.027	0.686
12 (Cimet 1)	0.7	29	1	..		0.77	36	0.87	22.10
13 (Cimet 2)	1	20	60	1.4		0.97	0.10 (gain)	....	.....
14 (Rezistal 5)	0.31	11	36	2		1.4	....		
15 (Hybnickel S)	0.15	17	21	.		1.7	....	....	...
16 (Cyclops 17-B)	0.20	6.5	2	1		1.7	....	....	...
17 (Block tin)	..	..	..			..	2.68	0.053	1.346
18 (Ferro Molyb. A 111)	..	..	..		Mo, 5.75	.....	57	1.07	27.18
19 (Delhi cast)	0.45	17	3	..		4.4	...	.....	.....
20 (Bethlehem chrome steel)	0.35	15.5	0.3	..		4.5–6.9*	...	....	.
21 (Silchrome)		18.5	0.4	3.0	W, 3.5	5.7	....		..
22 (Delhi rolled)	0.09	20.0	..	.		6.5	....		.
23 (Enduro A)	0.09	17.0	0.35			14.0	.. .		
24 (Duraloy)	0.32	23.5	1.1			17.0	..		...
25 (Chrome iron)	0.13	14.8			V, 1.2	17.0	..		..
26 (Uniloy 2825)	0.30	28.3				19.0	.		..
27 (Chrome iron)	0.13	14.0				34.0			
28 (Electrolytic iron)	0.02	.	..	0.01		43.0			
29 (Chrome iron)	0.20	25.0	.			59			
30 (Uniloy 1409)	0.09	12.4	0.5			84			
31 (Vanadium alloy steel)	..	13.6	.		V, 0.5	97			
32 (Rezistal 7)	0.9	5.5	0.3			101			
33 (Carpaloy 1)	0.1	14.0				109			
34 (Ascoloy 33)	0.09	10.5				143			
35 (Carpaloy 3)	0.27	20.0			V, 0.7	174			
36 (Uniloy 1809)	0.10	18.8	0.5			179		..	

* Range of triplicate samples.

Table 2

RESULTS OF CORROSION TESTS

IN UREA PILOT REACTOR

	Sample	Non-Ferrous Composition C %	Cr %	Ni %	Si %	Loss Mg./sq. cm.	Relative Penetration
1.	Chromium	-	-	-	-	0.21 gain	0
2.	Tantalum	-	-	-	-	0.10 gain	0
3.	Duriron	-	-	-	14.5	2.4	1.0
4.	Nickel	-	-	-	-	13.2	4.3
5.	Illium G	0.5	21.5	58.5	1.4	12.5	4.4
6.	Rezistal 4	0.23	18.0	22.5	2.9	37.0	13.9
7.	Lead	-	-	-	-	67.4	17.3
8.	Aluminum	-	-	-	-	55.4	59.9
9.	Enduro KA 2	0.15	18.0	8.5	<0.75	308.0	114.3
10.	Tin	-	-	-	-	506.0	252.1
11.	Zinc	-	-	-	-	Complete Solution	

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day and 7 day tests at 142°C. (288°F.) and 50 to 75 atmospheres. It appeared from this work that operation under the given conditions would be reasonable with lead, silver, chromium and nickel liners, and that various chrome-nickel alloys also would have application.

The same year further work by K. G. Clark and V. L. Geddy produced relative corrosion penetration figures for various metals in a test autoclave operated at somewhat higher temperature, 165°C. (335°F) and approximately 110 atmospheres (Table 2). It can be seen that results in the two tables do not agree on actual corrosion rates, but that those materials with lower rates do generally correspond.

Test Data on Corrosion

Additional, more recent data in Tables 3 through 6 show results of corrosion tests in actual operating reactors.

From these tables it is again apparent that several materials are satisfactory in urea reactor service, although the order of preference is by no means clear.

Table 3

LOCATION OF SPECIMENS:

Urea Reactor 3 ft. below top head of reactor in liquid - spool was mounted horizontally next to vessel wall.

AERATION:

Moderate

TOTAL TIME IN TEST:

115 days

AGITATION:

Slight

TEMPERATURE:

Ave. 181 °C
357 °F

REMARKS:

Type 316 ELC is used in construction of this plant. No failure encountered but general corrosion observed.

METAL	SAMPLE	CORROSION RATE in./yr. Ave.	
Titanium	1	0.0031	
Ni-o-nel	1	0.009	
Carpenter 20	1	0.010	
Hastelloy C	1	0.017	
316 ELC SS	1	0.030	
Ni-o-nel	2	0.061	
Silver	1	0.025	Destroyed in test
Silver	2	>0.025	Destroyed in test
Aluminum 1100	1	>0.061	Destroyed in test
Aluminum 1100	2	>0.063	Destroyed in test
Carpenter 20	2	>0.070	Destroyed in test

Table 4

LOCATION OF SPECIMENS:

Urea Reactor directly on top of sparger plate in bottom of reactor.

AERATION:

Some slight amount of air

TOTAL TIME IN TEST:

58 days

AGITATION:

3400-3800 lb/hr. of NH_3, CO_2, Urea soln. thru 31-½" ID vessel

REMARKS:

Type 316L (½" liner) stainless steel sparger plate in use. One plate failed in three months by general corrosion. During this test, corrosion was less than in the past as judged by iron in product and condition of sparger plate.

METAL	SAMPLE	CORROSION RATE in./yr. Ave.	
Type 304 SS	1	0.0018	Etched
Type 202 SS	1	0.0031	
Type 302 SS	1	0.0042	Lightly etched
Type 202 SS	3	0.0056	
Type 302 SS	2	0.0090	Lightly etched
Type 201 SS	1	0.024	Heavily etched
Type 202 SS	2	0.096	Missing after test
Type 202 SS	4	0.11	Missing after test
Type 304L SS	1	·0.12	Missing after test
Type 201 SS	2	>0.17	Missing after test

Difference in corrosion rates of duplicate specimens and complete disappearance of Type 304L makes value of test doubtful. The conditions of exposure apparently varied along the length of the rack.

It is also apparent that location of samples in the reactor has a definite effect. Thus one sample located a short distance from another may have a markedly different rate of corrosion. This may be indicative of actual differences in reactor conditions, not of the questionable validity of test results.

Oxygen

There has been considerable work done on the effect of oxygen on reactor linings; however, there is not a great deal of information available on corrosion related to oxygen content. Table 7 illustrates the effect of oxygen on titanium corrosion and Table 8 gives information on the combined effect of sulfur and oxygen. Thus for titanium the results illustrate that oxygen decreases the corrosion rate and sulfur increases it markedly.

The data in Figure 9 show that the reduction of corrosion rates as oxygen increases is more pronounced with stainless steels than with titanium. This is one of the reasons for the preference given presently to stainless reactor linings, when adequate oxygen content is present.

Table 5

LOCATION OF SPECIMENS:

Urea Reactor on top of sparger in bottom of reactor.

AERATION:

Moderate to Slight

TOTAL TIME IN TEST:

125 days - Out of service six months

AGITATION:

Extensive: 3400 to 3800 lb./hr. throughout.

TEMPERATURE:

Ave. 190 C
375 F

REMARKS:

Type 316L sparger has failed by general corrosion. Disagreement between duplicate samples on two support rods may be due to sparger flow pattern, but opens results to question.

METAL	SAMPLE	CORROSION RATE in./yr. Ave.
Zirconium	1	< 0.0001
Type 309 SS	1	0.0007
Type 329 SS	1	0.0010
S.S. Carpenter 20	1	0.0011
Ni-o-nel	1	0.0011
Type 316	1	0.0011
Type 317 SS	1	0.0013
316L SS	1	0.0013
Type 304 SS	1	0.0015
Type 304L SS	1	0.0016
Hastelloy F	1	0.0019
Type 202 SS	1	0.0020
316L SS	2	0.0030
Cu - Mo	1	0.0030
Tantalum	1	0.0034
316 Sensitized	1	0.0041
Titanium	1	0.0068
Hastelloy F	2	0.0070
Type 316	2	0.0089
Inconel 700	1	0.019
Type 309 SS	2	0.055

SAMPLES DESTROYED IN TEST
304 Sensitized
Type 310 SS
Type 330
Illium G
Nickel
Monel
Hastelloy C
Inconel
Inconel X
Incoloy
Incoloy 804
Incoloy 901
Nimonic 75
Cast iron
Ni-Resist Type II
Duriron
Type 325

Table 6

LOCATION OF SPECIMENS:

Pilot plant reaction autoclave in open glass tubes immersed in reactor.

TOTAL TIME IN TEST:

7 days

TEMPERATURE:

180 °C
355 F max.

REMARKS:

Test specimens 15 mm. diameter x 30 mm. long. Pressure about 250 atms. (3750 psi) max.

METAL	CORROSION RATE in./yr. Ave.	
Silver	0.033	
Stellite	0.39	
Monel	0.39	
Al Bronze	0.42	
Lead	0.42	Actual corrosion plant autoclave
M7 (18 Ni, 8 Cr, 7 Mo)	0.85	

Table 7

LOCATION OF SPECIMENS:

In reactor, position not given.

AERATION:

None

TEMPERATURE:

Ave. 196 °C
385 °F

AGITATION:

Considerable

REMARKS:

Pressure 260 atmospheres.

METAL	S cpds g/cu m	S cpds ppm by wt	CORROSION RATE in./yr. Ave.
Titanium (all tests) O_2 ppm			
44	0.012	6.0	0.0040
380	0.015	7.5	0.0014
790	0.011	5.5	0.0008
2360	0.012	6.0	0.0008

Table 3 gives the results of a 115 day test, with the samples near the top of a 316 ELC lined reactor, in which air was being introduced. Note the relative positions of titanium and 316 SS, and the variation in two samples of Carpenter 20. Aeration was probably responsible for the destruction of both silver specimens.

Table 4 again shows data from samples suspended in a 316 ELC lined reactor. They cover different materials and at a different loca-

Table 8

LOCATION OF SPECIMENS:

In Reactor - Position not stated

AERATION:

None

TOTAL TIME IN TEST:

33 to 63 days

AGITATION:

Considerable

TEMPERATURE:

Ave. 176 °C
349 F

REMARKS:

Pressure 240-250 atmospheres

O_2	8-9 ppm	9-250 ppm	0.3-0.5%	1-1.5%
S cpds.: g/cu m(ppm)	0.004(2)	0.02(10)	0.1(50)	0.5(250)
METAL	IPY	IPY	IPY	IPY
Titanium	0.0024	0.0033	0.016	0.089
Titanium 10-15 Cr	0.020	0.026	0.091	0.54
Titanium 6-7 Cr	0.0033	0.0035	0.033	0.18
Titanium 2-4% Mo	0.0021	0.0026	0.011	0.14
Lead	0.0037	0.015	0.34	Destroyed
Monel alloy 400	0.023	0.25	Destroyed	Destroyed
Inconel alloy 600	0.025	0.35	Destroyed	Destroyed

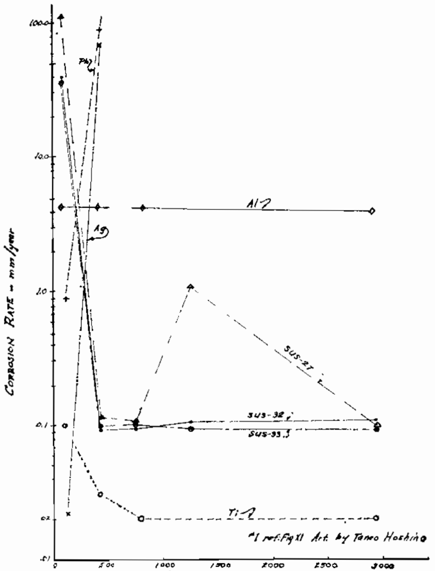

Figure 9

tion. The wide variation in corrosion rates is probably due to nonuniform conditions on top of the sparger. The object of this table is to show the difference between the rates of corrosion that can be obtained with the same materials in the same reactor.

Table 5, at relatively high temperature, shows zirconium at the top of the list, and other samples again with widely varying corrosion rates, as much as 80-fold in the case of 309 SS. Titanium is far down the list, maybe due to location or possibly the sample had been improperly heat treated before testing. Worthy of notice in this test are the many materials that proved to be unsatisfactory.

Table 6 gives results of a pilot test for a short period. It shows silver at a high corrosion rate but significantly better than other materials. In this case air was not used. The lack of oxygen proved the downfall of all materials but silver.

Silver and lead both react ununfavorably to oxygen content as illustrated in Figure 9. They also react unfavorably to a combination of oxygen and sulfur compounds. Limits for satisfactory operation of reactors with relatively thick silver linings have been set by one operator at 25 ppm O_2, when there is 300 ppm sulfur in the CO_2 used.

Process Considerations

Use of higher temperatures in reactors results in increased conversion of ammonia and CO_2 to urea. For example, if a given mixture at 180°C would provide a yield of 60%, the same initial mixture at 200°C might provide a yield of 65% of the CO_2 introduced.

Thus a more expensive liner with capacity for higher temperature operation may be justified, because either the same size reactor can provide more capacity, or recycle facility cost will decrease for the same output.

Summary of Materials in Commercial Use

Stainless Steel—316 ELC appears to be an economical material for urea reactor liners. It is used with various amounts of oxygen and in thicknesses of approximately ½ inch. Finish on the interior of the vessel and design to allow for even flow of materials and even distribution of oxygen are important factors in maintaining a protective oxide film on the liner.

Temperature limit is approximately 200°C (392°F).

Cost of material for a shaped stainless steel liner might be $2.50 per pound. Finished cost will depend on the fabrication technique used.

Titanium—Although know-how for titanium fabrication is limited, it has been used successfully in urea reactor design. Titanium is not as dependent on oxygen for satisfactory service life, thus eliminating requirements for oxygen injection. Also because of a lower corrosion rate, the period between inspection shutdowns may be increased and the cost of upkeep lowered.

Titanium treatment before installation is important in maintaining its resistance to urea reactor corrosion. Proper annealing can reduce titanium corrosion by as much as 80%.

Thickness of titanium liners is as low as ⅛ inch in clad material. They can be installed by two or three of the major vessel fabricating shops in the U.S. Various installation techniques are used. Besides clad plate in lower pressure units even solid titanium has been employed.

Cost relative to stainless steel is two or three times on a weight basis.

Temperature limit is approximately 200°C (392°F).

Zirconium—First use of zirconium for reactor lining produced failure in welds, which could not be X-rayed because of installation technique. Later design produced a satisfactory liner which loosely fits inside the pressure vessel, with a purge between the shell and the liner. At present, either the purged liner or one in which the steel shell is shrunk on the liner is used.

Zirconium liners have been approximately ⅜ inch thick. They can be fabricated by techniques and welding similar to that used on titanium. Corrosion of zirconium in urea reactor service is practically nil.

Cost relative to stainless steel is about 4 or 5 times on a weight basis.

Temperature limit is approximately 215°C (420°F).

Silver—Long a standard with many designers, silver has generally been replaced with stainless steel using oxygen injection.

Thickness of silver linings has been, in some cases, as much as ¼ inch.

Cost of silver (min. $24/lb.) is now considered prohibitive when compared with 316 ELC, titanium or zirconium on an over-all basis.

Temperature limit is approximately 200°C (392°F).

Lead—One of the earlier liner materials, lead has now largely been replaced by others, except in the oil slurry process, wherein no oxygen is used and oil coating lowers the corrosion rate of the lead.

General

Figures given herein on cost cannot be taken as indicators of comparable completed vessels. The complete vessel cost will depend on items that are related to the lining design, but not necessarily dependent upon it.

A comparison of the various corrosion data presented does not allow a definite conclusion as to which is the best lining. The answer will be determined in large measure by process and equipment considerations. One designer may have adapted his process and equipment to one material, with as good a result as obtained by another designer with a different liner.

Conclusion

While the information in this report is necessarily brief, it is apparent that there are several satisfactory lining materials for urea reactors, as well as several factors to be considered relative to their selection.

Some of the important ones are:

1. Process to be used
2. Pressure vessel fabrication technique
3. Availability of manufacturing facilities
4. Availability of repair facilities.

The data contained in the tables indicate that results of tests with corrosion spools in urea reactors can be frequently contradictory and sometimes misleading. And that generalizations cannot be made except on the basis of actual plant experience.

Acknowledgment

The information and data presented has been obtained from several sources, and from private communications. Further information can be found in the following references:

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Moderator Pelitti: Thank you, Russ.

Next on the panel is Philippe Moraillon. Mr. Moraillon received his Chemical Engineering degree in 1945 from the Ecole Nationale Superieure de Chimie in Paris. In 1946 he joined the Chemical Department of Saint-Gobain, which was later merged with the Chemical Division of Pechiney.

In Rouen, Mr. Moraillon played an important part in the development of many Pechiney-Saint-Gobain's fertilizer and phosphate processes. For the past three years he was Manager of fertilizer operations; first at Montargis and then at Bordeaux. He is presently assigned to the Pechiney-St. Gobain main office in Neuilly as Chief Engineer of the Fertilizer Division.

Mr. Moraillon has been active in technical meetings in Europe, and has presented papers at some of the conferences of the International Superphosphate Manufacturers Association. He has recently conducted a survey on the use of plastic materials in a number of fertilizer plants, and will report to you on European experience with the use of plastics for fertilizer applications.

Some European Experiences with the Use of Plastics in Fertilizer Plants

P. Moraillon

People who have known the fertilizer industry some twenty years ago should no doubt remember that wood and lead were widely used for reaction tanks, gas or vapor ducts, sulfuric and phosphoric acid piping, launders, scrubbers, stacks, etc. After operating for some time under the usual severe conditions, these materials underwent considerable deterioration and their maintenance cost was high. It is no wonder then that as soon as plastics became available, they received wide acceptance from fertilizer manufacturers and that their use spread quickly, in spite of some early failures caused by insufficient knowledge of their properties and lack of experience of equipment manufacturers.

No doubt this audience is well-acquainted with the use of various plastics in the States. So, my topic will be limited to European experience, mainly French, with the use of plastics in the fertilizer industry. The information I have collected covers a great number of French plants, a few in the Netherlands, Belgium, Italy, and also equipment supplied by French manufacturers to plants in Spain, Jugoslavia, U.S.S.R., Morocco, Lebanon and Senegal.

We will review successively the use of different plastics in sulfuric acid handling and metering, superphosphate manufacture, phosphoric acid manufacture, granulated fertilizers production and bagging.

Sulfuric Acid—Handling and Metering

The manufacture of phosphoric acid, superphosphate and some grades of granulated fertilizers consumes sulfuric acid.

Piping

Rigid unplasticized PVC pipes are extensively used for acid concentrations between 70 and 94% H_2SO_4.

Normal PVC is usually satisfactory when the temperature is not over 40°C. For instance in a plant in Nantes, a pipe 79/90 mm. in diameter and 250 m. long has been in service since 1954.

Some plants prefer high impact unplasticized PVC (type II), which fears neither shocks nor cold. This type of PVC, however, is sensitive to ultra-violet rays, which decrease the resistance to impacts. This is why suppliers advise to coat the outside of the pipes with a special aluminum paint.

For higher temperature, PVC hooped by fiberglass-reinforced polyester is used, which is also shockproof. This construction allows a temperature up to about 100°C, with weak acids. It is widely used in fertilizer plants in France for sulfuric acid pipes several hundred meters long.

Polyethylene does not appear to be as popular for this service. Anyway, let us mention a pipe, 700 m. long, 90 mm outside diameter, 8 mm thick, which supplies a fertilizer plant near Brest with 70% sulfuric acid. It is built up with 50 and 100 meters lengths, connected by polyfusion. This pipe was designed for a temperature of 40°C and a pressure of 4 atmospheres.

Some sulfuric acid piping in solid polypropylene also exists. The particularly high expansion coefficient of this material must be considered for proper installation.

Small tanks—Feeders

More and more plastics are being used in the construction of small tanks and feeders for sulfuric acid.

In a Bordeaux plant, a sulfuric acid pumping tank, 1.70 m. in diameter and 1.25 m. high was fabricated entirely of solid polypropylene, 15 mm. thick at the bottom and 10 mm. thick on the walls. Another pumping tank, narrow and high, (diameter 0.50 m., height 6 m.), is made of 4 mm. thick PVC, hooped by fiberglass-reinforced polyester, 6 mm. thick.

Sulfuric acid rotary dip feeders, weir gauges, are often fabricated of normal rigid PVC, high impact unplasticized PVC, polypropylene, or fiberglass-reinforced polyester.

98% Sulfuric Acid

For cold 98% acid, some plants use rigid PVC piping, which lasts about one and a half year. The same material is used for rotary dip feeders.

A factory in Toulouse has been working since 1965 with polyethylene pipes for 98% acid and oleum.

In sulfuric acid dilution units, the water sparger is often made out of solid teflon.

Manufacture of Superphosphates

The detachable upper part of some horizontal continuous mixers is fabricated of steel reinforced normal PVC or of 12 mm. thick fiberglass-reinforced polyester.

The mobile vertical wood walls of an old model Broadfield den (1948) were replaced in January 1966 by fixed fiberglass-reinforced polyester panels 10 mm. thick. After producing 200,000 tons of ordinary superphosphate, the lower part shows wear up to 0.50 m. from the bottom and will have to be replaced.

The exhaust hoods on continuous dens and fume ducts have been fabricated of thermoplastic materials for the last fifteen years. At the beginning, normal rigid PVC was used, or else PVC hooped by fiberglass-reinforced polyester. Such PVC ducts are still in operation in several plants, but in most cases the high gas temperatures of 80 to 90°C, thermal expansion and the silica deposits have led to rather costly maintenance. Presently, the general trend is to use either polypropylene with welded polypropylene stiffeners, or fiberglass-reinforced polyester. In the last case, the inside surface of the wall must be resistant to hydrofluoric acid. For that reason, a Dacron or vinyl mat is used in the resin-rich interior layer, and fiberglass mats and rovings in the outer zone, to give the necessary strength.

Scrubbers

Spray nozzles in old brick or concrete scrubbing towers are now made out of PVC. Spraying or splashing impellers are in PVC, strengthened by glass-reinforced polyester.

In recent plants, solid polypropylene is replacing rubber-lined steel in the construction of scrubbing towers. For instance, in a plant in Rouen, gases flow through two empty spraying towers in series, 1.70 m. in diameter and 5.50 m. high. Both towers are fabricated of 10 mm. thick polypropylene. Fluosilicic acid comes out at 10% concentration, and is used for the manufacture of sodium fluosilicate. Precipitated silica is separated on a continuous vacuum drum filter entirely made of solid PVC.

The Fluosilicic acid tanks are made out of steel-reinforced PVC and the piping of high density polypropylene.

Another plant, which does not recover the Fluosilicic acid, has only one polypropylene tower, built up by winding on a hot cylinder (1.80 m. diameter) an extruded polypropylene ribbon, a part of each turn overlapped by the next.

Steel reinforced PVC is also used for the construction of ducts, scrubbers, and entrainment separators.

This material, which we have already mentioned, is available as plates, obtained by laminating hot unplasticized PVC on both sides of an ordinary perforated steel sheet. According to the manufacturer, these plates have a coefficient of thermal expansion similar to steel and very good mechanical resistance.

Exhaust fans

Fan materials vary from plant to plant. In some cases the fan housing is of rigid PVC, while the impeller is of stainless steel.

In other cases the housing is made out of steel-reinforced PVC.

This PVC with its metallic core is also used for the protection of the fan impeller; plates of this material are cemented and bolted on the ordinary steel impeller. The heads of the screws holding the plates to the steel are protected by PVC patches cemented and welded on them.

In a plant in Balaruc, the housing has been in normal PVC since 1959, while a 1.40 m. diameter ordinary steel impeller, lined with reinforced polyester, has been in service since 1964 and stands up perfectly.

Finally, in a plant in Rouen, the housing is fabricated of polypropylene and the impeller of Uranus B 6.

Stacks

The exhaust stacks are currently made out of PVC, or polypropylene and for greater heights requiring a high strength, of fiberglass-reinforced polyester. Such is the case in a factory in Jugoslavia, where a French manufacturer has supplied a layered polyester stack 2.9 m. in diameter and 23 m. high. Another manufacturer has erected, in France, a stack 1.20 m. in diameter and 40 m. high.

Manufacture and Use of Phosphoric Acid

The field of applications of plastics is even wider than in the case of superphosphates.

a. *Reaction*

Rotary dip feeders for recycled phosphoric acid: rigid PVC.

Mixers for sulfuric and phosphoric acids: polypropylene, fiberglass-reinforced polyester, teflon.

Roof of reacting tanks:

- entirely fabricated of PVC plates stiffened with PVC beams which hang from the structural frame supporting the agitators (Bordeaux 1963). Some panels accidentally broken have been replaced by high impact PVC.
- steel-reinforced PVC, with two inner perforated plates, 10 mm. total thickness, roof diameter 14 m. (Rouen, January 1967). The general behaviour is satisfactory, but the welds are brittle and the underside of the cover became slightly discolored.
- reinforced polyester (17 m. diameter in a factory in Yugoslavia).
- concrete, lined underneath with a PVC sheet, or with a PVC coating applied by spraying, or with a polyester coating.

Exhaust hoods and ducts on the reacting tank:

- normal PVC—PVC hooped by fiberglass-reinforced polyester —polypropylene. Numerous installations (France, Netherlands, Italy, Greece, Morocco, Lebanon, Senegal).

Scrubbing:

- normal PVC: vertical scrubbers (diameter 2 m. and 2.35 m.—height 4.50 m.) in Rouen, Bordeaux, Avignon, with an internal polypropylene perforated tray.
- reinforced polyester, scrubbing tower filled with polypropylene balls between two grids. Diameter: 3 m.—height: 12 m. (Rouen 1965). Wall thickness: 10 to 12 mm. Vinyl mat inside (able to resist HF and H_2SiF_6) After some months of operation, the wall showed some wear in the zone of polypropylene balls. A coating of epoxy resin on polypropylene mat has been applied on the worn part for reinforcement. Since then, the resistance is satisfactory. The polypropylene balls must be replaced every 18 months.

Exhaust fans:

- made out of the same materials as the fans of superphosphate palnts.

Stacks:

- normal PVC—PVC hooped by fiberglass-reinforced polyester —polypropylene.

b. *Filtration*

Slurry pipes: they are usually made out of reinforced rubber hose, but parts of them, such as the elbows, are sometimes in propylene.

Filter feed tank: polypropylene.

Horizontal rotary vacuum filters: the wear plates of the filtrate valve are often made of Keebush G, a formaldehyde phenol resin with a graphite load which makes it self-lubricating. Life: abut 2 years. Teflon is also used.

Vacuum lines:

- normal PVC — high impact PVC.
- PVC hooped by fiberglass-reinforced polyester.

Vacuum filtrate receivers:

- small diameter: thick wall normal PVC (12 mm.) or polypropylene.
- larger diameter: fiberglass-reinforced polyester.

Scrubber before vacuum pump:

- PVC — polyester.

Phosphoric acid pipes under pressure or vacuum:

- normal PVC—PVC hooped by fiberglass-reinforced polyester —high impact PVC.
- solid polyethylene piping has also been used in some plants, but crackings appeared after a period of operation.

Exhaust hoods over filters: PVC — fiberglass-reinforced polyester.

Gypsum disposal pipes: normal PVC — high impact PVC — PVC hooped by fiberglass-reinforced polyester—polyethylene.

These pipes, generally several hundred meters long, and even 7 km. in a factory in Greece, are partly above and partly below ground. The exposed sections, made out of normal or high impact PVC, or reinforced PVC, show a good resistance. On buried sections some failures occurred, due probably to earth moves. High or low density polyethylene is to be preferred in that case.

Expansion joints:

- Expansion joints on phosphoric acid pipes are often Hypalon bellows. To connect gypsum pipes, rubber sleeves protected on the outside by a PVC tube which limits swelling by liquid pressure are often used.

Filter cloths:

Nowadays, filter cloths are most of the time of monofilament polyethylene or polypropylene. Vinyl chloride and Saran are usually no longer used for that purpose.

c. *Evaporation*

Forced circulation phosphoric acid lines:

Fiberglass-reinforced polyester is beginning to be used for this purpose. Pipes of 250 and 350 mm. diameter are used in a Bordeaux factory. The body of the strainer located in the recycling system to stop the big solid particles is also made of reinforced polyester.

Piping to storage of hot concentrated acid: high impact PVC —PVC hooped by fiberglass-reinforced polyester—polypropylene.

Circulating or surge tank for concentrated acid:

In a Bordeaux factory, this tank, 2.5 m. diameter and 1.70 m. high, is made out of 15 and 10 mm. thick polypropylene, with a stiffening steel band halfway from the ground. Acid temperature is 85–95°C.

Vacuum flash head:

In Spain, a French manufacturer has supplied a flash head, 2.90 m. diameter and 8.30 m. overall height, entirely made out of fiberglass-reinforced polyester — 38 mm. thick.

Vacuum condenser: reinforced polyester.

Barometric leg: normal PVC—reinforced polyester.

Vacuum lines:

- between flash head and condenser: reinforced polyester.
- between condenser and vacuum pump: normal PVC — high impact PVC — polypropylene.

d. *Storage and decantation of phosphoric acid*

A French manufacturer has built:

Storage vessels of 4 m. diameter and 4 m. high, of reinforced polyester 7.5 mm. thick, for 60°C acid, and 9 mm. thick for 115°C acid.

Thickeners of reinforced polyester, inside diameter 7.50 m., cylindrical height 7.50 m., contents 300 cu.m., average wall thickness 20 mm. (for a factory in Spain).

Manufacture of Granulated Fertilizers

Here, also, plastics have numerous applications.

Hoppers for raw materials

Internal coating of rigid PVC to facilitate flow of solids.

Vibrating feeders

To avoid sticking, they are coated with PVC (which lasts two years), or with teflon, which is more efficient but weaker.

Granulator inside lining

In a Balaruc plant, the 2 m. diameter ammoniator granulator is coated inside with 3 mm. thick fiberglass-reinforced polyester.

Exhaust hood, ducts, and stacks of granulator, cooler, dryer

According to the gas temperatures and to the required mechanical resistance, these units are built up in rigid PVC, plain or hooped by reinforced polyester, in steel-reinforced PVC, in polypropylene either solid or polyester-hooped, or in reinforced polyester.

Let us remark, by the way, that in a plant without scrubber, the upper outside part of the dryer stack, over the roof, is made out of rigid normal PVC although the gas temperature reaches 100°C.

In another plant, this same part is made out of polypropylene.

Scrubbers

The scrubbers in granulated fertilizer plants use either water when it is only necessary to prevent air pollution, or phosphoric acid when the ammonia must be recovered from the preneutralizers, the granulator and even from the dryer if the fertilizer contains diammonium phosphate.

The following materials are used:

PVC hooped by fiberglass-reinforced polyester for operation at low temperature. For instance, a scrubbing tower in a plant near Avignon has a diameter of 2 m. and is 7 m. high. The inner PVC is 5 mm. thick, as well as the outer polyester reinforced by three fiberglass rovings.

The tower is filled with PVC Raschig rings.

Steel-reinforced PVC:

In a plant in Toulouse, the gases exhausted from the cyclones after the dryer are washed in an impingement-type horizontal scrubber, 2.60 m. wide, 2.90 m. high and 6.10 m. long. The material used is over-chlorinated PVC, reinforced with a perforated steel sheet. Over-chlorinated PVC was chosen on account of its resistance to high temperature (100–110°C).

Polypropylene hooped by fiberglass-reinforced polyester:

Towers of 2 m. diameter and 7 m. high (Rouen) or 3 m. diameter and 13 m. high (Greece) have been built. With this kind of construction, some failures have occurred as the internal polypropylene separated from the polyester, probably because of the considerable difference in thermal expansion.

Reinforced polyester:

Towers of considerable dimensions are fabricated by a vertical winding machine spinning around a fixed mandrel, by a semi-continuous process including successive demoldings. The following have been realized with that process:

In Bordeaux a tower of 4.50 m. diameter, 9.35 m. over-all height and 0.12 mm. thick, the following reinforcing materials have been used, starting from the inside:

• 1 Dacron	150 g/sq.m.	corrosion-proof
• 3 Glass-fiber mats	300 g/sq.m. each	
• 5 Glass-fiber rovings	500 g/sq.m. each	mechanical reinforcement
• 1 Glass fiber mat	300 g/sq.m.	
• 5 Glass fiber rovings	500 g/sq.m. each	

This tower has been constructed close to its final site and moved there, whole, with a crane.

For a plant in U.S.S.R., the same manufacturer has constructed, in his own factory, four scrubbing towers of 7.50 m. diameter and 15.70 m. over-all height, 15 and 18 mm. thick. On account of shipping requirements, it was made in several sections, to be assembled after reaching the ultimate destination.

Weight of each tower: 13.5 tons.

Entrainment separators

Units of this type, installed downstream of some scrubbers, have been made out of PVC, either hooped by reinforced polyester or steel reinforced, or else of fiberglass-reinforced polyester.

Exhaust fans after scrubbers

Same materials used as for superphosphate fans.

Fertilizer Bagging

To reduce the build-up of fertilizer inside the automatic batch scales, several plants use PVC coatings.

In a plant, the discharge doors of the scale buckets are made out of polypropylene. In another plant, the bucket itself is entirely made out of polyester.

In order to improve the sliding of bags on inclined chutes and on plates at the discharge of bag conveyors, rigid PVC or, sometimes, polyethylene coatings are used.

Almost all the fertilizers in Europe are now shipped in 50 kilo bags made out of 15 to 25/100th mm. thick polyethylene sheet. A few years ago, PVC had been tested for this purpose and abandoned, on account of its lack of flexibility at low temperatures.

Conclusion

The use of plastics in the manufacture of fertilizers shows numerous advantages: corrosion resistance, lightness, non-sticking properties, ease of fabrication, easy repairing of thermoplastic and polyester equipment, relatively low cost.

The most economical material is usually plain PVC, which should be used every time the temperature allows it, either the normal impact type, or the high impact type.

With higher temperatures, one has a choice between PVC hooped by fiberglass-reinforced polyester, PVC with internal metallic reinforcement, polypropylene, and reinforced polyester.

Polypropylene units, especially pipes, are usually more economical than reinforced PVC units, on account of the rather high cost of the reinforcement operation.

Process piping and equipment made out of PVC hooped by reinforced polyester are usually cheaper than the same entirely made out of fiberglass-reinforced polyester. In the first case, the resin used is cheaper, since a high chemical resistance is not necessary.

On the contrary, polyester is presently the first choice every time a high mechanical resistance is required, particularly at temperatures over 80°C.

Reinforced polyester may also be used as a lining.

In both forms, reinforced polyester will likely replace more and more rubber coatings, maybe even anti-acid brick linings. If we take into account the phenomenal growth of this material in the past few years, we may guess that it will not be long before phosphoric acid reactors of big capacity are made out of reinforced polyester.

MODERATOR PELITTI: Thank you, Philippe.

The next panel member is R. C. Berry. Bill has an impressive record of experience in the operation and maintenance of fertilizer plants. I first met Bill 10 years ago at the Texas City plant of Smith-Douglass, where we exchanged notes on our respective experiences with pumps for phosphate slurries. Prior to that he had been with Best Fertilizers on the West Coast, and later became the resident engineer at the Illinois Nitrogen plant at Marseilles, Illinois. In 1965 Bill became resident manager of construction for the fertilizer complex which Borden Chemical undertook to build at Palmetto, Florida. He is presently Chief Engineer of the Chemical Division for the Smith-Douglass operation of Borden. Bill will give you an evaluation of materials of construction from the point of view of the plant operator.

Materials of Construction and Plant Operators

R. C. Berry

I would like to discuss with you today, problems of evaluation of materials of construction from the standpoint of plant operators, without attempting to explore in depth or detail specific materials, since there are others on this panel more eminently qualified to do this.

Ours is an emerging industry, in that we do not have the wealth of experience and established processes that some of the older industries, such as the petroleum industry, have at their disposal. In our case, many of the materials of construction are new to their application and, frequently, the success in their use will vary widely from one plant to another. Since the industry is constantly changing, it is incumbent upon those of us responsible for the selection of materials of construction to be as well informed as it is possible for us to be.

It has been said that the half-life of an engineer in these times is approximately 5 years. While the state of our present knowledge of materials of construction may be hard to define, it could be reasonably assumed that some of the materials we are now using may not be applicable 5 years from now. It is also quite possible that new materials, as yet undeveloped, will bring radical changes to the construction of our facilities.

Since both the fertilizer industry and its technology are relatively young, it does not appear reasonable to conclude that only one material of construction is the proper answer for any given application; much experimentation and development are going on at this time which may provide alternate or better answers. From the point of view of the plant operator, the major problem related to development in this field is that of proper evaluation of the new materials as they become available to us.

Several factors govern effective evaluation of materials of construction, and to demonstrate some of these factors I will cite a few instances from my own experience. The first factor I would like to discuss is what I call the foolishness factor. This factor is exemplified by an experience that we had in our Texas City plant approximately 10 years ago. At that time we, like all others in the industry, were having trouble with breakage of evaporator tubes. In an effort to overcome this problem we enlisted the aid of the International Nickel Company to prepare test spools for us, to be installed in the upper liquor chamber of Swenson LTV evaporators. These test spools consisted of some rather exotic materials, untried as yet in phosphoric acid service.

The installation of the test spools was supervised by a young engineer in our organization. After approximately 2 weeks the upper liquor chamber was opened to inspect the spools, and it was found that they had disappeared. Investigation showed that they had deposited themselves in the lower liquor chamber of the heat exchanger, and further investigation revealed that the young engineer had hung the exotic test spools in the chamber with a piece of Type 304 stainless wire which, of course, was less resistant to the environment than any of the materials being evaluated on the spool. This is an example of what I call the foolishness factor.

Variables introduced into the process will sometimes bring about unexpected changes in the corrosion rate of the materials involved. We experienced this in our digestion circuit where, in an attempt to increase our capacity, we supplemented our vacuum cooling with air injection cooling. We began to notice a marked decrease in the corrosion rate of the Type 316 agitator shafts. We concluded that vacuum cooling created an oxygen deficient atmosphere that was detrimental to the oxide film on the stainless steel agitator shaft, and that the addition of air cooling replaced the oxygen that was being removed in the flash cooling process. Whether this analysis is chemically correct or not, we know that it did work, and can only conclude that had we not introduced this variable we would have continued to experience severe corrosion of the agitator shafts.

Another factor in the selection of new materials of construction is the thoroughness with which the evaluation is made and the care exercised to avoid any haphazard type of experimentation. An example of the haphazard type of evaluation occurred some years back when we were considering the use of a new kind of plastic pipe. We had been using lined metal pipe and were experiencing difficulty from external corrosion. The new material appeared to be an excellent solution to this problem and, in an attempt to check its suitability, we installed several spool pieces replacing straight sections of the lined metal pipe. Based upon this rather haphazard evaluation we decided that the new plastic pipe would do the job, and proceeded to make an installation of a complete phosphoric acid evaporator piping system.

Only after placing the new piping in operation did we discover that the fittings had an inherent weakness, and that it was impossible to maintain operation for any reasonable period of time on account of breakage of the plastic fittings. We further found that the fittings were not constructed to ASA Standards and could not, therefore, be readily replaced with rubber-lined steel fittings or other fittings having the necessary strength for the service.

This points out that an evaluation of materials of construction for an integrated system should be extended to all of its components, rather than limited to some sections of it, and related to the actual service to which the system will be subjected.

When new materials are being considered for existing applications, or new applications for available materials, both the user and the supplier have responsibilities for the proper evaluation of the material and the application.

The supplier has a responsibility to state the qualities of his material clearly and honestly. Too often we have all been asked to consider materials that were claimed to be performing miracles in our industry. In reality, only very few new materials have been developed in the last few years that could even come close to being called miracle materials. We have all witnessed the development of fluorocarbons, epoxies, polyesters, and similar materials that have alleviated some of the problems which had plagued the industry. These, however, are for specific applications, and cannot be considered cure-alls. In addition, the more expensive materials must be evaluated from the economic standpoint since, as our industry is constantly revamping and rebuilding facilities, the cost of new materials must be balanced against the expected life of the plant or facility as a whole. Sometimes it is just not economically feasible to apply the more exotic materials to some of the applications in our industry.

The supplier also has a responsibility to provide as much of a system as he is able to do, rather than only component parts, which are often difficult to apply because they are not compatible with other components or materials of construction.

In fairness to the user, the supplier, and the material being evaluated, the supplier also has the responsibility to follow up, to make sure that his material is being properly evaluated and applied. There have been many excellent materials that have been rejected by some plants because of improper evaluation. And when a material that seems to be doing a good job in one plant is found to be totally unsatisfactory in another, it may merely be a case of improper application rather than a real difference in performance.

The user has a responsibility to maintain open lines of communications with the suppliers and to look upon them as a source of information rather than as a nuisance. One of the mistakes that young engineers make is in not taking enough advantage of the knowledge available to them through the sales representatives. With the technology of our industry constantly changing, the specialized knowledge that sales representatives have of their materials and products provides an easy way for plant operators to keep up with new developments and materials.

The user also has a responsibility to the supplier and to his own company to see that the sales representative is placed in contact with the proper man in the user's organization. Too often excellent materials of construction may be overlooked because the vendor does not talk to the man who is thoroughly familiar with the problems, or who has the authority or desire to institute the program of material evaluation.

Cost of evaluation is always a

consideration, since both the supplier and the user are reluctant to spend a great deal of money on it. Many materials potentially suitable for specific applications do not get considered at all, because both parties feel that the other should bear the cost of the evaluation. This is especially true in smaller companies that do not have Research and Development departments.

There is no easy answer to this problem, since both sides have valid arguments. But a joint effort on the part of material suppliers and fertilizer producers, through a panel or committee composed of experts and industry representatives, with the cost borne and the results shared by all participating companies, may provide a solution to the problem of evaluating new materials and products that is both less expensive and more effective.

Regardless of how it is accomplished, it is essential that the strongest possible effort be made to eliminate errors in the selection of materials of construction. With the fertilizer industry becoming more and more competitive, and confronted with steadily rising operating and maintenance costs, only those companies that make a concerted effort to reduce construction and maintenance costs through new and improved methods and materials can be sure to survive and operate successfully. We must all, therefore, direct our efforts toward more effective communications between suppliers and users, more scientific and thorough evaluation of materials, and more direction and purpose toward the growth and maturity of our industry.

Moderator Pelitti: Thank you, Bill.

The last member on our panel is Ken Harrison, Executive Vice President and Director of Acalor Chemical Construction of Canada, Limited.

Mr. Harrison is a graduate of the North Staffs Institute of Technology in the U.K. He is also a member of the National Association of Corrosion Engineers.

After being associated for a number of years with Acalor in the United Kingdom as Chief Engineer, where he gained extensive experience in the development and application of linings, Mr. Harrison formed the Canadian company, and has been responsible for the development of many of the Acalor lining systems.

He will talk to you about custom linings for reaction vessels in fertilizer plants. Acidproof membranes and carbon brick linings are his specialty.

Developments in Attack Tank Linings

K. Harrison

Broadly speaking, reinforced concrete has for some time been lower in cost than steel for large tanks; hence a large number of wet process phosphoric acid plants built in recent years have used Attack Tanks with a concrete shell. For corrosive service, however, concrete requires a protective lining.

The selection of lining materials which can give long life and low maintenance at an economic level is not an easy task, especially under the conditions prevailing in the digestion of phosphate rock, which combine temperatures in excess of 180°F, a mixture of highly corrosive acids, plus a fairly high degree of abrasion.

For other process tanks in the system, a natural or synthetic rubber lining, or one of the plastics (such as PVC) is adequate without brick sheathing, providing the correct grade is selected and properly applied. However, the elevated temperatures, acids, abrasion and risk of physical damage during maintenance, occurring in a reactor make a brick lining or sheathing essential.

The brick sheathing, does:

a. Provide thermal insulation barrier for the membrane.
b. Protect the membrane from physical damage.

Components of the Lining System

The most economical lining material which will resist hydrofluoric, as well as the other acids, in phosphate rock digestion is carbon brick. Silica based materials will, of course, be severely attacked by fluorides, even at extremely low concentration. The corrosive effect of HF is cumulative and even with materials of very low absorption ultimate disintegration is certain.

Carbon Brick

Carbon bricks set in a well formulated furane phenolic resin cement, with pure carbon fillers, are in common use and do provide excellent service life.

Several years ago, it was considered necessary to use carbon bricks with very low ash content, that is 1% or less. However, experience has shown that carbon bricks with very low ash content, 7% will resist the fluorides present in the slurry with no evidence of deterioration, with the added advantage of improved resistance to abrasion. Consequently, we now favour the high ash content brick, which are less expensive.

This type of lining has been installed in several large tanks, and in some cases with a thickness on side walls of only 2½″. Total area covered has ranged from 10,000 to 30,000 sq. ft.

Performance has been excellent, with no sign of fluoride attack and minimal wear due to abrasion after several years of service.

In that carbon bricks have a fairly high absorption, up to 20% by weight, an impervious membrane between the bricks and concrete is always required. Even if impervious bricks were used, a membrane would still be essential, as it is a practical impossibility to install a lining which involves from 40,000 to 120,000 pieces jointed with a resin mortar, without some minor cavities or hair line cracks.

Membranes—Asphaltic Base

The most frequent cause of leaks or failures in Attack Tank linings has always been the membrane. It is annoying and time consuming, and an extremely expensive proposition, to remove and install a perfectly good carbon brick lining in order to repair or replace the membrane.

Earlier practice for concrete vessels was to use hot applied asphalt, about ¼″ thick; it is still specified today for some applications. The alternate was a sheet material, manufactured from petroleum tar and reclaimed rubber.

Both materials have been fairly successful, but have the disadvantage of being difficult to apply, which makes them quite expensive in terms of labor. This is particularly true with hot applied asphalts, because of the difficulty of building up the required thickness on large vertical surfaces. To give body and strength to the membrane, layers of fiberglass mesh were introduced.

In wet process phosphoric acid Attack Tanks, this method is not recommended, because if any part of the fiberglass is exposed or insufficiently covered with the asphalt it will be attacked by the fluorides. The risk of failure is then very great, because the acid attack will progress through the fiberglass mesh by what can be described as "wick action."

Rubber Lining

Natural gum rubber is an ideal membrane material for Attack Tanks because of its excellent resistance to the acids present in the reaction. Application and vulcanization of rubber in sheet form to large concrete surfaces, however, is extremely difficult, and the costs are prohibitive.

The logical answer was to spray what can best be described as a semi-vulcanized dispersion of natural gum rubber. The big problem to overcome was the spraying technique, which involved finding the correct temperature, ventilation and method of heating the air in the vessel, as well as obtaining the correct temperature of the substrate. This we overcame, but most important of all, the finished product is only slightly more expensive than the types of membrane already mentioned, and without the attendant risks of an early failure.

The system is essentially an underlay coat, based on natural rubber latex mortar ⅛″ thick, followed by the sprayed natural rubber also ⅛″ thick. It can be (and often is) applied to "green" concrete.

Our first large installation in an Attack Tank was for the Western Co-op. Fertilizers plant in Calgary, Alberta. It is of interest to note that three sides of this particular tank are exposed to the severe winter climate in Calgary. The fact that this particular membrane can be physically stressed between −40°F and +185°F removes any risk of failure should temperature cracks develop in the concrete. At temperatures up to 120°F it can be elongated to three times its original length. This would suggest that for future installations in cold climates, it is not essential to enclose the Attack Tank in a building.

Our next applications were on multi-compartment concrete tanks, of which we have now done five on this continent. The more complex design of the vessels and the multiplicity of the surfaces to be protected provided a strong incentive to develop a conductive underlay between the concrete and the sprayed rubber, so that electrostatic spark testing could be performed before the brick lining was installed.

The technical difficulties in terms of correct formulation, and selecting of a conductive component, to ensure successful field application in large areas without shrinking or cracking, and providing of a suitable substrate and bonding medium to ensure good adhesion of the sprayed rubber were of considerable magnitude, but eventually we were able to overcome them. Spark testing can now be performed with conventional equipment set at 15,000 volts.

Our first installation using the conductive system was at the Electric Reduction Company fertilizer plant at Belledune, New Brunswick. The technique was also used at the Imperial Oil plant at Redwater, Alberta, and will be applied in a new large plant in Iran.

Monolithic Linings

While the rubber membrane-carbon brick system provides a satisfactory answer to the problem of protecting the inside surfaces of large concrete reactors, its cost is relatively high. Can an alternate system be developed to provide equal performance, but at a lower cost?

To the layman, a monolithic lining would appear to provide a logical answer. For example, filled trowelled-on epoxy resin materials are in wide use for protection of concrete floors, up to a thickness of ¼″. Protection requirements for process vessels, however, are much more stringent, as the consequences of lining failures are infinitely more costly.

Let us consider the problems and prospects of development of a monolithic system for large concrete digestion vessels.

The essential porperties required by such a system are:

1. To resist various combinations of highly corrosive acids, up to temperatures of 200°F for indefinite periods.
2. Resist abrasion.
3. Have the ability to bridge contraction cracks which may develop in the concrete shell. Hence, it must be, and remain, flexible.
4. Have a co-efficient of linear expansion approximately equal that of concrete.
5. Must not creep, shrink or swell due to the operating conditions, or other factors, otherwise structural failure of the lining may occur.
6. Be easily applicable.
7. Be easy to patch in worn areas.
8. 100% impermeable.
9. More economical than membrane and carbon brick system.

As none of the materials presently available for monolithic linings is expected to be superior to carbon brick, we may start with the assumption that about the same thickness as for carbon brick will be needed for a given set of conditions.

Assuming that all requirements except #9 are met, let us take a look at the cost that must be met for the material.

A lining sytstem based on 3″ carbon brick set in resin cement, over a ¼″ membrane, will have a finished thickness of 3⅜″, and weigh 30 lbs/sq.ft. Installed cost, including labor and supervision, and freight to job site (1300 miles), is about $13/sq.ft.

A carbon filled resin cement applied at the same thickness would weigh 25 lb/sq.ft. and its installed cost would be about $18/sq.ft. for furane and $19/sq.ft. for epoxy. This is $5.00 to $6.00 per square foot more than the rubber-carbon brick system.

For a monolithic lining to be attractive, I would suggest that it should cost about 20% less than the carbon brick system. This means that material costs, taken at 50% of the installed cost, should be in the order of 20 cents per pound. This is way below current prices of available resins and fillers which would be suitable for the conditions of this application. Furthermore, we have not yet found all the answers to the technical requirements.

Therefore, even aside from the technical problems which have yet to be solved, we have to conclude that monolithic linings are not yet a substitute for the conventional membrane and brick sheathing system on the basis of cost.

MODERATOR PELITTI: Thank you, Ken.

The panel is now open for questions from the audience.

RONALD D. YOUNG: Rico, I was going to ask the panel what is really the present feasibility of lining non-pressure vessels with an alloy such as Hastelloy or titanium? What are some cost comparisons?

MODERATOR PELITTI: Let me see, your question refers to the lining of non-pressure vessels?

MR. YOUNG: Yes, just regular reaction vessels.

MODERATOR PELITTI: Reactor vessels with titanium, or with any of the more expensive alloys. Are you referring to a sandwich type construction or a clad type construction?

MR. YOUNG: Either clad or lining, just some means to use these materials at a lower cost.

MODERATOR PELITTI: I believe that the cladding of carbon steel with stainless steel has been considered in a number of cases, and there have been some applications in the phosphoric acid field. Unfortunately, I personally do not have any report on the results that have been obtained with it, or a later history of what has developed in these plants.

I believe there has been a great deal of reluctance to accept the type of construction indicated, because frequently there is no warning of impending failures. If you have a thin layer of a protective material, subject to show any amount of corrosion, then as soon as you go through it you might lose the whole reactor and shut down the plant with serious losses. Therefore, the economy of construction derived from the clad type material does not appear to be too attractive to anybody, at least on an extensive basis.

I might turn this over to Allen. Do you have any comment?

MR. E. A. TICE: I might make a couple of comments. As Rico said, the stainlesses are available as clad plate. For example, Lukens Steel Company offers a range of stainless steels for cladding on steel.

Usually we like to see these applications go for those materials where the rate of corrosion of the stainless is quite low, so that you don't corrode through and have failure of the entire unit.

Specifically, the Hastelloys I do not believe are available yet as clad material on steel. I don't think that Lukens have, for example, developed the technique of cladding Hastelloy C on steel. Perhaps Hastelloy G may fit in here, but we have to have some markets for the material before a steel company such as Lukens will undertake to develop the cladding technique.

Titanium can be applied by the new explosive bonding technique, which Du Pont has come up with. This is a rather expensive way to put materials together but there are definite applications, for example, bonding titanium to thick steel. We think of rather thick applications of steel and a very thin layer of the alloy for this explosive bonding technique to be economical. Some very thick tube sheets have been made this way, for example.

You can weld overlay also, as another technique. I believe in some of the urea reactors where stainless has been used, the heads have been applied by weld overlay techniques, and some of the major fabricating companies have procedures for putting down weld overlay in a multipass technique.

MODERATOR PELITTI: Okay. Now your question.

A MEMBER: I should like to add regarding the cost of the various alloys that show high resistance that, of course, the use of any alloy has to be related to its expected life; and are these two alloys justified, considering their price?

MR. TICE: It is a good question. I think we have to, again, weigh the particular application. The Jessup Alloy may sell at a price, and I would not like to be quoted — of the order of $1.65 a pound, as a base price for plate material. Now, this is more than 316 stainless, but undoubtedly there are going to be some applications where it can be justified. Perhaps the components in attack tanks, or agitator equipment might provide applications where this can be justified.

I think the Hastelloy G and the Inconel 625 alloys that I mentioned are even more expensive. Hopefully, if we go through the procedure that Bill Rushton would like us to follow to evaluate the evaporator tubing, and we hope to do this, we may be able to justify the economics of these alloys here.

But it is always a problem. I do not have the answer, I'm sure.

SAME MEMBER: What is the cost factor between, say, a 316 alloy and Hastelloy G?

MR. TICE: I don't know. I don't have these in my head. I think it's about 3 or 4 to 1.

A MEMBER: I have a question for Mr. Tice of INCO. In high nickel alloys is there any correlation between the molybdenum content and the pitting type of corrosion?

MR. TICE: Did I understand you, do I have any correlation between pitting —

SAME MEMBER: And the molybdenum content.

MR. TICE: — and the molybdenum content? We are trying to evaluate pitting resistance. We don't really have a good laboratory test. We have tried to use a ferric chloride solution and a crevice.

For example, a rubber band put around the specimen gives you a nice crevice, to assess the alloy behavior versus pitting resistance in ferric chloride.

Another good solution for pitting is aerated seawater, and we have subjected all of these new alloys to long-time exposure at our test location in North Carolina. In aerated seawater we will get barnacle growth, which gives us lots of chances for pitting to occur.

We find that when we get up to this Inconel 625 composition of about 9% molybdenum we have freedom from pitting.

So I think in the chrome-nickel system at about 9% molybdenum we have freedom from pitting, at 4 to 5% we can still get some pitting.

THE SAME MEMBER: With 317 stainless normally it is 3 to 4%.

MR. TICE: Did you mention 317?

SAME MEMBER: Yes.

MR. TICE: It can still pit in seawater and in the ferric chloride test, at least in the work we have done. It's a lot better than 316 but not completely immune.

SAME MEMBER: Another question is about the wrought alloys. What would you consider as a minimum hardness to insure moderate resistance to erosion?

MR. TICE: I don't know that I can give you a number.

SAME MEMBER: I have another question directed to Mr. Rushton of Swenson.

You mentioned a while ago that the temperature resistance of natural rubber lining in evaporators and the hopper usually ranges around 200 degrees, so you are limited. Is it possible just to use a better heat resisting rubber; for instance, butyl rubber for the hopper lining and increase your temperature so you can get more effect of the evaporation?

MR. RUSHTON: Evaporation systems generally operate under vacuum, and to date the rubber liners at least have been hesitant to apply butyl linings, or any of the synthetic linings, under the vacuum conditions that exist there. Their bond strengths I don't believe are good enough yet to allow use in this sort of vessel. The vacuum would tend to pull the rubber off the steel.

SAME MEMBER: You mean, the bonding is never as good as for natural rubber? The bonding between the metal and the rubber?

MR. RUSHTON: The bond between natural rubber and steel is an excellent bond, yes, and it is better than it is for the synthetic rubbers.

MODERATOR PELITTI: If there is no further discussion, I would like to thank both the audience and our panel members for their cooperation and if anybody can think of additional questions where they wish to obtain more precise answers, as always happens after the meeting, all of the panel members will be happy to be available for discussion outside the meeting room.

I would like to remind you that if we have time, and this is up to Dr. Sauchelli, there will be a movie shown immediately following the meeting.

I would now like to turn the meeting over to Dr. Sauchelli.

CHAIRMAN SAUCHELLI: Thank you, Enrico. How long will that take?

MODERATOR PELITTI: About 15 minutes.

We can dismiss the group, and those who really want to stay to see this movie, which I understand is a very interesting and valuable one prepared by Mr. Moraillon, may remain here.

You have been a very patient audience.

(The Session adjourned at five-fifteen o'clock p. m.)

Thursday Morning Session, Nov. 14, 1968

The Round Table Meeting reconvened at 9:00 o'clock a.m.
Albert Spillman and Vincent Sauchelli, Moderators

MODERATOR SAUCHELLI: Before we start our regular proceedings, it is a pleasure to call your attention to Mr. Edwin Wheeler, the new President of the National Plant Food Institute. Mr. Wheeler.

MODERATOR SAUCHELLI: Ed, do you want to make any remarks?

MR. WHEELER: Vince knew he was safe in calling on me because I don't have any notes or any speech prepared. I am glad to see you. As you know, this is my first time attending the Round Table. I know something about its function and I know a good deal about its importance to our industry. I hope that while you are here you will feel free to drop by our shop. We are busy with some changes being made in the Institute and apparently there are more changes in the wind than on some of the slides I saw yesterday. Thanks very much, Vince, for giving me a chance to say hello.

MODERATOR SAUCHELLI: Thank you. We are glad to have you here. Al, the meeting is yours.

MODERATOR ALBERT SPILLMAN: Good morning, gentlemen. I hope all of you will have a nice stay in Washington and we hope you enjoy our program.

This morning we have a full program with some very interesting subjects; Improvements in Mixing Plants, Efficiency of Bulk Blend Mixers, High Efficiency Bulk Storage, Improvements in Bagging Systems, we have two papers on Improvements in Bagging Systems, Elemental Phosphorus Production and Usage, and a very important subject, Safety in the Fertilizer Plant.

Our first discussion this morning is titled "Mixing Efficiency of Fertilizer Bulk-Blending Equipment." This paper was prepared by G. L. Bridger and I. J. Bowen, Georgia Institute of Technology. It is my pleasure to present to you our good friend Dr. Leon Bridger, Director, School of Chemical Engineers, Georgia Institute of Technology, Atlanta, Georgia, who will discuss and present this subject. Dr. Bridger, please.

Mixing Efficiency of Fertilizer Bulk-Blending Equipment

G. L. Bridger and I. J. Bowen*

Summary

Tests were made of the efficiency of mixing of fertilizers in six bulk-blending plants and of one pilot plant scale mixer. The plant scale mixers tested were a cylindrical rotary mixer, a concrete mixer, a ribbon mixer, a vertical tower mixer, a cone mixer, and a screw mixer. The pilot plant mixer tested was a Munson rotary mixer. Mixing efficiency was judged by deviation from average analysis of a series of samples taken during discharge of the mixer.

Best mixing was achieved by the screw conveyor mixer, which is a continuous mixing unit, but proportioning of the raw materials was poor, so that the product was badly off specifications (17-18-11 instead of 15-15-15). The Munson rotary, cylindrical rotary, and ribbon mixers gave good mixing. The concrete, cone and vertical tower mixers gave poor mixing, and sample analyses varied excessively from beginning to end of the discharge period.

Introduction

Bulk blending of fertilizers has grown to be a major segment of the industry in the past few years. It was estimated that there were 1,536 bulk blending plants in the United States in mid-1964.[1]

The equipment used in bulk blending plants for mixing fertilizer materials is of many types; a wide variety of both batch and continuous systems is used. It is recognized that differences in mixing efficiency of the various types exists, but little quantitative information is available on this subject.

It has been shown that if fertilizer raw materials of the same particle size range are well mixed, little segregation will occur even if the materials are of different densities and shapes.[2] However, if the particles differ significantly in size, segregation can take place during discharge from the mixer and in subsequent handling.

There are, therefore, two problems in producing and delivering to the soil a homogeneous bulk blend fertilizer, (1) obtaining good mixing at the point of production, and (2) prevention of segregation of the fertilizer components in subsequent handling.

The present study was undertaken to determine the ability of several types of mixers being used in commercial operations to produce a homogeneous bulk blend fertilizer. Study of the degree of segregation in subsequent handling was beyond the scope of the present investigation.

To accomplish this objective, large batches of specially sized ammonium nitrate, high analysis superphosphate, and potassium chloride were prepared at the TVA chemical plant at Muscle Shoals, Alabama. The particle sizes were chosen so that there were slight differences between each of the three materials, but not enough to prevent a homogeneous mix to be made and discharged from the mixer without excessive segregation. The materials were bagged and a total of two tons sent to each of various mixing plants in the Southeastern United States. Two one-ton mixes were made at each of the plants, except when a continuous system was used, in which case a single two-ton run was made. A series of samples was taken at the mixer discharge at equal time intervals over the entire discharge period. The samples were analyzed for N, total P_2O_5, and K_2O, and the variations in analysis were used to judge the effectiveness of mixing.

Experimental

A. Materials

Table I shows screen analyses and chemical analyses of the raw materials.

B. Description of Mixers

1. Cylindrical Rotary Mixer

This mixer was cylindrical and had the following dimensions: diameter = 78 inches, length = 32 inches. It had a 1-ton batch capacity and operated at a speed of 12 RPM.

The rotary mixer was on two wheel drive rubber-tired trunnions which provided the rotary motion for the cylinder. The interior discharge was actuated by air operated controls.

The raw materials were conveyed by payloader to a weigh hopper which discharged into the 1-ton rotary mixer. The blended fertilizers were then discharged from the mixer into an elevator which conveyed the blend into a truck outside the building.

2. Concrete Mixer

The concrete mixer was a 2-ton rotary batch type with a fixed, inclined axis and helical flights. With mixers of this type, which

Table I. Screen and Chemical Analyses of Materials

Screen Analyses (Tyler)

Material	% by Weight (Cumulative)							
	6	8	10	12	14	16	20	-20
Ammonium nitrate	0.1	[illegible]	[illegible]	92.3	96.3	98.4	99.4	0.6
Granular high-analysis superphosphate	0	[illegible]	[illegible]	61.5	78.0	88.6	94.7	5.3
Potassium chloride (red granular)	0.3	[illegible]	[illegible]	[illegible]	87.8	91.4	94.3	5.7

	% by Weight of Screen Fraction							
	+6	-6+8	-8+10	-10+12	-12+14	-14+16	-16+20	-20
Ammonium nitrate	0.1	[illegible]	[illegible]	[illegible]	4.0	2.1	1.0	0.6
Granular high-analysis superphosphate	0.0	[illegible]	[illegible]	[illegible]	16.5	10.6	6.1	5.3
Potassium chloride (red granular)	0.3	[illegible]	[illegible]	[illegible]	[illegible]	3.6	2.9	5.7

	Chemical Analyses, % by Weight						
		P_2O_5					
	N	Total	C.I.	W.S.	F.A.	K_2O	H_2O
Ammonium nitrate	[illegible]	----	----	----	----	----	----
Granular high-analysis superphosphate	----	[illegible]	1.6	[illegible]	[illegible]	----	0.9
Potassium chloride (red granular)	----	----	----	----	----	59.8	----

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* Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia.

are similar to those used on concrete ready-mix trucks, the blend was discharged by reversing rotation; this caused the helical flight to move the blend upward and out of the mixer. The mixer was charged by gravity flow from a weigh hopper. It discharged through a chute which conveys the blend to a bucket elevator which conveys the material to another chute and then to the truck.

The geometry of the mixer was comparable to a frustum of a cone with a small diameter of about 3 feet and a large diameter of about 6 feet. The mixer was positioned horizontally with its axis slightly inclined, the center of the large end was about 20 inches lower than the center of the smaller end. The mixer working capacity was 2 tons. The drum speed was 14 RPM.

3. Ribbon Mixer

The ribbon mixer had a 1-ton capacity. It had a U-trough design and a total internal volume of about 50 cubic feet. Overall dimensions were 30 inches wide by 38 inches high by 9 feet 10 inches long. The unit had two multiple ribbons blending flights with a double extra heavy pipe and trough of steel. The blender gate was located at one end and was air operated.

Fertilizer materials were conveyed to the mixer by payloader. The mixer was located on weighing scales which were adjusted to zero after each mix. Mixing was accomplished by the rotating spiraling motion of the ribbon blades and the mix was discharged at one end of the blender through the hydraulically operated discharge gate. From here it fell by gravity to a screw conveyor where it was conveyed to bucket elevators and to a discharge chute to a truck.

4. Vertical Tower Mixer

This mixer was developed by TVA and is described by Achorn and Meline.[3] The tower, which is made of wood, is 4 feet square by 28 feet high. The top 4 feet is used as a collecting hopper. The floor of the hopper is in the form of a trap door. The lower 24 feet of the tower serves as a mixing section and is provided with five baffles. Two diagonal flights extend across each baffle. In operating the tower, the raw materials are weighed and then elevated to the retaining section with the gate closed. When all the materials have been added, the gate is opened, and the mixing of the materials is accomplished as they pass over the steps and flights of the tower. This system is designed for the weighing and mixing of 1-ton batches of fertilizer. Production rates of 14 tons per hour may be obtained with it.

5. Cone Mixer

The cone mixer had a capacity of one ton. From overhead storage bins, raw ingredients were gravity fed into a weigh hopper. The raw mix was then belt conveyed to bucket elevators which conveyed it to a vibrating conveyor. The material flowed to the cone mixer by gravity around the upper inverted cone and to the closed top gate. The mix was retained momentarily at this point. The top gate was opened and the material flowed around the middle inverted cone to the bottom gate which was closed. After a momentary retention the bottom gate was opened and the material flowed around the bottom inverted cone and out the discharge chute to a truck.

Mixing was accomplished as the fertilizer materials flowed over and around three inverted cones.

6. Screw Conveyor Mixer

The screw conveyor mixer had specifications as follows:

size—12 feet long by 5 feet wide by 7 feet high
weight—4,000 pounds
belt—endless, 5 ply, extra-heavy duty
motors—belt motor is 2 HP; double gear head auger motor, 1½ HP
auger—specially designed mixing unit.

The screw conveyor mixer had a capacity of producing 20 tons of blend per hour. A master control panel electronically activated the motors to elevate the raw ingredients to overhead bins, operate the mixer and re-elevate the finished product.

Raw ingredients from overhead bins fed into the sloping floor of the blender under the gates onto the endless rubber belt. A baffling system, plus a mixing auger blended the fertilizer. The blended material was then transferred to truck or was bagged.

Prior to mixing, the bulk densities of the raw materials that were used in the test were determined so that the feed gates could be set. The bulk density of the ammonium nitrate, superphosphate and potassium chloride were 55.0, 64.2, and 67.2 pounds per cubic foot, respectively.

7. Munson Rotary Mixer

This mixer operated at a speed of 20 RPM and had a 15 cubic foot capacity. It was mounted in a horizontal position. Its geometry can be described as a cylinder joined by a cone frustum closure on one end and a hemispherical closure on the other end. The diameter of the drum was 42 inches and the overall length was about 36 inches. The mixer was operated by a gear at one end connected by a shaft driven to an electric motor. It was charged through a door located on the cylindrical part of the drum. It discharged through a manually operated door located on one end of the mixer. No tilting of the mixer was necessary during discharge, because the internal blades move the mix up and out through the opening of the discharge end. The size of batch used in this mixer was 500 pounds.

C. *Test Procedures*

1. Mixing

(a) Two batches were made in most tests. Each batch weighed 1,975 pounds, except for the pilot plant scale mixer test.

(b) The following amounts of raw materials were used:

Raw Material	*Amount, Pounds*
Granular Ammonium Nitrate (33.4-0-0)	900
Granular Superphosphate (0-52.4-0)	575
Granular Red Potassium Chloride (0-0-59.8)	500
Total:	1,975

These proportions of materials would result in a mixed fertilizer of the following analysis, based on the analyses of the materials:

N	15.2%
Total P_2O_5	15.7%
Available P_2O_5	15.2%
K_2O	15.2%

(c) The mixer was charged with raw materials and operated for one minute, except in the case of the ribbon mixer, which was operated for five minutes.

2. Sampling

(a) A small quantity (about 100 grams) of each raw material was removed from each bag used in the test and placed in separate containers. When samples were collected from the raw materials of both mixes they were riffled into two quart samples, placed in moisture-proof containers and identified. This constitutes a composite sample of each raw material representative of the two mixes.

(b) Ten-quart buckets were used to collect 20 samples (or as many as practical) from the mixer discharge of each test mix. In most cases, two quarts of blend per bucket were collected from the discharging stream of blend. The samples were collected at timed intervals from the start of discharge to the end of discharge.

When all of the samples were collected from a test mix each was riffled into two quarts, placed in moisture-proof containers and identified. This operation yielded identical samples, one of which was used for chemical analysis and one of which was placed in reserve. Forty quart samples were obtained when all 20 samples were riffled.

3. Sample Preparation

(a) One quart-size sample was ground in the Mikro-Samplmill in half-quart batches. An 0.039 inch round hole screen was used in the mill during grinding. After grinding the two batches were combined and riffled to a 2-ounce sample. This sample was placed in a moisture-proof container and identified. This operation was performed as rapidly as possible to avoid moisture absorption by the sample. The mill was thoroughly cleaned after each grinding to avoid contamination of the next sample to be ground.

4. Chemical Analyses

Standard AOAC procedures were used to determine nitrogen, total P_2O_5, and K_2O. Listed below are the methods used.

(a) *Nitrogen.* Devarda Method — official. Paragraph 2.053, page 17, Association of Official Agricultural Chemicals, 10th edition, 1965.

(b) *Total* P_2O_5. Volumetric Ammonium-Molybdate Method—official. Paragraph 2.026, 2.027, 2.028, page 13, Association of Official Agricultural Chemicals, 10th edition, 1965.

(c) K_2O. Volumetric Sodiumtetraphenylboron — official. Paragraph 2.083, 2.084, 2.085, page 23, Association of Official Agricultural Chemicals, 10th edition, 1965.

Results and Discussion

A. Interpretation of Results

The following method was adopted to analyze the results from the tests. The deviation of each plant nutrient determination from the average was used as a measure of the failure to achieve perfect mixing of a single sample. Although this deviation also reflects variations due to sample preparation and analytical error, it is believed that the latter are relatively small compared to variations due to imperfect mixing.

The average deviation for each plant nutrient for an entire test indicates the probable difference between a sample taken at random during the discharge of the mixer and the average composition of the entire batch. The average composition of the test batch may be in slight error since the individual samples do not represent precisely the same fraction of the total batch, but since the number of samples is large this error is probably small.

Plots were made of the deviation of each determination from the average versus sample number to show any trends in variation in analysis during the discharge period. A flat curve would indicate no variation in composition from beginning to end.

Screen analyses were made on each sample and these were averaged for each particle size range. Weighted screen analyses for each particle size range were calculated from the screen analyses of the raw materials and compared with the averages of the mixture samples to determine whether degradation took place in mixing.

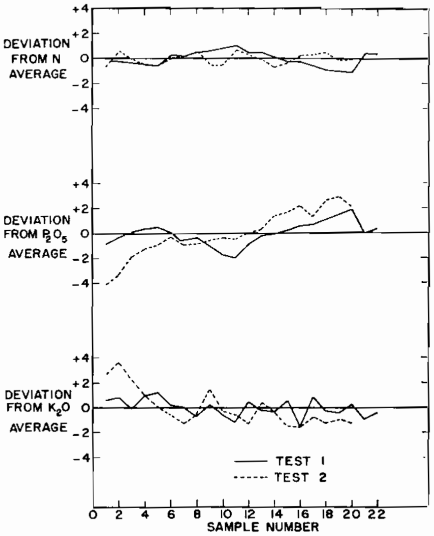

Figure 1
Cylindrical Rotary Mixer Tests

B. Cylindrical Rotary Mixer Tests

The results of the cylindrical rotary mixer tests are shown in Figure 1. Average deviations were greatest for total P_2O_5 (0.70 to 1.49), less for K_2O (0.59 to 1.07), and lowest for nitrogen (0.52 to 0.32). Analyses of individual samples ranged from 15-12-18 to 15-18-14. There was a slight trend for P_2O_5 content to increase as discharge proceeded. There was no degradation in particle size.

This mixer did a good job of mixing on the whole.

C. Concrete Mixer Tests

The results of the concrete mixer tests are shown in Figure 2. Average deviations were rather large (1.17 to 2.15). There was a very pronounced increase in P_2O_5 content as discharge proceeded, with corresponding decrease in

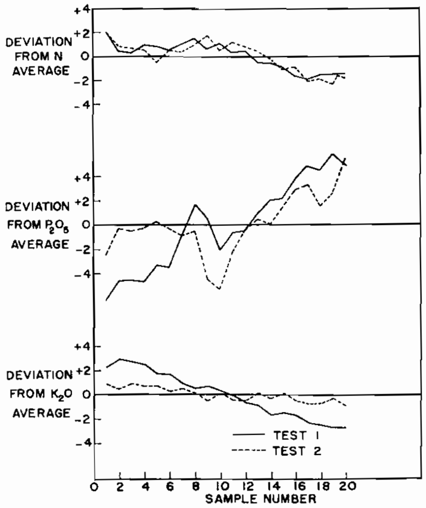

Figure 2
Concrete Mixer Tests

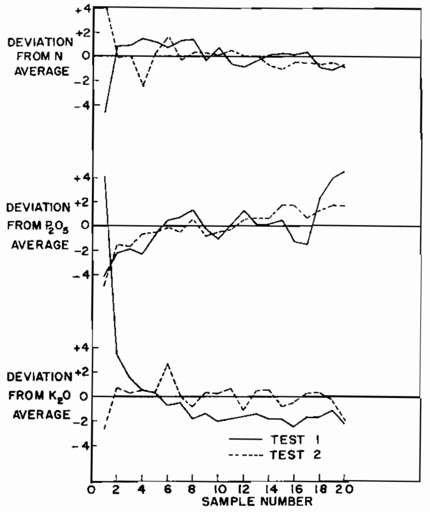

Figure 3
Ribbon Mixer Tests

N and K_2O. Individual samples varied from 17-13-17 at the beginning to 14-23-12 at the end. Screen analyses showed no significant degradation in particle size during mixing.

Mixing in this unit must be rated as poor.

D. Ribbon Mixer Tests

The results of the ribbon mixer tests are shown in Figure 3. The average deviations were large (0.76 to 2.43). Except for the first and last samples, there was no pronounced trend in sample analysis as discharge proceeded. Individual sample analyses ranged from 10-11-33 to 13-20-13. Screen analyses showed no appreciable degradation.

Mixing in this unit was considered good.

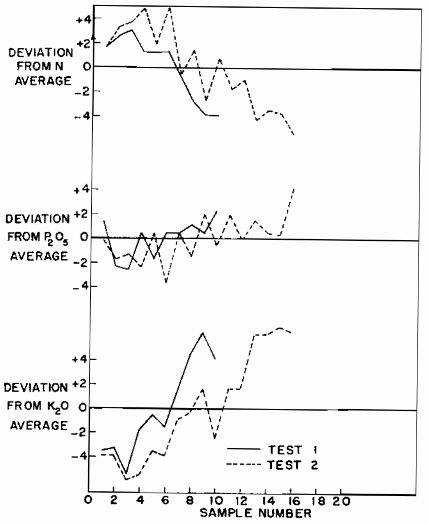

Figure 4
Vertical Tower Mixer Tests

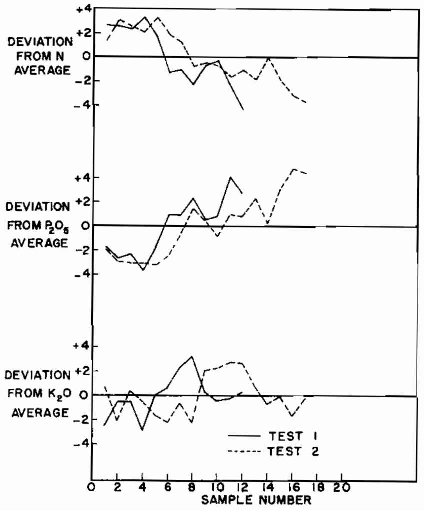

Figure 5
Cone Mixer Tests

E. Vertical Tower Mixer Tests

The results of the vertical tower mixer tests are shown in Figure 4. Average deviations were greater than for any other mixer tested (1.33 to 3.78). There were pronounced trends in all three nutrients as discharge proceeded. Analyses of products ranged from 15-17-12 to 8-20-22. There was no appreciable degradation in particle size.

The mixing in this unit must be rated as poor.

F. Cone Mixer Tests

The results of the cone mixer tests are shown in Figure 5. Average deviations were large (1.17 to 2.15). There was a pronounced decrease in N content and a corresponding increase in P_2O_5 content as discharge proceeded. Analyses of products ranged from 17-13-13 to 11-20-15. There was no appreciable degradation in particle size.

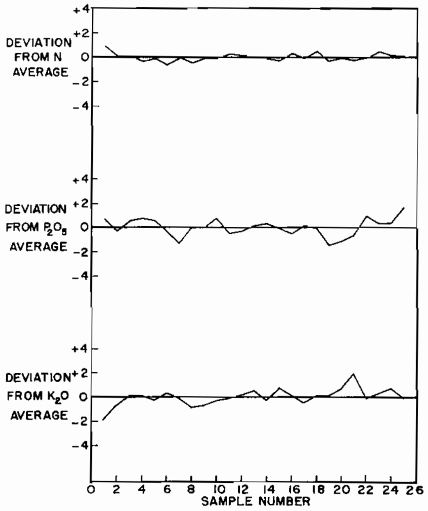

Figure 6
Screw Conveyor Tests

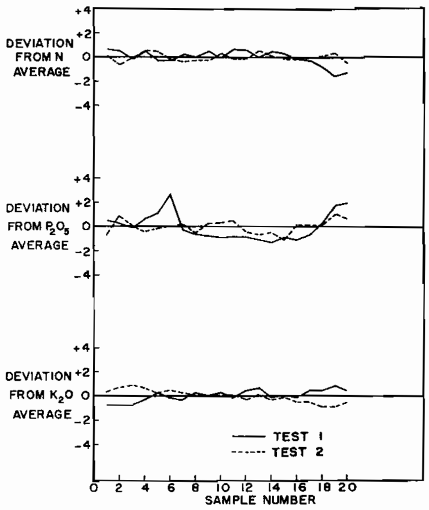

Figure 7
Munson Mixer Tests

Mixing in this unit must be rated as poor.

G. Screw Conveyor Mixer Tests

The results of the screw conveyor mixer tests are shown in Figure 6. Average deviations were the lowest of all tests made (0.23 to 0.59). There were no pronounced trends in plant nutrient content. The composition of the product was very uniform from beginning to end of the mixing period, but the average analysis was 17-18-11, indicating that proportioning of raw materials was poor. This was borne out by the fact that the ammonium nitrate and superphosphate bins were emptied before the potash bin, and sampling was stopped when all three materials were no longer being fed into the mixer. Screen analyses showed no degradation of materials.

It must be concluded that whereas uniformity of material feed rates and mixing in the screw conveyor mixer were very good, the raw materials proportioning was poor.

H. Munson Rotary Mixer Tests

The results of the pilot plant Munson rotary mixer tests are shown in Figure 7. Deviations from average analyses were low (0.27 to 0.93). There were no pronounced trends in sample analysis from beginning to end. The average product analysis was about 14-17-15. There was no appreciable

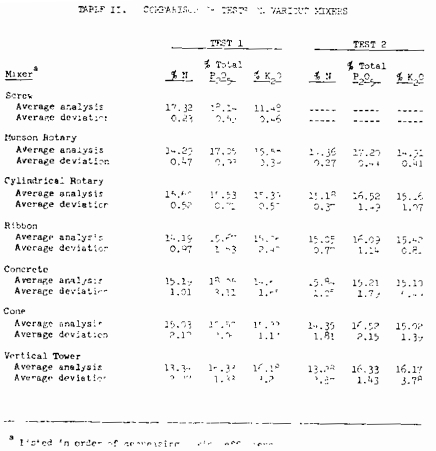

TABLE II. COMPARISON OF TESTS OF VARIOUS MIXERS

Mixer[a]	TEST 1 % N	TEST 1 % Total P_2O_5	TEST 1 % K_2O	TEST 2 % N	TEST 2 % Total P_2O_5	TEST 2 % K_2O
Screw						
Average analysis	17.32	[illegible]	[illegible]	-----	-----	-----
Average deviation	0.23	[illegible]	0.46	-----	-----	-----
Munson Rotary						
Average analysis	14.29	17.25	[illegible]	[illegible]	17.20	[illegible]
Average deviation	0.47	[illegible]	[illegible]	0.27	[illegible]	0.41
Cylindrical Rotary						
Average analysis	[illegible]	[illegible]	[illegible]	[illegible]	16.52	[illegible]
Average deviation	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.07
Ribbon						
Average analysis	14.19	[illegible]	[illegible]	15.05	16.09	[illegible]
Average deviation	0.97	[illegible]	[illegible]	[illegible]	1.14	[illegible]
Concrete						
Average analysis	[illegible]	[illegible]	[illegible]	[illegible]	15.21	[illegible]
Average deviation	1.01	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cone						
Average analysis	[illegible]	[illegible]	[illegible]	14.35	[illegible]	[illegible]
Average deviation	[illegible]	[illegible]	[illegible]	1.81	2.15	[illegible]
Vertical Tower						
Average analysis	[illegible]	[illegible]	[illegible]	[illegible]	16.33	16.17
Average deviation	[illegible]	[illegible]	[illegible]	[illegible]	1.43	[illegible]

[a] Listed in order of decreasing [illegible]

change in screen analysis after mixing.

The overall performance of this mixer is rated as good.

I. Comparison of Mixing Efficiency

The best index of mixing efficiency is believed to be the average deviation from the average analysis of each plant nutrient. Based on this criterion, the various mixers are listed in order of decreasing mixing efficiency in Table II.

The mixer giving best mixing, namely the screw conveyor, unfortunately produced a product badly off the desired analysis of 15-15-15 because of the poor proportioning. It is evident that the raw material feeders delivered a uniform flow of materials to the mixer, and mixing was good, but the flow rates were not as desired.

The Munson rotary mixer, the cylindrical rotary mixer, and the ribbon mixer gave good mixing, and there was no decided difference in analysis of samples from beginning to end of discharge, except for the first and last samples from the ribbon mixer.

The concrete mixer, the cone mixer, and the vertical tower mixer all gave poor mixing, both with respect to average deviation and variability of sample analysis.

All of the mixers except the screw conveyor mixer were operated batchwise, and the raw materials for each test were fed as measured batches; this was done by feeding the proper number of bags, each of which has been weighed, and making a final weight adjustment of the entire batch which was weighed on scales. If the raw material analyses and batch weights were correct, the average analyses of the mixes should have been exactly 15.2%N, 15.7% total P_2O_5, and 15.2% K_2O. In some tests the average analyses differed significantly from these figures. This could have been due to many reasons, such as contamination, errors in weighing the raw materials, nonuniformity of sampling pattern, errors in sample preparation, and errors in analysis. However, these errors should not affect the validity of the use of average deviation as a criterion of mixing, even though they would affect the absolute values of the plant nutrient content.

Conclusions

1. The best mixing achieved in the tests was by the screw conveyor mixer, but because of poor proportioning the product analysis was substantially off specifications.

2. Good mixing was achieved by the Munson rotary, cylindrical rotary, and ribbon mixers.

3. Mixing achieved by the concrete, cone, and vertical tower mixers was poor.

Acknowledgments

This project was supported financially by the Division of Chemical Development of the Tennessee Valley Authority. In addition, several of the TVA personnel assisted in planning and carrying out the tests, including Frank Achorn, Frank Anderson, Ralph Cunningham, Al Gordon, George Hoffmeister, Robert Meline, and L. M. Nunnelly.

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2. Hoffmeister, G., Watkins, S. C., and Silverberg, J., *J. Ag. and Food Chem. 12,* 64-69 (1964).
3. Achorn, F. P. and Meline, R. S., *Commercial Fertilizer and Plant Food Industry 110,* 32-33 (1965).

MODERATOR SPILLMAN: Thank you, Dr. Bridger for that very fine report. We had a good many requests last year and the year before for this type of a discussion. We appreciate Dr. Bridger coming here today to discuss this very fine study. We are ready for questions.

Those of you who have any questions, please give us your name, your title and the company you represent.

ROBERT E. ROBINSON: Atlanta Utility Works. I, of course, am a manufacturer of rotary mixers. I would just like to ask Dr. Bridger if he has any information regarding the mixing of unequal quantities in a batch, for example, the mixing of trace minerals or very small quantities of some ingredients into a batch?

Was anything done in this, Dr. Bridger?

DR. BRIDGER: No, we did not do that in this study and I don't know of any other information that I have on that.

MR. SAMUEL STRELZOFF, Chemical Construction Company: I am curious to know whether you have taken into account the difference in density of your various materials. After all, each of these fertilizers has a different density and when you use that in the rotary mixer maybe you have some factor that really didn't help you in mixing it properly because of the variation in density of these materials.

DR. BRIDGER: The three materials certainly were not identical in density. I do not have the information here. However, it has been shown by TVA that the most important single factor in bulk blending with respect to segregation is the particle size rather than the density or the shape. Density has some effect but relatively minor as compared to the particle sizes.

MR. THOMAS BARNHART, U.S. Steel: In the case of your cement mixer, I have two questions relating to it.

Number one—Was the mixer baffled for cement mixing or was the baffling specifically altered for fertilizer blending?

Number two—Were there any tests run to determine the increased retention time and its relationship to the efficiency of mixing?

DR. BRIDGER: The answer is no in both cases. The mixer was, I believe, just a standard concrete mixer, not altered, and we ran the one test only at one-minute mixing time, because this was standard practice in the plant. That's all we were after, to find out how good a job they were doing according to their standard practice.

MR. ROBERT SORENSON, American Oil Company: I notice that all of your mixers were operated at rated capacity, where your concrete mixer just had half its rated capacity. Don't you think, maybe, this had some effect on the outcome? Many pieces of equipment operate at a lower efficiency if they don't take their rated charge.

DR. BRIDGER: Perhaps — The concrete mixer was rated for two tons of concrete, not two tons of fertilizer, so you couldn't get two tons of fertilizer in it. This simply was what the plant considered the maximum operable capacity of this particular mixer.

MR. ALBERT HENDERSON, Wilson & Toomer Fertilizer Company: What type of screw conveyor did you use in these tests?

DR. BRIDGER: It was simply an auger. It was designed as a mixer. It was a solid auger running the length of the mixer. I can't describe it further than that.

MR. RICHARD GILBERT, American Cyanamid Company: I would like to hear some comment on the significance of these tests. Of course, we would all like to get the best mix that we can get but, if we dump this one-ton batch into a spreader and drive it out in the field and spread it, unless we've got deviations of, oh, 20 per cent, it isn't going to be noticeable in the crop yield, although the farmer may notice stripes in his field, if we have very high nitrogen in one part and very low in another. But if we put the correct amount in to give us the ratio we want of each nutrient and dump it into a spreader and spread it on the field, how important is it that we get a very complete mix?

DR. BRIDGER: Certainly some of the difference here would probably not show up agronomically in the field. You would have to have a very pronounced imbalance in the NPK proportion before you begin to see it in the crop response. I think from the more practical significance of these tests it is whether or not the state inspector will get a bad sample.

MR. GILBERT: That's important too, of course, but, if the state inspector samples the spreader the way he ought to and mixes his sample the way he ought to, we could almost put the stuff into the spreader in layers and he'd get a reasonably good sample.

And if he took stream samples as you have done, again, and composited a number of samples and mixed them, he would come up with an average which would be pretty close to the guarantee, I think, wouldn't he?

DR. BRIDGER: That's right. His average would be pretty close but his individual samples might be badly off.

MODERATOR SPILLMAN: Thank you, Dr. Bridger.

MODERATOR SPILLMAN: Our next paper will be given by Walter J. Sackett, Jr., Executive Vice President, A. J. Sackett & Sons Co. Walter will discuss a most interesting subject, "High Density Storage and Automated Bin Filling System." His message should be of interest because of the economics possible, getting the most storage per cu. foot of space and loading and unloading bins with practically no segregation. Walter please:

High Efficiency Bulk Storage

Walter J. Sackett, Jr.

The subject of my talk is the New Sackett High Density Storage and Automated Bin Filling System. To many of you, gentlemen, who are highly technologically oriented, this may sound like a very drab subject. After all, when you attend the normal pre-construction planning meeting for a new facility, the typical attitude is, "Well, we need a building which will hold so many tons of raw materials and so many tons of products. It will be of steel and corrugated asbestos construction and we'll put it here. Now, let's get to the meat of this thing . . . the process." Perhaps your attitude is different, but in most cases, storage is the area that receives the least amount of attention. After all, our main objective is to make the stuff. We know we've got to put a certain amount of material into bins and ship it, but what's so tough about that? We've got to make it first! The real problems are in the process technology, not in storage . . . people have been storing fertilizer for a *long* time! What kind of problems can we run into there? We eventually find out . . . it may be several years later, but eventually we find out what problems there are.

With all the tremendous strides our Industry is making in this age of progress, it seems to me that occasionally it might do us all some good to walk back along that path from whence we came, just to see if there is something that we might have missed along the way. Once in a while, we'll be amazed to find some pretty basic items that are bottlenecks in our operation. Most of the time, these things are pointed out to us by someone who is much less familiar with our particular operation than we. This is natural because each of us, after living with a plant or operation for any length of time, gets to feel that we know our operation like nobody else. But, one day along comes Joe Smith, who knows nothing about our situation, and asks some naive questions, which we answer easily because, after all, we are the experts around here.

Later when we think about the conversation, we realize that in a couple of cases the questions were answered with the main explanation being, "Well, we've always done it this way." Perhaps not in those exact words, but the text of our answer essentially amounts to that. Then, being the conscientious individuals that we are, we try to answer the questions more effectively to ourselves. And, because each of us is subject to his particular job pressures—deadlines, production schedules, etc. — we don't have too much time to dwell on these matters and even if we do come up with a solution, it's put off and, in many cases, forgotten.

Sackett has been in the business of serving our Industry for 71 years and while we've seen it advance in most areas, there are a few that have received very little attention.

A common complaint we hear from today's manufacturer goes like this. "I could have sold 50% more tonnage this year if I'd only had the goods. I've got to have more storage, but I've completely built up my plant to the property limits and the land adjacent to the property is either not for sale or so costly that it is prohibitive. I have a good central location and a substantial investment in my plant and equipment, so I don't want to rebuild at another location. What can I do to increase my storage capacity?"

Another common complaint, especially since the advent of granular fertilizers is, "I can't seem to get a consistent quality product. My customers complain that they get large granules in one shipment and small granules in the next. What can I do to make the quality of my product more consistent?

We have been hearing these questions for a long time now and have decided to shape up and see if we can't supply some answers. We think we've got some!!!

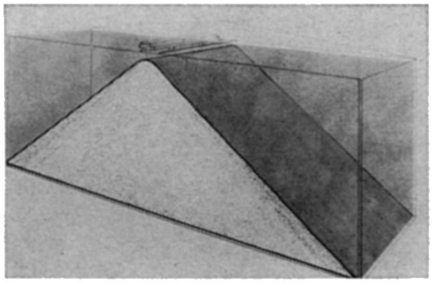
We've got something novel, but better than that . . . workable . . . in our new High Density Bulk Storage Building which we'll show you shortly, by means of slides. Because of the angle of repose of the pile, it's not possible, under normal plant conditions, to completely fill the bins without using considerable manual labor.

With our High Density Storage concept, this "filling the voids" is made possible by using a new building design and equipment which will level load the total volume available to us. Thus, we can now store almost twice the amount of material per square foot of floor area that we could by conventional methods. We have been issued patents* for the "Automatic Bin Filling System", which will level load this building. Because of this new and unique level loading method, one of the remaining serious problems of particle size segregation will be essentially eliminated. Material egress from this new storage building may be accomplished by under-floor belt conveyor means or floor operated front end loaders operating thru newly designed permanent bin fronts.

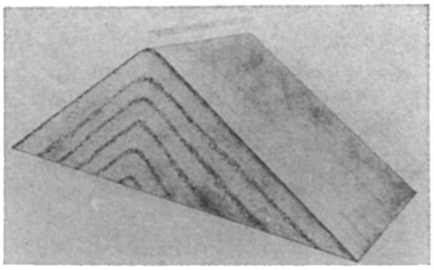
Slide No. 1

For years we've been making little piles, big piles and medium size piles around our fertilizer plants. Our normal procedure is to take our finished goods from process by conveyor or overhead tram car and put it into an open bin, similar to that shown on this slide. This is normal procedure—nothing wrong with it *until* you find yourself short on storage, land at a premium, and in your own plant you've got no place to go but UP! Then, what do you do??? Simple!!! You go UP.

After all, when you consider that with this type of storage you are wasting anywhere from 30 to 50% of your actual under-roof bin volume, you've got to go up. The volume as shown in pink on this slide is strictly wasted. OK, how do we fill it up? Easy! We put a front bulkhead on the bin. Fine, but that in itself does not do anything for us because the angle of repose of the pile will, all of a sudden, start shoving our conveyor thru the roof before we've filled up any of the wasted volume. No sweat! We'll put a slinger on the conveyor and fill 'er up that way. Well, this makes some sense, until you consider that the second complaint was about particle size segregation and I don't think there is a much more effective segregator than a slinger. This will compound a problem that already exists with the normal single point bin loading methods.



Slide 1
Normal Open Bin Storage



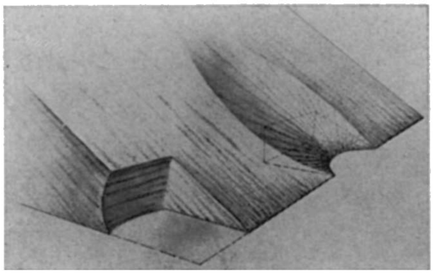
Slide 2
Stratification and Segregation
Single Point Loading

Slide No. 2

As you can see by this cutaway section of a typical pile, we've already got more of a segregation problem than we like to admit or have been able to do anything about. To anyone who has ever been in a fertilizer plant, this is a familiar sight. As the material comes off the belt conveyor, it starts to cone since all the material is being fed to the bins at one point. As it cones, the larger granules roll down the slope of the pile farther than the smaller ones. This segregation of materials plus the "in bin cooling" forms the stratification, or layering, of the pile. Hence, as we ship material from this bin, we're going to get different size particles as we work our way thru the various layers. Not only that, but when we send our front end loader operator to the bin to ship this material, he further accentuates the segregation problem.

Slide No. 3

As is shown in this view of our pile, the front end loader has arrived and carted away his first few scoop fulls. If the pile remained stable, the area removed by the scoop would look like that pictured in the lower left hand corner. But, our pile is not stable (or at



Slide 3
Intensified Segregation Caused by Scoop Unloading

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* Covered by U.S. #3,319,808, U.S. #3,342,352, U.S. #3,406,847, Canadian #776,344, Canadian #782,196 and Other Patents Pending.

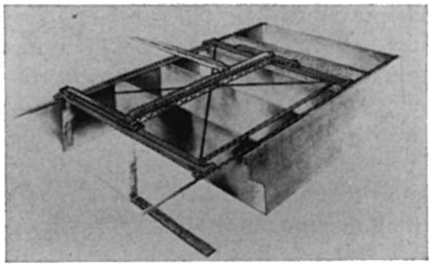
least, we certainly hope not) and it converges on the void left by the scoop. This is shown up in the middle of the pile. When it converges, naturally, the larger granules fall into the void first; thus intensifying our segregation problem.

Well, I've spent quite a bit of my time here telling you gentlemen something you already know! —We got problems!! What do we think we can do about our problems? I'll show you!

Slide No. 4

Here, we show our High Density Bulk Storage Building. This is a high rise single or multi-bin storage building provided with automatic bin filling equipment. It is the combination of these new building and equipment components that, for the first time, makes possible an automatic level loading of the building, which is to say, the attainment of maximum bulk storage within a given area. For this building, we have based our construction on reinforced concrete, although steel is employed in some areas, particularly the roof enclosure above the bins. With this method, we bring our carefully screened material to a central point of the storage building where we feed our automated bin filling equipment. This new bin filling equipment is made up of several components joined together to form an "H" shaped conveying system which moves on rails throughout the building over the bins.

A breakdown of the components making up this unique conveying system reveals a combination of two (2) bridge-mounted laterally reversible self-propelled shuttle belt conveyors with a third longitudinally reversible self-propelled shuttle belt conveyor with its supporting framework connecting the two bridges together. Thus, this conveying system transfers the incoming feed to any bin in the plant.



Slide 5
Operator Selects Bin

Slide No. 5

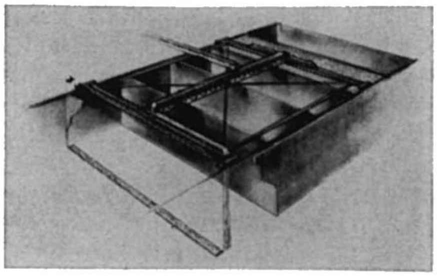
Our operator first selects the bin into which this particular grade is to go. Once he has manipulated his main shuttle into position, he then starts feeding material to the bin. A creeper gear is actuated on the lateral shuttle and it starts moving across the length of the bin feeding material on the floor of the bin as it goes.

Slide No. 6

When the conveyor reaches its terminal point on one side of the bin, it activates a limit switch which reverses both the creeper gear, which is moving the conveyor along the length of the bin, and the belt travel, so that it now feeds the opposite half of the bin.

Slide No. 7

Once a cycle is made, a creeper gear on the main shuttle is activated and by means of a timer moves a pre-set distance further down the width of the bin as shown by the red arrow.



Slide 7
Shuttle Is Activated Once Cycle Is Made

Slide No. 8

By a repetitive use of the sensing devices, the conveyor again starts laterally across the building putting down another layer of material on the floor immediately adjacent to the first.

Slide No. 9

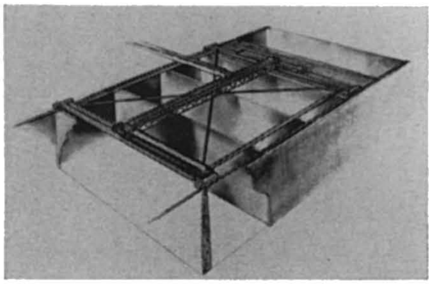
This automatic level loading cycling is repeated back and forth across the bin until it is full. During this process, *not once* do we form a coned pile.

Slide No. 10

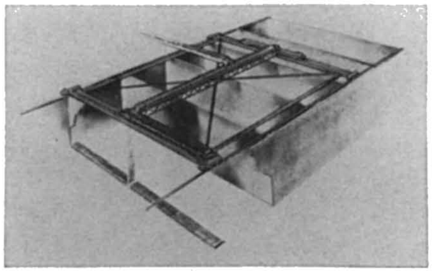
Now, with this method of storage, we may unload our material in a number of ways:

(1) We may have just a plain floor slab with fixed openings which will feed the material much like an animal feeder to our front end loader . . . OR

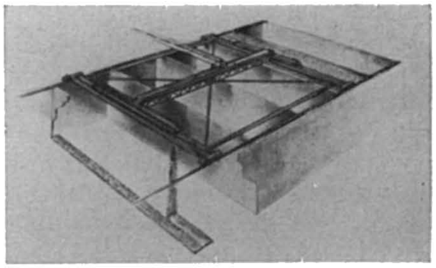
(2) We can install a tunnel under our slab containing conveyors which will transport material to our shipping unit. These conveyors are fed by large charging hoppers built right into the floor of the bin with heavy grated covers. The material flowout of the bins is controlled by a console in



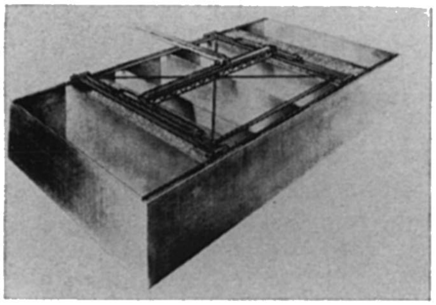
Slide 4
High Density Bulk Storage



Slide 6
High Efficiency Bulk Storage



Slide 8
By Repetitive Sensing Devices Conveyor Again Starts



Slide 9
Automatic Level Loading Cycle Repeated Back and Forth

the shipping department. When shipping is running low in a certain grade, we merely activate the hydraulic or pneumatic gate at the bottom of the correct bin and automatically feed material to the shipping unit. Naturally, with a flat bottom bin all of the material will not run out by gravity; a small amount will remain. We keep our openings in the bin wall of such size that our front end loader operator can push the remaining material into the hoppers.

With this system, we have increased our storage tremendously per square foot of area and helped stop the segregation that normally comes with single point bin loading. Along with this, we have another built-in advantage. Since a very small percentage of our product requires that we handle it by front-end loader, it follows that we will need considerably fewer front-end loaders around the plant. With fewer front-end loaders in the plant, we have eliminated:

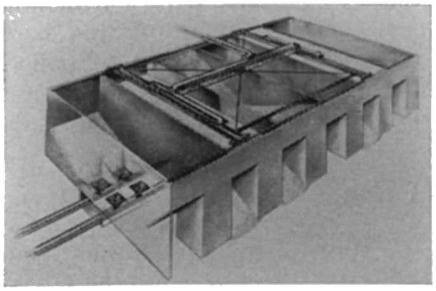
#1—The degradation of product which naturally comes with its being handled by a front-end loader.

#2—The manpower that is required to operate these machines.

#3—The fuel to power them.

#4—The high maintenance expense that's required to keep each machine operating.

As we all know, these are big expense items and constant headaches to our plant management personnel.

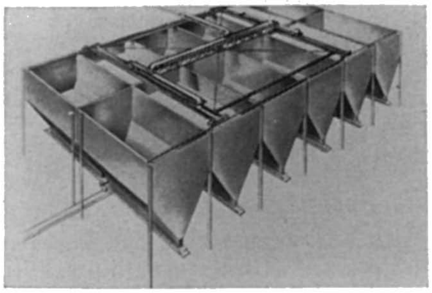


Slide 10
High Efficiency Storage Floor Type

Slide No. 11

This slide shows our New High Density Storage Concept applied to an overhead or multiple hopper system. In this case, we have a middle bulkhead which doubles the number of hoppers. Each of these hoppers is provided with a belt conveyor at the bottom, each in turn transferring the flow to the main longitudinal conveyor taking the material from storage to the processing or shipping area. Belt scales of the in-transit variety may be incorporated with the cross conveyors to give us better inventory control. Or, any number of blends may be made by pre-set weighing elements built into each hopper conveyor. Thus, this system opens up new opportunities for many industries and fills a growing need for an almost countless variety of prescription blends as well as single materials.

This new Automatic Storage Method will permit you to sell a better product . . . sell more of it . . . and at a larger profit by eliminating much of the labor and maintenance that must be charged against each ton that is shipped.



Slide 11
High Efficiency Storage System Overhead Type

Moderator Spillman: Thank you, Walter. That is looking into the near future, I would say, looking into the crystal ball. Do you have any questions for Walter?

A Member: The last slide you have shows that material will be fed to the belt conveyor at the bottom of the silos. Now what provision do you have if the material sets in the silo?

Mr. Sackett: Several methods and further studies are in the works. We have answered the question as far as increasing storage capacity and the segregation problem. We have to assume that the material has been properly dried and cooled and is in good flowable condition.

Moderator Spillman: Walter, have you done any figuring on the cost economics of the Sackett "High Density Bulk Storage" compared with present conventional bulk storage per ton or per square foot area.

Mr. Sackett: I think that we could say that our construction costs would be somewhat higher, however, not much higher than present conventional storage because, after all, we are spending on a per ton basis. In the overall savings, maintenance and decreasing our personnel required to operate the machines around the plant, etc., I think that here is where the savings will show up.

Moderator Spillman: Do we have any other questions? Thank you, Walter, for your excellent paper.

Moderator Spillman: Our next two discussions bring to the Round Table technological improvements in bagging operations.

The companies they represent have contributed valuably to previous Round Table Sessions.

First, Robert Dean, Engineering Manager, Fisons Limited, Suffolk, England will discuss "High Speed Filling, Sealing and Handling Plastic Bags". Mr. Dean, please.

The High-Speed Filling, Sealing and Handling of Plastic Bags in the Fertilizer Industry

Robert Dean

Introduction

In 1963, Fisons decided to make a gradual change from multi-ply paper bags to polyethylene (P.E.) bags.

At that time, the following P.E. bags were available:

1. face valved bag, heat sealed top and bottom,
2. open mouth bag made from extruded P.E. tube, with bottom end sealed by the manufacturer.

Large scale field experiments on both types of bags demonstrated that the open mouth bags after heat sealing gave a hermetically sealed package, whereas the face valved bag did not, resulting in damage to the fertilizer by moisture. The valve bags also suffered severe damage around the valve opening when being filled.

At the present time, all our bags are of the open mouth P.E. type, but during this year a further investigation was carried out to evaluate block-ended valved sacks of more modern design (these would still not provide a hermetically sealed package). A changeover would have increased our present bag costs by 3.63 shillings (0.435 dollars) per ton of fertilizer. With sales in excess of one million tons per annum, the minimum increase in operating costs would have been in the order of £181,000. (434,000 dollars) per annum.

Under these circumstances it is most unlikely that our Company policy, in respect of open mouth sacks, will be changed and developments described later will still be applicable even if a change to open mouth gusseted P.E. sacks was subsequently introduced.

Summary of Position to Date

This paper describes our development of a system for bagging and handling of fertilizers in plastic bags of a .008″ and 0.010″ thickness at the rate of 1,200 bags per hour to palletised store.

Initially, to handle plastic bags a pneumatically operated sack holder for filling purposes and a heat sealer unit to seal the open top of the bag were purchased. It was apparent that although plastic bags were easy to fill and seal, the characteristics of the filled bag were such that they could not be stored satisfactorily due to excess air, and damaged bags amounted to approximately 6%.

The bag filling and handling rate over a shift of 8 hours averaged 600 bags per hour, each of 112 lbs with a team of:

Chargehand	1
Shovel Operator	1
Filler	1
Sewer or Sealer	1
Outloaders or Palletisers	2
Fork Lift Operator	1
Total	7

This method of operation can be expressed as 85.7 bags per operator per hour.

There were four major problems that had to be solved before the standards required could be attained:

a) filled bag characteristics had to be such that it could be easily handled and palletised,

b) excessive damage to bags by handling equipment,

c) it was necessary to develop a high-speed and economic method of palletising,

d) it was necessary to increase the rate of operation in a single bagging line.

Bags are now filled and handled at a rate of 1,200 per hour with an average of 1,000 bags per hour over a shift of 8 hours, into palletised store 30 bags high, i.e. 5 pallets high each having 6 layers of 6 bags with damaged bags running at less than ¼%. The team comprises the following:

Chargehand	1
Shovel Operator	1
Filler	1
Sealer	1
Palletiser Operator	1
Fork Lift Operator	1
Total	6

This can be expressed as 166.6 bags per operator per hour, an increase in productivity of almost 100%, and the details of how this has been achieved are outlined below.

Filled Bag Characteristics

At the beginning of the operation the handling of the bagged fertilizer was very difficult, due to excess air trapped in the bag after filling and sealing causing ballooning which made it difficult to produce a stable load for transport, and it also reduced the palletised storage capacity by 40% as safe storage limited the height to 3 pallets, each pallet having 5 layers each of 5 bags. To overcome this problem, 8 micro holes were made in each bag during manufacture, but this did not solve the problem because dissipation of air through the holes was too slow.

A bag vibrator and fixed sides conveyor unit was designed and installed under the filling spout and the bag shape was maintained until sealing was complete (Fig. 1). This enabled us to expel the excess air from the granular mass and to maintain the bag at a thickness which allowed the materials to fill the bag more efficiently. This, followed by top folding to expel excess air above the mass before sealing, gave a good shaped package without ballooning, but with sufficient air content to keep the material free flowing.

This resulted in a vast improvement in handling the bags and the normal storage of pallets i.e. 5 high, each of 5 layers, was obtained with safety.

Excessive Damage to Bags

During the conversion from multi-ply paper bags to plastic bags it was apparent that equipment which would handle paper bags was not satisfactory for plastic bags, due to an unacceptable high rate

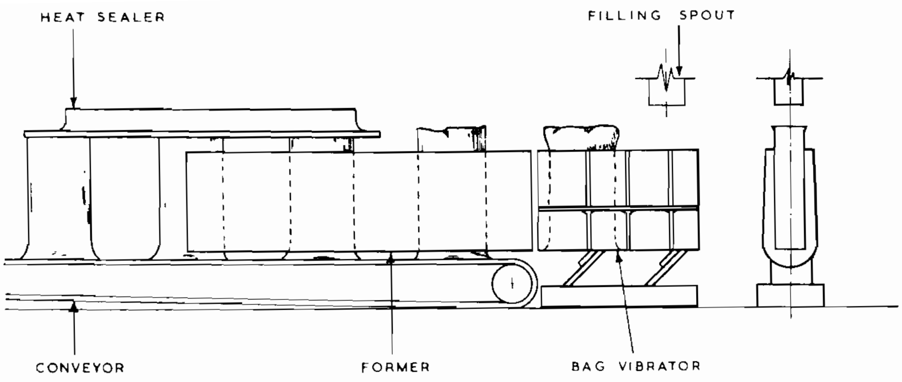


FIGURE I FILLED BAG FORMING AND SEALING

of bag damage. The major causes of this were:

a) tears in plastic film caused by fouling obstructions during transportation,
b) sliding of bags down chutes causing granules to pierce the plastic film from the inside,
c) rubbing of the bag by supporting members when in the upright position causing the same fault as (b),
d) twisting of the bag to change direction causing creases in the plastic, which tended to initiate a crack after a period of storage in cold weather,
e) pressure during storage forcing splinters and corners of rough pallets to pierce the plastic,
f) the back support frames of the forks on the forklift trucks caused damage due to impact when picking up the pallet, and during transportation when the backward tilt of the mast was adopted.

These problems were tackled systematically by redesigning the equipment as follows.

a) All obstructions or side guides were removed from the transportation system and bags made to travel in the centre of all conveyor belts. Bags are accurately positioned at the start of the conveyor system by pneumatic pushers actuated by the bag itself (Fig. 2).
b) Polytetrafluoroethylene (P. T. F. E.) lined loading chutes were limited to a length of 3 ft. and only allowed as a means of safe working, i.e. to enable operators taking bags at the end of a conveyor to work well away from any moving parts.

   Spiral chutes were replaced by spiral gravity roller conveyors when height had to be lost.

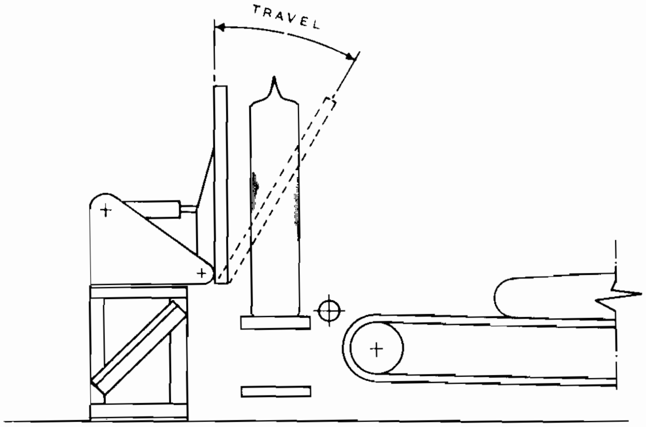


FIGURE 2 BAG PUSHER

c) When bags travelled in an upright position following the filling and sealing operation, the vibrator and former had shaped the bag so that it was free standing and would travel without the need for guide boards.
d) When the conveyor system required a change of direction, then mechanically driven curved slat conveyors were used to avoid chutes and twisting of the bag (Fig. 3).
e) A standard pallet was designed laying down a strict specification as follows.

   All boards to have corners rounded to a radius of ½ inch where they can contact the bag.

   The two surfaces, which contact the plastic, must be smooth planed and free from splinters.

   The gap between boards must not exceed 2½ inches so as to provide maximum area of timber to support the load, commensurate with an acceptable weight and cost.
f) The back support frame of the fork-lift truck was replaced by a full plate which eliminated corners and provided a larger surface area to take the pressure.

When these modifications had been carried out it was found that the handling and storage system was no longer a limiting factor to output, and that the bag damage was less than ¼%.

Palletising and Storage

The palletised bags were of a tied pattern of 5 to a layer, 5 layers per pallet and 5 pallets high, giving storage of 125 bags over a floor area of approximately 25 sq. ft. (equivalent to the pallet area). This gave an unused pallet area of 10/15% due to bag sizes permitting free space between bags.

Experiments were carried out

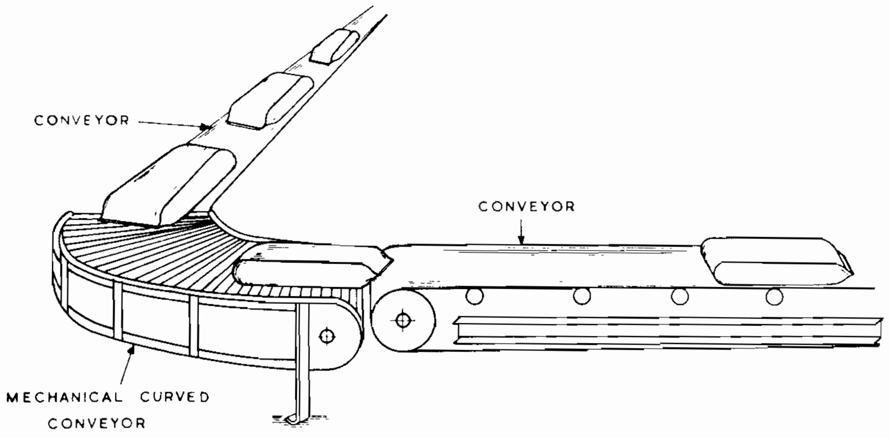


FIGURE 3 CONVEYOR DIRECTION CHANGER

with a non-tied pattern having 6 bags per layer and 6 bags high which provided 36 bags per pallet, (Fig. 4) an increase in capacity of 44% which resulted in considerable savings in the purchase of pallets. For the last three years this pattern has been used successfully when storing 5 pallets high which provides storage of 180 bags over an area of 25 sq. ft. approximately (equivalent to pallet area) an increase of storage capacity of 44%.

It was decided to look at the problem of palletising and storage of bags at a rate of 1,200 per hour, and a study was made of manual, semi-automatic and fully automatic methods of palletising. The conclusions were as follows.

a) *Manual Palletising*

To achieve a rate of 1,200 bags per hour would have required two stations each manned by two men, i.e. a team of four operators.

b) *Semi-Automatic Palletising*

In this case a machine is used to reduce the work content to that of one man, who is engaged in forming the pattern of the bag layer which is then delivered to the pallet. It was felt that a high rate of bagging could be adversely affected by tying production to a man who was expected to handle one bag every 3 seconds without a break. As the palletising stations are in all cases remote from the bagging plants, relief could not be given by the chargehand and under these circumstances it would have been necessary to have two men operating transportation and palletising.

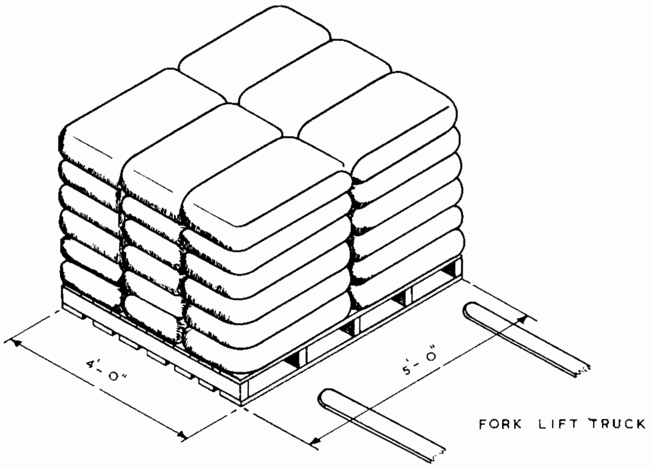


FIGURE 4 FORMATION OF PALLET LOAD

c) *Automatic Palletising*

A machine which had been successfully established in operation elsewhere was not known and it was necessary to collaborate with a manufacturer of a machine on an experimental basis and to carry out the development work jointly. This we have been doing since September 1965 with The Lawrence Engineering Company Limited who made the prototype machine. The machine has now reached a stage where satisfactory operation can be obtained continuously over a 5 day week provided that a maintenance period of 3-4 hours per week is allocated. Many changes in design have overcome troublesome or unsatisfactory parts.

A major problem that was encountered during the early operation was that the filled bags reaching the palletiser tended to be thinner at the top than at the bottom of the bag (wedge shaped) and the extent of this varied, depending upon the density of the material. With a non-tied formation which gave 6 layers each of 6 bags, the cumulative effect of the variation in thickness led to bad stacking in the store. It was found that this problem could be overcome by an operator allowing 6 bags to go forward, and then turning the next 6 bags through 180°, then 6 bags to go forward and so on therefore cancelling out the effect of the wedge shape on a pallet with an even number of layers.

To eliminate the need for this manual assistance a novel mechanism which automatically turned each alternate set of six bags through 180° was designed (Fig. 5). The unit is also used in the conveyor system to turn bags through the required change of direction.

Development of High Speed Bagging Plant

The potential capacity of the handling and palletising system

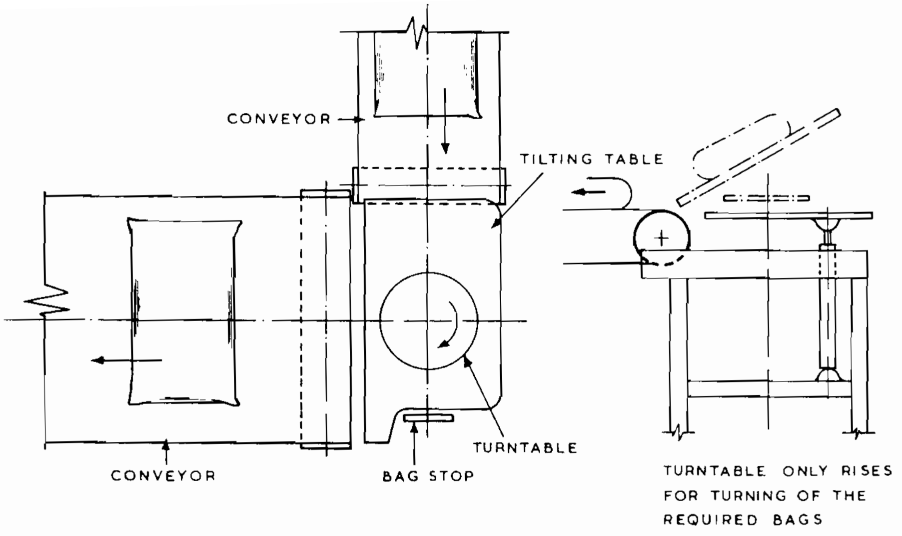


FIGURE 5 BAG TURNER AND DIRECTION CHANGER

was now 1,200 bags per hour, but a single line bagging output was still only 600 bags per hour. Considerable effort was devoted to the development of a new unit which would provide 1,200 bags per hour from a single bagging line and at the same time retain such desirable features as — low maintenance, simplicity and reliability.

Feeding and Filling of Bags

A study of the system which was used initially, i.e. one man putting a bag onto a single spout, waiting for the filled bag to partially move away in the bag vibrator before placing another bag on the spout, showed that:

time was wasted,
work was tedious, done in one standing position,
working conditions were not good due to the operator being in close proximity to the filling spout.

It was obvious that given the right conditions and no delay, an operator could emplace a bag on the spout every 3 seconds.

The considerations in the new design were as follows:

a) the condition of the empty bag supply was not sufficiently uniform to allow automation,
b) the operator must be uninterrupted,
c) good working conditions must be provided,
d) male or female labour must be able to operate,
e) 1,200 bags per hour must be filled,
f) identification of weighing machine for check weighing must be provided.

To fulfill these requirements a Turret Bag Feeder was developed (Fig. 6). This consists of six separate bag feed hoppers traversing on a track. At the point of putting on the bag the travel is in a straight line and this also applies at the point of filling, which is diametrically opposite to the operator. The straight parts of the track are required to feed the bag whilst filling in line with the bag vibrator.

Each hopper is an individual unit provided with its own drag link from a central drive shaft, thus allowing the variation in centres as they traverse the circuit.

Approximately 200 empty bags, lying flat with open mouth towards the operator, are positioned on a magazine conveyor directly below the position of emplacement. To put a bag on the travelling hopper the operator places a thumb or finger in each end of the mouth, which opens the top of the bag sufficiently to place over the closed spout which is fitted with gravity operated bag holders.

The bag is carried forward to the filling position where the top is mechanically opened by the spout and held against P.T.F.E. pressure plates, during travel for filling purposes. After filling, the spout closes and the hopper rises above the top of the bag for return to the operator.

The operator can sit on an adjustable seat, or stand as preferred, and his arm movements are minimised to ensure the least discomfort in carrying out a tedious operation.

The six hoppers are fed by three Simon E.P.G. type weighing machines, each capable of 600 bags per hour, but are operated at 400 bags per hour to ensure maintenance of accuracy and long life.

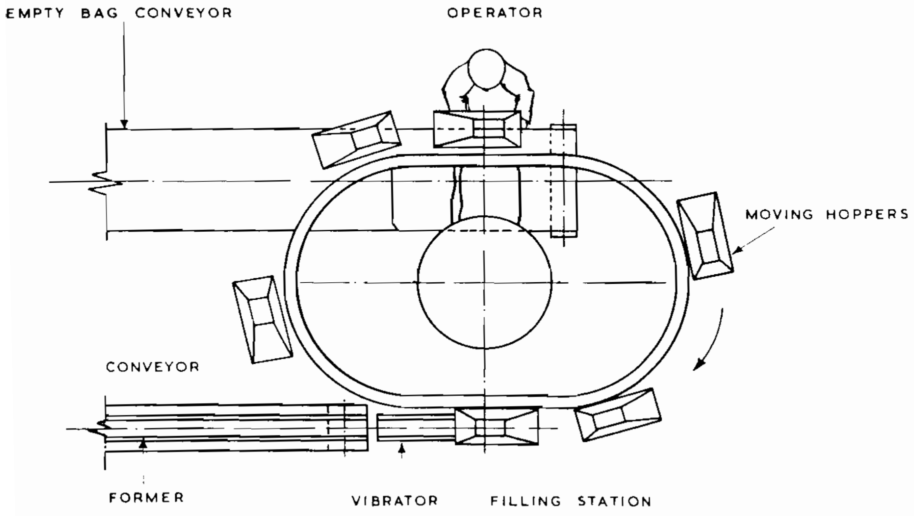


FIGURE 6 TURRET BAG FEEDER

The same weigher always fills the same two travelling hoppers as they are married together and are identified by colour.

Blue weigher feeds 2 blue hoppers
Red " " 2 red "
Yellow " " 2 yellow "

This provides identification for check weighing and in the event of maintenance being required by one weigher then the operator does not feed bags to the two corresponding hoppers, and a reduced output to 800 bags per hour results.

As the empty bag passes a point just prior to entering the bag vibrator, it passes through an ultra-sonic sensing device which signals to the weigher that a bag is attached. If a bag is not attached then the senser is not activated, and the weigher will not discharge.

After two years' operation, this bagging machine has given full satisfaction in all aspects when operating at the rate of 1,200 bags per hour.

Preparation of Filled Bag

The need to vibrate and form the filled bag was discussed under heading (3) Filled Bag Characteristics.

The bag vibrator and conveyor fixed sides have been fitted into the high-speed bagging plant and the details are as follows.

The empty bag enters the vibrator and the spout is opened, pressing the walls of the plastic bag against P.T.F.E. coated pressure plates. Filling commences and when approximately 20 pounds weight of fertilizer has entered the bag the weight overcomes the side pressure support, and the bag settles gently onto the bottom of the vibrator, reducing shock load to a minimum, but the top is still supported by the pressure plates to prevent collapse of the bag before filling is complete.

The top of the bag is moving continuously whilst being filled and the vibrator is adjusted to provide the same speed to the bottom of the bag, which ensures that the bag remains upright.

As the vibration of the contents of the bag is commenced at an early stage this ensures maximum efficiency of air removal throughout the package, but consolidation of granules is such that free flowing properties are still maintained.

The sides of the bag vibrator are lined with P.T.F.E. 1/8″ thick, this has reduced side friction to a minimum and has a life of over 2 years when operated for 120 hours per week.

This machine could handle more than 1,200 bags per hour and has been proved completely reliable with low maintenance costs.

Maintenance of the Shape of the Bag

The bag passes immediately from the vibrator on to a slat conveyor with fixed sides so that the shape of the bag is maintained until sealing is complete, after which the bag retains its formed shape in an upright position without any side support.

The fixed sides are of plywood, lined with P. T. F. E. and placed above the slat conveyor with a clearance of 1/2 inch. They are approximately 2 feet high with internal measurement between the sides the same as that of the vibrator.

Heat Sealing Unit

The operator passes the folded bag top into the machine where it is contained between two steel P.T.F.E. coated bands. Electrical heating bars are applied to the other side of the bands and heat transfer melts the plastic whilst under pressure exerted by the bars. This is followed by cooling, carried out in a similar fashion to the heating, and the cooling medium is water which passes through the bars.

On leaving the machine the seal is hot, but sufficiently cooled to be self-supporting, i.e. does not fold over.

A unit with a band speed of 45 ft. per minute will handle 1,200 bags per hour satisfactorily if regular daily maintenance is given.

Patents

The following items of equipment:—

(a) Filled Bag Forming and Sealing,
(b) Bag Turner and Direction Changer,
(c) Turret Bag Feeder,

described in this paper form the subject matter of applications for patents in the name of Fisons Limited in the principal countries of the world.

Acknowledgments

The Author wishes to thank the Board of Fisons Limited—Fertilizer Division for permission to publish this paper.

The Production Team at Fisons Limited, Ipswich factory for all assistance and forbearance during the development.

All Colleagues who assisted in providing the necessary items complementary to the paper.

MODERATOR SPILLMAN: Thank you Mr. Dean. I have been around fertilizer production many, many years, I have visited many plants, I have seen many efficient bagging operations but, by golly, Mr. Dean, you have one that you ought to be proud of. Thank you for your excellent discussion.

MODERATOR SPILLMAN: Do we have any questions for Mr. Dean? He has given us an outstanding talk and a very interesting illustration of their high efficiency bagging operation.

MR. ROBERT ROBINSON, Atlanta Utility Works: I would ask Mr. Dean to repeat his figures at the end of his talk that one lift truck operator can handle what tonnage up to a distance of 60 yards.

MR. DEAN: The fork lift truck driver is part of the team. The team consists of the shovel operator, the charge man, the foreman, if you like, the man putting the bags on, the man sealing the bags, the transporter, palletizer man and the fork lift operator. They all have to operate at 60 tons an hour.

The fork lift man has to handle this 60 tons an hour, however, at the same time he has to put in empty pallets. All of this work we have timed and he can do this quite satisfactorily but he is limited to distance from the palletizer to the point of storage of 60 yards.

MR. ROBINSON: Thank you.

MODERATOR SPILLMAN: Mr. Dean, how many changes do you make in an 8-hour shift or do you go right on through each shift bagging one grade of fertilizer?

MR. DEAN: We try. What we do now in this particular factory that you saw, we have limited bulk storage in our factories these days. We have gone to bag storage mainly because high nitrogen compounds require protection and we have found that the best way to protect them is to put them into bags. We have pans, say, on the order of 1,000 tons where one of the two granulating plants fill and we completely discharge that pan before we change grade. We very rarely feed to a customer direct from the plant. We always feed from the store so that we do maintain the bagging rate and don't require changes of grade too often.

We estimate to do about 350 tons a shift. I would say we change grade every two shifts or something on that order.

MODERATOR SPILLMAN: I noticed in the movie that you practically had no breakage. Do you have records on the percentage of breakage in your bagging operation?

MR. DEAN: I did say, I thought earlier, that we did start off in the early days with 6 per cent breakages. We are now down to a quarter of one per cent. That is not damage. That is due to a bad fill when the bands are getting worn and haven't been changed in time. This is the only damage we get.

In all of our developments we have a technical department which has worked very well with us. They have developed techniques for testing damage to the plastic film. Everything we have done they have checked and we do not damage the film in any way, shape or form.

MR. JOHN HORDYCH, Union Bag Corporation: How many different unit weights do you put up and what are they?

MR. DEAN: Do you mean weights of each individual bag?

MR. HORDYCH: Weight per bag, yes, sir.

MR. DEAN: We put up in England what we call one hundredweights, which is 112 pounds. The only variation we have made from that up-to-date is 50 kilos, which is 110 pounds. Our company is investigating smaller packages and this is why we talk of 1,200 bags an hour, because, if they reduce say to 56 pounds, to be ridiculous, then our tonnage per hour would be halved. The tonnage per hour would be halved but the number of bags still filled would be the same.

MR. HORDYCH: The pallet size. Is that about a 60″ x 60″?

MR. DEAN: The pallets are 5′ x 4′. Our pallets have been especially designed for our purpose. We have a very strict code and all of our works must stick to this. That is that all of the timbers, the tops of the timbers, where they can contact the bags are smooth planed. All of the corners which can come into contact with the bags must be proper corners of half inch radius. This is part of the exercise to reduce damage. This is our standard now and the manufacturers of pallets in the country are conforming to our standards very well indeed.

MR. JAMES G. MACARTHUR, Gulf Oil Co.: Do you use tape, I couldn't tell from the movie?

MODERATOR SPILLMAN: Do you use tape in your bag-closing operation?

MR. DEAN: We do not. We rely on the heat seal of the plastic.

MR. MACARTHUR: Thank you.

MODERATOR SPILLMAN: Thank you, Mr. Dean. We appreciate your coming here and we appreciate your message.

MODERATOR SPILLMAN: Our second paper on bagging operations "St. Regis Bagging System Improvements" will be discussed by Robert F. Schrader, Product Manager, Packaging Systems, St. Regis Paper Co., West Nyack, N. Y. Mr. John H. Dively, Marketing Manager, St. Regis and Mr. Schrader edited this paper. Mr. Schrader, please.

St. Regis Bagging System Improvements

Robert F. Schrader and John H. Dively

For many years your industry was the number one user of Multiwall Bags. Then in the early 1960's dry and liquid bulk started to make inroads into bag usage as better facilities for handling bulk became available.

As a result some of you either postponed or delayed at least modernization of bagging facilities in an attempt to concentrate on bulk.

As most of you are aware though, there will always be a need for bagged goods because of the various factors of weather conditions, row application, topography, and other factors which we will discuss later.

For that reason today we would like to detail the facts about bag usage, the improvements to bag packaging which allow efficiencies in bag handling, and the increase in profits which bags can contribute to your total marketing efforts.

We will show you how one company — W. R. Grace — uses modern bag packaging facilities in conjunction with bulk to increase *their* ability to supply *all* the customers in their marketing area — thus contributing to their overall profitability.

And finally we will touch on the very latest developments in bag packaging systems—the recently developed ones as well as those coming in the near future.

As we implied earlier — your industry is no longer the largest user of Multiwall Bags — you are second to animal feeds.

But, as the slogan of the Advertising Campaign of the Ford Motor Company was a few years ago — "There's a Ford in Your Future" So we believe "There's a Bag in Your Future", and that an important percentage of the fertilizer produced in the 70's will be shipped in bags.

But before we enumerate why we believe this and show you how it can be done, let's first take a look at the recent history of bag usage by your industry. Chart #1 shows what has happened to bag usage since 1963, when it hit a high of 450 million bags. Even though fertilizer production was increasing, bag usage plateaued because of dry bulk and liquids. No definite trend sent in until 1966 when bag usage

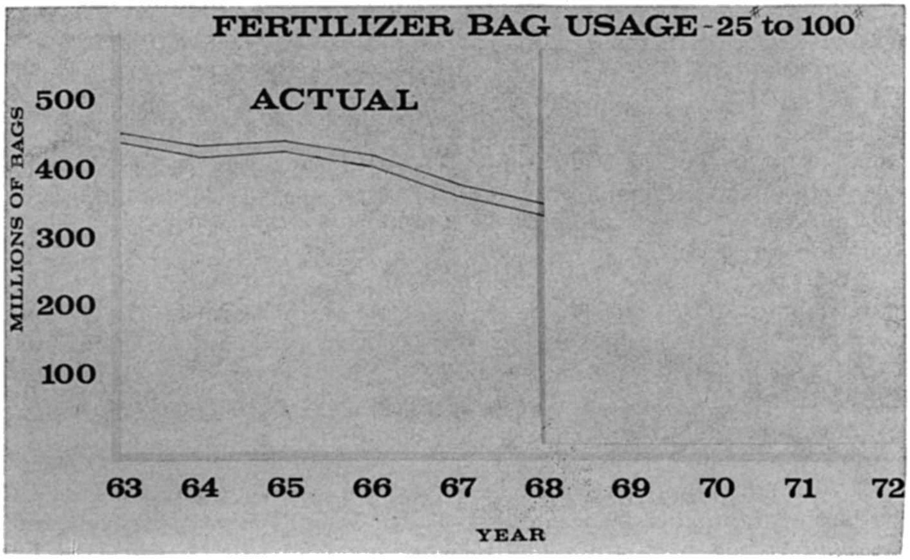


Chart 1
Fertilizer Bag Usage—Actual

dropped by 5%. This was followed by a 10% drop in 1967. But, this does not mean that bagged shipments are *dead* — in fact, they are *far from* it. For the year ending June 30, 1967, USDA reports that 57% of mixtures, and 24% of direct application primary nutrients — a total of 15,488,000 tons—*were bagged.*

Now let's take a look at Chart #2 and see what we believe will happen to bags during the next five years. In the year 1968—we expect another 10% drop—but by 1969 we expect the curve will begin to flatten out as shown on the top line, rather than continue downward as shown on the bottom line. This is similar to the history of bag usage in the feed industry when bulk approached the 50% level. And this situation should exist at *least* through 1972. And here are the reasons why.

1. Bags are still the most convenient method of handling and applying fertilizer to millions of acres of row crops.
2. Conventional trucks can be used for delivering bagged goods.
3. Regular farm buildings or warehouses can be used, to store bagged goods until the day it is needed.
4. The *average* plant that produces chemically combined fertilizer can ship at least as many tons of bagged goods per day as dry bulk goods, because most plants have more bagging mills than bulk stations.
5. With all of our technical know-how no one has yet fully solved the problems created by bad weather during the planting seasons. So far, bags have been the best answer.
6. And . . . perhaps most important of all, the correct bagging system, both bags and equipment, *improves* your service. This results in increased tonnage—frequently in both bags and bulk — because you can then *deliver the goods rain or shine.* The end result is increased tonnage and increased profits for you.

I think you will agree that these reasons are valid ones and that efficient bagging operations must be incorporated in the total operations, in order to provide the profits which are there for those who properly plan for them. As is true with the total plant planning, proper planning of bag packaging *and* distribution systems can benefit the planner, although it involves a lot of hard work.

Chart #3. A very good example of a properly planned and well thought out packaging and distribution system is located at this W. R. Grace Company complex in Henry, Illinois. This is one of the most modern and up-to-date bagging and bulk handling plants in the world.

This plant was located in this particular area to serve a market encompassing the state of Illinois and neighboring states. It is in this area, according to the USDA report for the year ending June, 1967, that the highest percentage of bulk shipments of mixed fertilizer existed. This, of course, is exclusive of those areas where irrigation is prevalent — i.e., Idaho, Utah, among others.

But, Grace recognized the need to supply the ultimate in service necessary for *all* the farm communities in this marketing area, and to have available (1) *what* the farmer wants, (2) *when* he wants it, and (3) *how* he wants it.

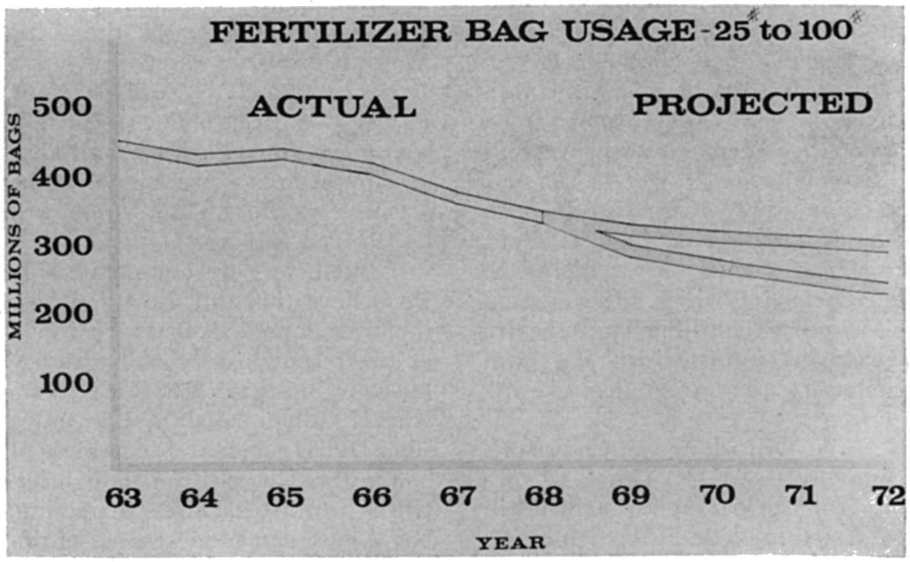


Chart 2
Fertilizer Bag Usage—Actual Projected

Chart 3
W. R. Grace Plant

Chart 4
Overall View Interior Packing Warehouse

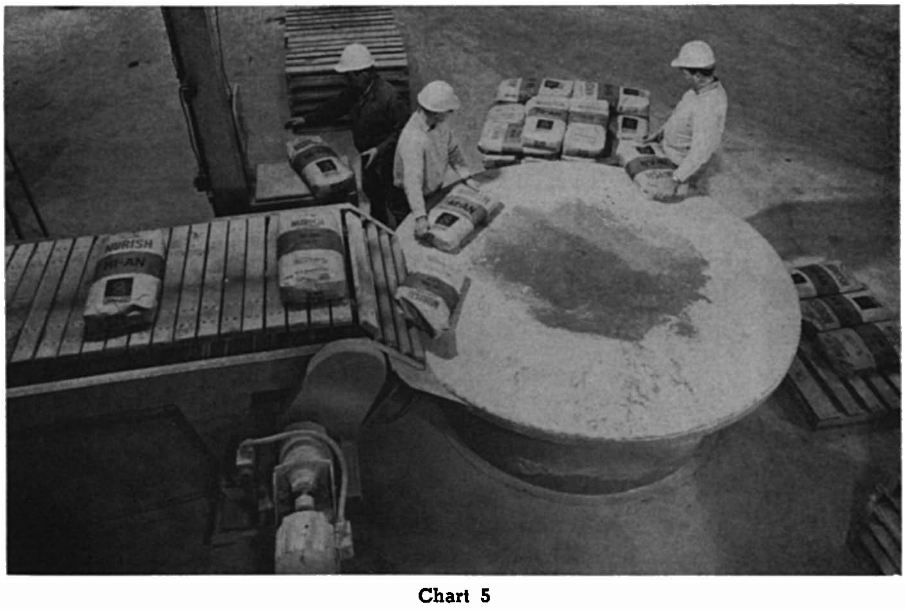


Chart 5
Bagging Operation—Palletizing Bags

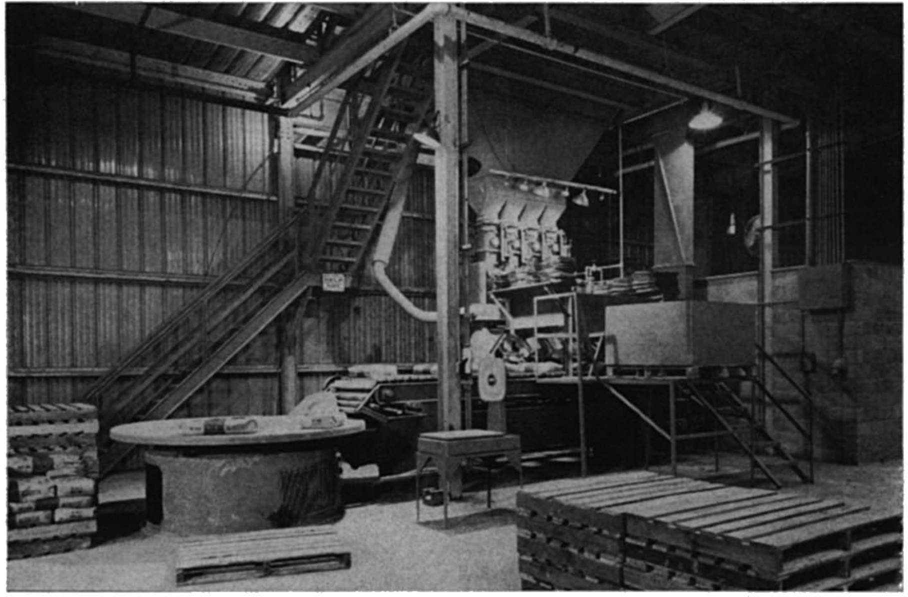


Chart 6
St. Regis 4 Tube Bagging Unit

The original planning called for this modern packaging and warehousing operation in keeping with all the latest technology used for their production facilities as well as bulk handling system.

This 100,000 ton per year plant was put on-stream in February, 1967, and is geared to ship 60% of their material in bulk and 40% of their output in the form of bagged goods.

Their bagging warehouse is a building 120′ × 240′, with a capacity for storage of 3,000 tons of filled bags. There are 2 truck-loading bays, each one 50 × 60 ft. and each with 4 truck loading docks and 2 railcar loading stations to insure prompt loading of truck and cars. Both trucks as well as cars can be loaded simultaneously if desired. You will note the packer is located in the center of the long wall with a car loading facility in either side. Having the truck bays on the other side allows the flexibility of loading both fast.

Chart #4. This is an overall view of the interior of the packing warehouse. Fork truck operators have easy access to the filled pallets of bags, truck bays, or railcar entrances.

Chart #5 and Chart #6 show the bagging operation which consists of a St. Regis 4-tube Force Flow packer, bag takeaway conveyor and turntable to assist in the palletizing of bags. This turntable not only acts as an aid in inventory of some bags, but also allows more than one pallet to be placed on the floor and loaded immediately after a pallet has been filled.

The bagging rate is approximately 26 bags per minute from the Force Flow Packer. On a normal day during the peak season, it is possible to pack out approximately 240 to 260 tons in 8 hours. The manpower required for packing is 1 packer operator, 3 men palletizing, 1 fork truck operator and one man servicing the area. In addition to this, there is a half a payloader charged to this operation, who divides his time to bagging as well as bulk. Chart #7.

Each of the truckloading docks shown at the bottom of the slide, has a capability of loading out approximately 30 tons per hour. This allows Grace an overall capability to load out more than 200 tons per hour because they have material available at all times in their 3000 ton warehouse.

The Grace operation incorporates all the basic requirements for a modern materials handling system for bagged goods. There are:

1. *Flexibility* to assure that customer service can be fast and efficient.
2. The *capabilities for packing and moving high tonnage* during regular working hours with minimum mill and packaging equipment.
3. *Low packing and handling costs* per ton of bagged goods moved.
4. Flexibility that permits the mills to operate at peak efficiency even when there are no trucks in the yards.
5. Flexibility that permits rapid movement of inventory to customer trucks.
6. Flexibility that will inven-

Chart 7
Closeup Bagging Operator

Chart 8
Warehouse Showing 3 Tier High Storage

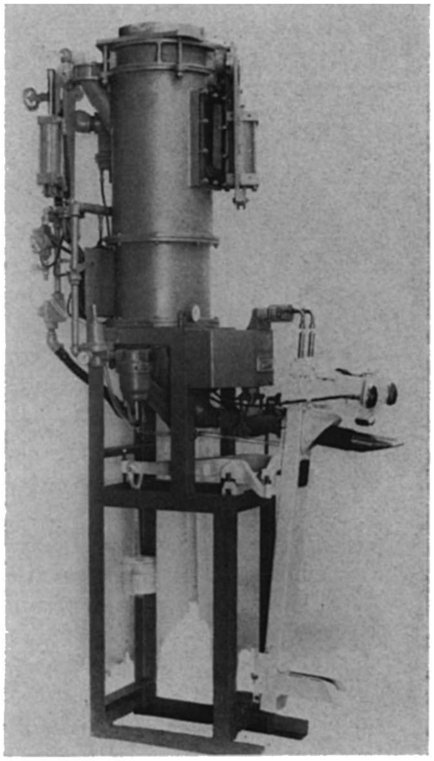


Chart 9
Model of Single Free Flow Packer

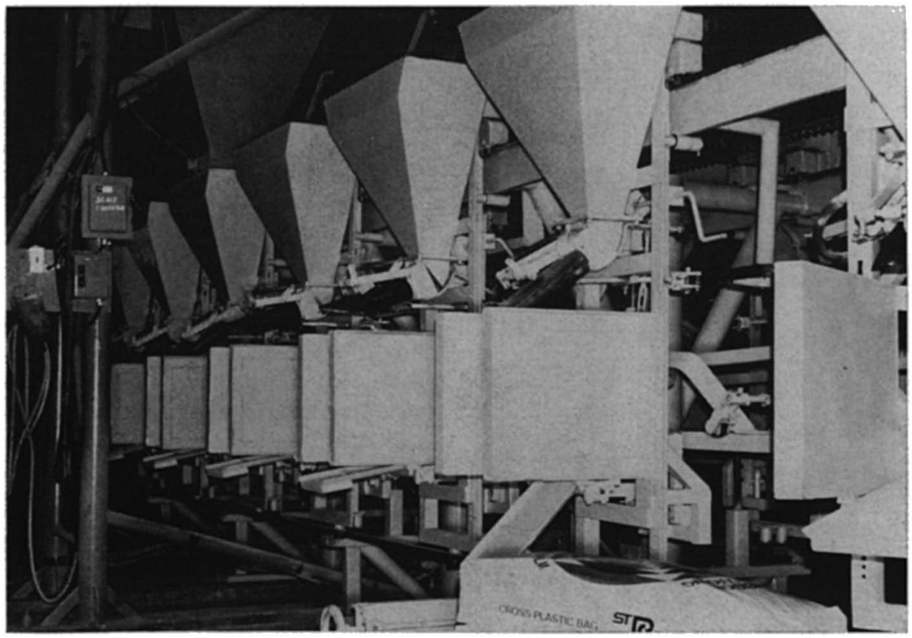


Chart 10
15 Tube Rotary Packer

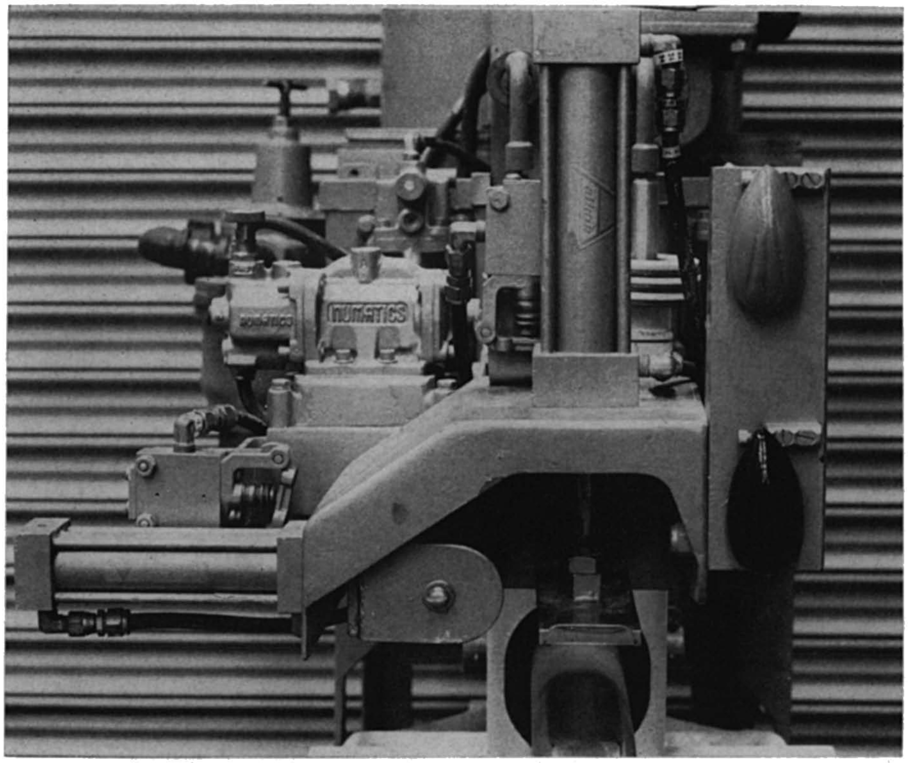


Chart 11
Device for Analysis Printing

tory all grades in the correct amounts at all times.

Chart #8. This warehouse type system has many advantages over the common bag to order system. These are:

1. Customer service is fast and efficient. All grades available from inventory and eight trucks can be loaded simultaneously.
2. Bagging crews can be intelligently scheduled and their utilization is unaffected by minimum or maximum demand of packed goods.
3. Inefficiencies are minimized in the bag packaging operation through elimination of frequent grade changes and the resultant short production runs.
4. Provides capability for handling large demands for packaged shipments but requires minimum mill and packaging equipment.
5. Economies over the conventional bag to order system can be realized through a 15%-20% improvement in the efficiency of bag shipping operations.

Since the time of the W. R. Grace startup, and still believing there's a bag in your future, we have continued to explore the needs of your industry and have perfected and successfully introduced to your industry, new bagging systems improvements covering the following segments:

1. Packaging Equipment
2. Bags (Paper & Plastic)
3. Bag Handling
4. Warehousing

Chart #9. First in the area of bagging machines there is the new low cost, high production model "J" Force Flow Packer. This machine was designed initially to supply a low cost single tube packer for the blending industry. Performance was *outstanding*. Refinements to the original design now allows this machine to be the standard for the industry. In 3 short years over 150 tubes of this machine have been installed for packaging all types of fertilizer.

Chart #10. Another recent innovation to valve packing is a 15-tube Rotary Packer which can provide packing rates up to 36 bags per minute. The gravity downspouts travel on an elliptical monorail and receive the pre-weighed charge as each travels beneath a pre-weigh scale. You will hear more about this machine as the initial commercial models are installed.

Chart #11 is a simple device for analysis printing.

Inventorying of bags with preprinted analysis for all the different grades being produced today is impractical. Blank analysis bags printed as needed is *the* solution. A device to print during the filling

Chart 12
Showing Analyis End Bag Printing

operation is this new bag clamp coder. It clamps the bag to the filling tube, and simultaneously prints the analysis on the top of the bag as it is being filled, and requires no additional labor or time. Printing Plates can be changed in a matter of seconds for analysis changes.

And look where the analysis is printed—on the end of the bag, where it can easily be seen when stacked or palletized in the warehouse. Chart #12.

Officials in Louisiana and Minnesota, where this system is used, have approved this method of analysis identification and several other states have it under consideration.

If the complete guaranteed analysis block must be shown, and requires a larger printed area, a newly developed high speed platen press, shown on Chart #11 can be used. It can print up to 20 bags per minute.

Shown at the lower part of this slide, is the printing job it is doing at a large fertilizer plant on the West Coast.

Chart #13. In the area of materials handling, there have always been the back breaking problems of manually palletizing filled bags—expecially on high speed packing lines. Automatic palletizers are one answer and have been put to use by a number of fertilizer companies. There has been *that* need, however, to fill the gap between manual palletizing and automatic palletizing—now there is available a one-man semi-automatic palletizer. This is called an air floatation palletizer, and utilizes an air plenum chamber which provides jets of air to virtually float the bag on a cushion of air. An operator can move a 100# bag with his fingertips to form the pallet pattern desired. The model shown here is operating at 12 bags per minute. Field experience has shown that with minor modifications speeds of up to 16 bags a minute and more will be possible soon.

And now last but certainly not least are improvements to the heart of any packaging system—the *bag* itself. The past several years have been the low density all polyethylene shipping bag having had only limited acceptance by your industry. Approximately 38 million units were used for fertilizer in 1967.

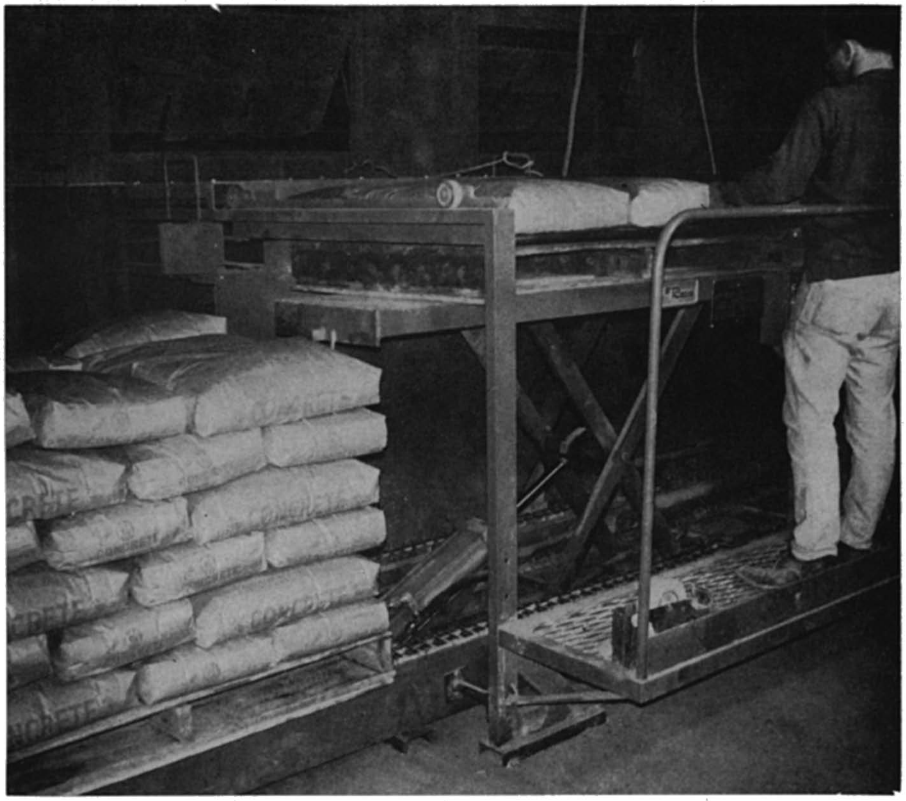


Chart 13
Palletizing Equipment

To date many have felt a better answer to solve the problems of moisture and acid resistance has been the film/kraft combination multiwall bag. Up to 200 million film kraft bags will be used by the fertilizer industry in 1968.

We have recognized the need for an even better packaging material to satisfy the requirements of today's critical products, as well as the *more* critical products you will be marketing in the next sev-

Chart 14
Cross Plastic Bag "Valeron Film"

eral years. One which provides superior moisture and acid resistance, superior puncture resistance, tear strength, and above all superior cost performance. Such a packaging material has been found in Holland and is manufactured by the Van Leer group of Companies. They call the material VALERON—Valeron is a laminated material composed of 2 specially oriented high density polyethylene films that are cross laminated with a special adhesive. This film is currently available in 2½ and 4 mil thicknesses.

During the past 24 hours, many of you have been trying to poke holes in this as well as tear it, and you have found this very difficult to do.

We are introducing bags made from this material in the United States and we call the bags "Cross Plastic Bags". We have made, tested and shipped all common types of bags, both sewn open mouth and valve. Chart #14.

Industry standard drop tests have been performed. The Cross Plastic bags have out-performed, not only the multiwalls containing free film, but also the all poly bags which were of 5,6&8 mil construction. Chart #15.

Drop test performance of polyethylene plastic bags diminish severely at temperatures below 15°F. Cross Plastic bags are not affected by these low temperatures.

The puncture resistance of both the 2½ mil cross plastic bag and the 4 mil cross plastic bag, is superior to 5 and 8 mil low density polyethylene as well as 4&5 ply multiwalls. Cross plastic bags made of Valeron film are superior in finger puncture resistance as well.

For most products, cross plastic bags made with either 2½ mil or 4 mil Valeron film, are superior in moisture vapor resistance to 5 mil and 8 mil low density polyethylene films.

The Valeron films combine high tensile strength with moderate elongation, providing the optimum in resistance to breakage. Chart #16.

The tear and tear propagation resistance, chemical resistance, snag resistance, and crease strength are superior to the low density polyethylene—and the empty bags can be disposed of by burning.

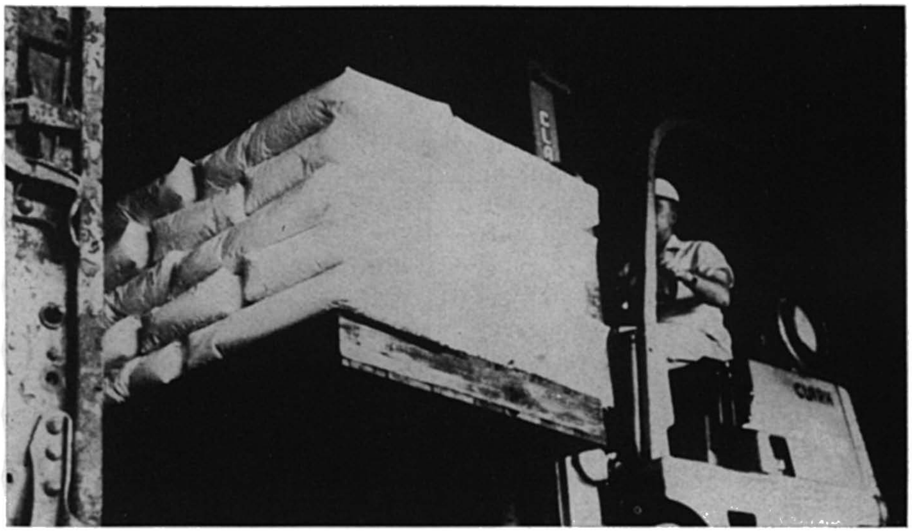


Chart 15
Tractor Moving Filled Pallet to Storage

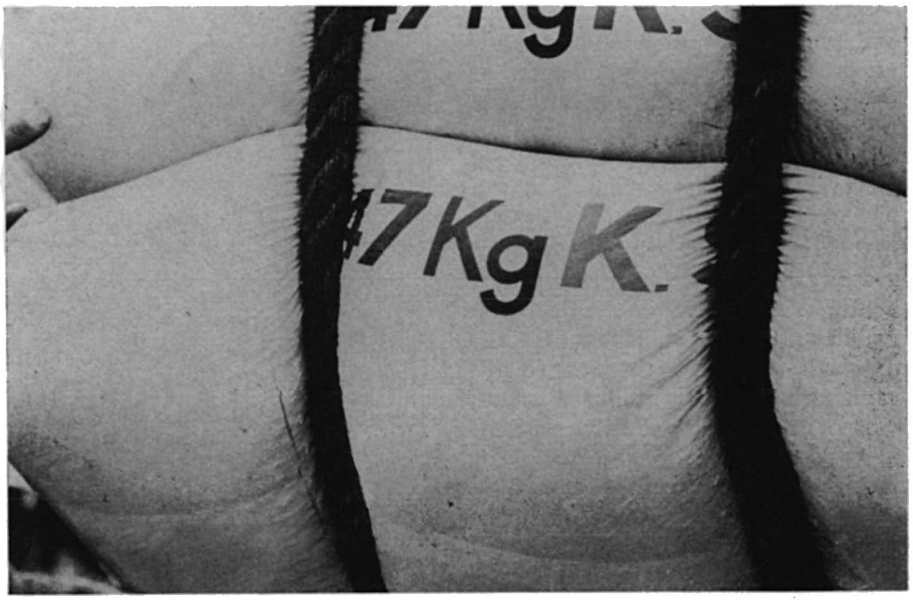


Chart 16
Valeron Film Bag on Sling for Boat Loading

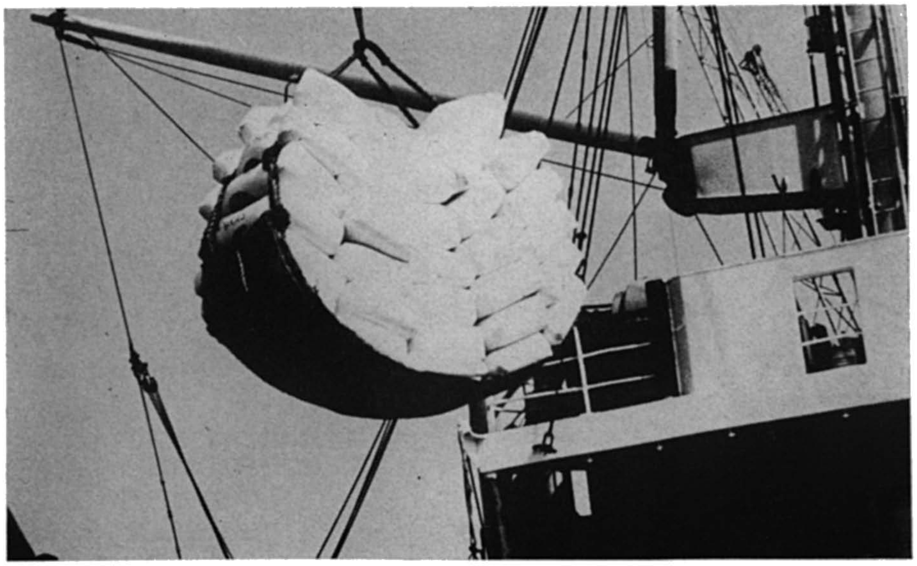


Chart 17
Full Sling Vinyl Bags Lifted on Boat

We have conducted initial marketing and bag performance tests on 10 products including granular fertilizer, granular triple super phosphate, ammonium nitrate, and lawn and graden products: Cross Plastic Bags have been filled, closed, handled, loaded and shipped with normal production equipment and under average shipping conditions. Storage tests are presently under way on several products including—triple super and ammonium nitrate.

The preliminary test results have been most encouraging—in fact, so encouraging that we believe that Cross Plastic Bags will for the first time make year-round packaging possible for your industry. And equally important, to some of you, provide a high performance, low cost export bag. Chart #17.

Gentlemen, these are the latest Packaging systems improvements in filling, product identification, filled bag handling, and the bag itself.

They are the result of development dollars being spent—knowing there's a bag in your future.

MODERATOR SPILLMAN: Thank you Mr. Schrader and Mr. Dively very much. Gentlemen this concludes the latest, up to date information on efficient bagging operations. We have time for several questions.

I have a question. Comparing costs with the regular paper bag, carrying an asphalt liner versus the plastic bag, what is the percentage differential cost?

MR. SCHRADER: As far as the economics go on a cross-plastic bag, it is comparable to the cost of a bag containing three-film polyethylene.

MODERATOR SPILLMAN: I will now turn the meeting back to Vince Sauchelli. Thanks, all of you, for your excellent cooperation.

MODERATOR SAUCHELLI: We want to squeeze in here at this moment the Treasurer's Report. It will be brief. We are not holding the regular business meeting. We will just have the report from our Treasurer. You all know our esteemed Secretary-Treasurer, Dr. Marshall.

Secretary-Treasurer's Report

Housden L. Marshall

HOUSDEN MARSHALL: Members of the Round Table. Your Secretary has been rather active this year. I have several items to bring to your attention.

On the program you will find a list of the back "Proceedings" that are available. If interested, send me a purchase order. I will mail to you and bill you. We do not have too many. If you are urgently in need of any Proceedings not available and you are willing to pay the cost for xeroxing them, I will have the job done for you.

Your secretary has made the usual issuance of meeting notices. We have promptly taken care of all the correspondence and the work that goes with getting up the program, writing to many people interested in our program and other secretarial work. Now the Treasurer's report:

Nov. 1, 1967—Cash on hand	$ 460.30	
Income during year	*8,643.25	$9,103.55
Total Cash to Account for	$9,103.55	
Disbursements		
1967 Meeting Costs	*$2,375.22	
Membership Lists 1967	267.86	
Proceedings Printing 1967	4,510.87	
Secretarial Office Expense	1,211.82	
1968 Meeting Cost-Preliminary	198.37	
Total Expenditures	$8,564.14	8,564.14
Balance on Hand Oct. 31, 1968		$ 539.41
I have an Equitable Trust Bank Statement showing our balance Oct. 31, 1968		$ 539.41

*Note includes $1,200.00 contributed for Cocktail Party and same amount paid to Hotel Mayflower.

Respectfully submitted,
HOUSDEN L. MARSHALL

MODERATOR SAUCHELLI: At the October 1967 T.V.A. Market Conference Hugh TenEyck made the following statement:

"The possibilities of low-cost elemental phosphorus from new hydroelectric installations, as well as from the potential availability of cheap atomic power, coupled with the other geographic combinations, make this material, elemental phosphorus, appear on the scene for the first time as a present or future competitive source of P205 for fertilizers."

It's a very interesting subject, this discussion around elemental phosphorus. We were fortunate to get Taylor Darden, Chemsultants, Inc., to discuss for us the potentials of elemental phosphorus for making phosphate fertilizers.

Mr. Darden was formerly on the staff of the T.V.A. research organization, he has given a lot of thought to this subject and he is now a consultant but the subject of elemental phosphorus for making phosphate fertilizers has engaged his time and attention and I am sure he has prepared a very interesting paper. Taylor, please.

Elemental Phosphorus Production and Use in Fertilizer Manufacture

Taylor Darden

Introduction

This is a subject which has been discussed and written about from every possible angle. When compared to the production of phosphate fertilizer by the mineral acid processes, it is as controversial as the continuing argument of public vs. private power, in fact, the two have been frequently linked together.

I remember helping to prepare a paper that was given in Seattle, Washington, when the Hells Canyon Dam, a public power project consisting of a single high dam, was being opposed by private power who wanted to build three low head dams, and the subject of the paper was the economics of fertilizer production via the elemental phosphorus route as opposed to the sulfuric acid route.

It has been fairly well documented that 4 mill power and $42.00 per long ton of sulfur delivered give comparable unit costs of P_2O_5 as phosphoric acid at a selected location.[1] I do not care to get involved in this continuing controversy.

I would now like to say a few words about the chemical element phosphorus, which while not pertaining directly to the subject, I found quite interesting and I hope you will.

Phosphorus has been associated with both the deity and the devil. It has the properties of both, and I'm sure those of you who have been connected with the operation of either the wet or thermal plants will agree with the latter.

An old alchemist working in a dungeon-like laboratory was the first recorded human being to see its greenish, white glow and because it glowed in the dark, he named it phosphorus from phosphor, the Bringer of Light, the Greek name for the Morning Star. The Morning Star became Lucifer, in Latin, and some early Christian Bible student associated Lucifer with Satan. So our first self-striking matches tipped with, oddly enough a mixture of sulfur and phosphorus, were called Lucifers. The sudden burst of fire and smell of brimstone smacked of the devil.

The human race knew the effect of phosphorus on plant growth long before they knew the agent. Grass grew greener and taller above a pile of buried bones, frequently human bones.

The old German alchemist, Brandt, in the year 1669, was the first recorded man to see elemental phosphorus. He was searching for the philosopher's stone which would turn base metals into gold. He had something, but he didn't know it. Neither did he associate his discovery with agriculture. His method of preparation would make a fairly good patent conception for what is done in an electric phosphorus furnace today. He took an organic solution containing phosphates, boiled it down to dryness, coked the organic material, added silica sand and heated the mixture in his furnace to a high temperature. All he got for his effort was a glow.

The government today has the philosopher's stone in the tax returns from phosphate production.

It is recorded that certain old kings used to have their political enemies and hecklers planted in their kitchen gardens. This served two useful purposes:

1. It took care of a troublesome fellow.
2. It fertilized the garden.

If we were not so civilized, what a solution our leading politicians could have to some of their political problems, and the press. Washington might be greener, too.

Now to aspects of the subject that are of today and the possibilities of the future.

Phosphorus Production

Since there has been so much published on the chemistry and mechanics of phosphorus production, I would like to refer you to the references listed at the end of this paper on these subjects and not discuss them here.

Phosphorus is still produced in the conventional electric phosphorus furnace which may vary in shape from an oval, round, or delta configuration; in electrode arrangement from "in-line" to "delta"; and the hearth may be stationary and/or rotating. The greatest change in the industry has been in the size of the furnace which has increased from about 5000 KW in the early thirties to 60,000-70,000 KW as of today. Furnaces between 50,000 and 70,000 KW are being operated in Russia, Germany, and FMC in the U.S.A.[2] A 70,000 KW furnace will produce phosphorus equivalent to 320 tons of P_2O_5 daily which is small compared to wet acid units at 1,300 tons P_2O_5 per day. This points out the need for larger furnaces; however, there are two main problems to be overcome, the first is that "scale up" has not been as predictable as expected, and the second is providing electrodes of adequate size and strength to carry the high electric current required. An educated guess by experts is that the electric furnace limit will be around 150,000 KW or about 700 tons P_2O_5 per day per furnace.[3]

The large furnaces that are successfully operating today are reported to be using the self-baking electrodes (Soderberge electrodes). It has been reported that the largest electrodes available are 68 inch diameter carbon electrodes[2] and they have given great difficulties due to overheating and breakage.[3]

It is reported that Russia is increasing phosphorus production by 1.2 million tons annually in four very large electric furnace plants. This production would require that each of the four plants has the equivalent of nine 50,000 KW furnaces. This appears a logical development for a country where distances are great, and the transportation network is limited. As far as is known there is nothing of this magnitude either under consideration or proposed in the U.S.A.

Outside of the increased capacity per unit which is common to all chemical processes, there have been no reported startling breakthroughs process-wise in the production of phosphorus.

The blast furnace route appears to be out of the picture, even though the capacity per unit can easily be built in at least twice than that of the present electric furnaces but due to capital investment, recoveries and process problems, it is not now attractive.

The T.V.A. and at least one commercial fertilizer company have been doing research on the reduction of phosphate rock in plasma furnaces. Also, there has been some work along this line by the use of hot gases in fluidized beds.

The opportunity for better heat recovery from the process appears to have possibilities in lowering the cost of phosphoric acid production by thermal methods. Some of these areas are:

1. Approximately 1.6 million BTU per ton are required to calcine the phosphate portion of the furnace charge. This amounts to about 15.0 million BTU per ton of phosphorus or 37% of the heat required to produce one ton of phosphorus. No known attempts have been made to recover this energy.
2. The recovery of the heat released when phosphorus is burned and hydrated to make phosphoric acid which amounts to about 25 million BTU or 60% of the heat requried to produce one ton of phosphorus.
3. The heat lost in the slag leaving the furnace is about 12 million BTU or 29% of the heat required to produce one ton of phosphorus.

It may be both uneconomical and technically impossible to recover the heat lost in the slag. The other two items offer definite pospects.

Albright and Wilson reportedly generate steam from Dowtherm heated by the combustion of phosphorus with dried air.

At a power cost of 3 mills per kilowatt hour, the heat requirement to produce a ton of phosphorus is about 45% of the total operating cost and the recovery of 75% of this heat would cut operating cost by about 34% or about $12.00 per ton.

The only energy recovered from the process in the U.S.A. today as far as it is known is the use of by-product carbon monoxide in the calcining operation, which requires about 70% of the CO produced. Some carbon monoxide may also be used to dry the silica and coke.

It will probably be in the development of a different kind of furnace for phosphorus production such as the fluidized bed type where heat recovery will be exploited to the fullest.

Also, if and when the shipment of phosphorus in considerable quantities to other locations for conversion to phosphoric acid becomes a reality, will the recovery of the heat from this source become important as the steam generated can be used in the storage, unloading, and processing operations.

Factors that May Influence the Selection of the Elemental Phosphorus Route to Phosphoric Acid Production for Agricultural Uses

Phosphate Rock

The general depletion of high grade deposits from previous skimming the cream off the milk mining practices are forcing some phosphate producers to consider methods of economically using the lower grade ores that are left. Ores containing what are considered high in iron and alumina, the booga-boos of the wet acid process, can be successfully processed by thermal methods. Within reasonable limits the Al_2O_3 content does not have any effect on the process and the Fe_2O_3 content only lowers the recovery of elemental phosphorus. The iron content is converted to ferrophosphorus which usually has some value as such. Processes have been developed to recover the iron and phosphate values and other metallic compounds such as vanadium may be contained in the ferrophosphorus.

There are a number of known phosphate deposits that are not suitable for wet process phosphoric acid production. Other deposits in the developing nations may be discovered which are of low grade and suitable for the thermal process.

Table I shows the composition of the phosphate portion of an electric phosphorus furnace charge using mixtures of low grade matrix and high grade phosphate rock from Florida, North Carolina and Idaho sources. Due to the high CaO/P_2O_5 ratios in both the Florida and North Carolina phosphate ores, the table shows a lower P_2O_5 content in the furnace charge from these ores than the Idaho phosphate, which is in the desired range. However, I believe that these lower grade ore combinations can be economically furnaced. The table also shows that the beneficiation step to produce the 68 BPL rock should be geared to remove as much as posslble of the calcite from the rock and still retain as much of the SiO_2 as possible.

When adding the difference in capital investment for the beneficiation plant, and a clarification section to wet acid plants that expect to ship most of their product as phosphoric acid, the investment gap between the two processes narrows. It narrows still further if superphosphoric acid is to be shipped because these facilities have to be also added.

The phosphate recoveries from mine to phosphoric acid are higher for thermal process than wet acid processes as shown in Table II. While advised that the ore as mined (matrix) should be deslimed with the inherent losses of P_2O_5 in this operation, before blending with the higher grade beneficiated ore in the case of Florida and North Carolina rocks, my calculations show that you obtain a higher P_2O_5 content in the phosphate plus silica content of the furnace charge without desliming. Of course, this may vary from deposit to deposit depending upon the CaO/P_2O_5 ratio and the SiO_2 content of the phosphate matrix. There is one thing common to both the wet acid and thermal processes and that is the higher the CaO/P_2O_5 ratio, the more acid and/or electricity will be consumed per ton of product.

Table I. Blends of Phosphate Matrix and 68 BPL Rock for Electric Furnace Charge Showing Grade of Furnace Charge and P_2O_5 Losses on Beneficiation

	Florida—Calcined Basis (Calc.)			N. Car.—Calcined Basis (Calc.)			Idaho Actual[1]
	Matrix	68 BPL	Furnace Charge	Matrix	68 BPL	Furnace Charge	Furnace Charge
P_2O_5, %	20.0	32.6	23.9	20.6	33.2	23.6	28.6
CaO, %	30.5	47.8	35.8	32.4	53.2	37.2	42.0
SiO_2%	37.0	10.0	28.8	38.3	2.1	29.8	23.8
Silica Rock Added, %	—	—	—	—	—	—	9.8
% P_2O_5 in Fce. Charge	—	—	23.9	—	—	23.6	25.6
% P_2O_5 Loss on Beneficiation	0	25	—	0	15	0	0
Ratio Matrix/68 BPL	2.3	1.0	3.3	3.3	1.0	4.3	(1)
SiO_2/CaO Wt. Ratio	—	—	.80	—	—	.80	.80

[1] Mixture of the high grade and shale beds as mined.

Power Cost

The advent of large nuclear power plants such as the T.V.A. Browns Ferry plant is expected to have a very significant effect on the cost of power. It is expected that this plant will produce electric power at 2.38 mills per KWH at the bus or around 4 mills delivered to the electric furnace plant. A breeder reactor now under development is expected to lower the cost of power still further[2,3]. More than half of the 2.38 mill cost cited above is from nuclear fuel and the breeder reactor is expected to produce almost as much fuel as it consumes.

The combination of nuclear power generation and the electric phosphorus furnace is a natural with the high load factor of the electric furnace permitting the nuclear reactors to operate at peak efficiencies.

A recent news release in C&EN News states that Kaiser Chemical is investigating this possibility in the Florida phosphate field.

As a matter of interest, one carload of nuclear fuel will produce as much power in a year as a 100 carload train of fossil fuel per day.

Transportation

Of the three major plant nutrients, nitrogen, phosphorus, and potash, most of the phosphate used for agricultural purposes is shipped in a concentration much lower than the other two as shown in Table III. In fact. it has been only in recent years that phosphates were shipped long distances in any form except as phosphate rock which contains only about 15% phosphorus. Even today the bulk of the phosphates exported is in this form.

Table II. Comparison of P_2O_5 Efficiencies From Mine to Phosphoric Acid by the Thermal and Wet Process Phosphoric Acid Routes

	Electric Furnace Process			Wet Acid Process		
	Florida	North Carolina	Idaho	Florida	North Carolina	Idaho
P_2O_5 Recovery from Matrix Use	100%	100%	100%	—	—	—
P_2O_5 Recovery on Conversion to 68 BPL Rock	75	85	Not Required	75	85	70
% Matrix Beneficiated to 68% BPL Rock	30	23.5	0	100	100	80
% P_2O_5 Recovered From Mine	92.5	96.5	100	75	85	76
% P_2O_5 Recovered During Processing to Phosphoric Acid	88	89	88	95	95	95
Overall P_2O_5 Recovery Mine to Phosphoric Acid	81.5	85.5	88	71.3	81.0	72.0

Most of the countries importing phosphate rock have a sufficiency of gypsum for both their agricultural and industrial uses without the need of using by-product gypsum for these purposes.

Elemental phosphorus has been safely shipped by rail, truck and water for many years. It is a non-corrosive material that may be shipped, stored and handled in mild steel equipment.

It is when phosphorus instead of phosphate rock is exported, that presents the most interesting economic picture. The T.V.A. has prepared an analysis of the cost of importing phosphorus into India and then converting the phosphorus into diammonium phosphate vs. (1) wet process acid from imported rock and sulfur and then producing DAP and (2) importing DAP from the U.S.A.[4] which shows that importing phosphorus is the cheapest of the three methods.

The conversion of phosphorus to phosphoric acid is much simpler and requires less capital investment than converting sulfur to sulfuric acid. Also, the phosphorus conversion plants present less of an air pollution problem.

A comparison of liquid (phosphorus) cargo water rates to various ports around the world from Tampa, Florida is shown in Table IV.

It is interesting to note that in most cases the liquid cargo rate is quite a bit lower than the dry cargo rate which also applies to the shipment of phosphate rock, DAP, etc., and this factor should definitely enhance the economics of the shipment of phosphorus vs. other phosphate containing compounds.

Albright and Wilson of England are now entering the field of producing phosphorus in Newfoundland and shipping the phosphorus to England for conversion to phosphoric acid. They have constructed two ships to carry the

Table III. Concentration at Which Fertilizer Materials May Be Shipped

Basic Materials	
Elemental Phosphorus	100.0 P
Ammonia	82.3% N
Potash as Potassium Chloride	50.0% K
Superphosphoric Acid (Wet Process)	30.0–32.0% P
Phosphoric Acid	22.0–24.0% P
Phosphate Rock, 74–76% BPL	15.0% P
Base Materials	
Triple Superphosphate	20.0% P
Di-Ammonium Phosphate	38.9% N + P
Calcium Metaphosphate	30.0% P
Ammonium Polyphosphate	42.0% N + P
Urea	45.0% N
Ammonium Nitrate	33.5% N

phosphorus to England and also carry phosphate rock from Florida to Newfoundland. The combination of dry cargo and liquid cargo ships probably played an important role in the overall economics of their particular case.

(Figs. 1 and 2, ship and cargo designs, respectively, were not clear enough to be reproduced.)

I am sure this is quite different from the usual tanker design for most liquid cargos and very similar to the liquid cargo section of the Albright Pioneer of Albright and Wilson which has already been launched.

One of the big advantages of the shipment of liquids over dry bulk cargo is the fact that minimum port facilities are required to unload the ship, as the necessary equipment, mainly pumps, are easily added to the ship's equipment.

I am a firm believer that each production locality and product market has its own economics, therefore, I have not worked out an economic comparison of the production and distribution of phosphates via the two processes discussed.

However, for those who are interested in this for a particular situation, and care to do their own calculations, the next table, Table V gives the approximate raw material, utilities, and products produced for the production of elemental phosphorus which will complete the economic picture.

Table IV. Approximate Water Transportation Rates from Tampa, Florida to Ports Indicated.

Port	Approx. Distance	Liquid Cargo Rate*	Dry Cargo Rate (Bulk)
Bombay, India	9,000	$10.35	$17.00
Madras, India	10,000	11.50	17.50
Calcutta, India	10,500	12.08	11.30
Singapore, Malaysia	10,900	12.54	17.50
Durban, South Africa	7,300	8.40	11.30
Beirut, Lebanon	5,900	6.79	10.20
Manila, Philippines	10,200	11.73	14.70
Freemante, Australia	10,300	11.85	12.50
Ravenna, Italy	6,600	7.59	9.10
Cartegena, Spain	4,200	4.83	8.50
Liverpool, England	4,000	4.60	7.40
Rotterdam, The Netherlands	4,300	4.95	6.80
Santos, Brazil	5,700	6.46	—
Buenos Aires, Argentina	5,600	6.44	—
Callo, Peru	2,200	2.53	—
Keelung, Taiwan	10,800	12.42	13.00
Cork, Ireland	3,900	5.49	7.40
Helsinki, Finland	5,200	6.48	—
Memphis, Tennessee	1,600	4.80	—
Paducah, Kentucky	2,300	6.90	—
St. Louis, Missouri	2,500	7.50	—
Clinton, Iowa	2,800	8.40	—
New York, New York	1,900	5.70	—

* Based on published rates of the American tanker rate schedule for dirty cargo and barge rate schedules on a ton-mile basis with water ballast return trip.[3]

The Use of Phosphates Produced from Elemental Phosphorus for Agricultural Purposes

Any fertilizer compound produced by the wet acid process can also be produced from phosphoric acid from elemental phosphorus in higher concentrations than possible by the wet acid process. As an example, DAP from wet acid has the analysis 18-46-0, a total plant food content of 64% while DAP produced from electric furnace acid, 21-53-0, contains 74% plant food.

In addition to fertilizer compounds when producing phosphorus, it is possible to produce animal feed grade phosphates without expensive purification steps and the direct production of pesticides is also possible.

The possibility of the development of high concentration fertilizer compounds, other than those that are now known from wet process acid is very limited. New fertilizer compounds from elemental phosphorus are possible. In fact, compounds made from phosphorus, ammonia, and air having a nutrient content up to 147 percent based on the P_2O_5 equivalent, have been made and agronomically tested that gave results comparable to standard fertilizers.

The use of a pure compound such as furnace acid always raises

Table V. Raw Materials, Utilities and Products.

(Tons per ton of phosphorus)	
Phosphate Rock	9.4
Coke	1.6
Silica	1.6
Electrodes	.017
Cooling Water	35.0
Phosphorus	1.0
Slag	8.1
Ferrophosphorus	0.946
CO Gas (82,000 SCF.)	2.8
Precipitator Dust	0.13

the point that wet process acid contains many of the trace elements needed for plant growth. I believe that these elements may be added to fertilizer in a form more available to plant, more economically than their natural inclusion in wet process acid due to the fact that their inclusion in wet process acid adds to the sludge removal and disposal problem.

References

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2. "Production of Basic Chemicals —Phosphorus", Striplin, M. M. Jr., Oak Ridge Associated Universities Annual Conference on Nuclear Energy, August 1968.
3. Private Communications.
4. "Economic and Technical Evaluation of Overseas Shipment and Utilization of Elemental Phosphorus for Fertilizer Production" Scott, W. G., Patterson, G. G., Gahan, Jr. and Hignett, T. P., T.V.A. January 1968.
5. Chemical Engineering Report No. 3 — "Production of Elemental Phosphorus by the Electric Furnace Method".

MODERATOR SAUCHELLI: Any questions? This is a very interesting subject. The future has tremendous possibilities for the phosphate industry. Did I see a hand there? Would you identify yourself and talk into the mike, please.

MR. RICHARD KULP: I would like to ask Mr. Darden the fluorine distribution from rock to finished product —

MR. DARDEN: It has been some time since I have gone back on these figures but the bulk of the fluorine goes out with the slag. Some of it is evolved and goes out with your phosphorus condenser water. So far as getting in the product, it does not get in the phosphorus which is converted to phosphoric acid.

MR. KULP: How about the fluorine that is evolved in the calcination?

MR. DARDEN: A lot of that depends on how high you calcine. I would say, if my memory is right, somewhere maybe from 15 to 30 per cent at a high temperature of calcining could be involved in the calcining step.

MR. RICHARD MACFARLANE, USS Agricultural Chemcial: I would like to ask if I misread the slide. I thought it said that the tons of ferro phos was 9.– something. Shouldn't that be .09?

MR. DARDEN: It probably is. I think .09 is correct, right.

MODERATOR SAUCHELLI: Ronald W. Young: (Dr. Young) TVA. Do you have any comments?

DR. YOUNG: No, sir, I would just say it was a very interesting presentation. We feel that worldwide phosphorus does offer some real opportunities for the future.

MODERATOR SAUCHELLI: I know TVA is doing a lot of work on this.

MR. WILLIAM ROSENBLOOM, Mobile Chemical: At a power cost in the range of 4 mills, what are we talking about in terms of cost per ton of P_4?

MR. DARDEN: I think it's somewhere around 10 or 12 cents a pound, which would be $200.00 to $240.00 a ton.

MODERATOR SAUCHELLI: Mr. Harding, do you have any comments–

MR. CHARLES HARDING: (Wellman Lord, Inc.) No, I agree with what he said.

MR. ARTHUR HURLY: Is there any economical method for recovering water soluble P_2O_5 from the precipitator dust?

MR. DARDEN: Yes, there is and also most precipitator dust contains some potash values also.

MR. HURLY: Then the question is: Is there any process for recovering this P_2O_5 that is in the precipitator dust, or phosphorus?

MR. DARDEN: In a lot of instances it is what you might say recirculated, added back to the furnace charge, blended in and for many years TVA sold precipitator dust as such. It is a very, very small portion of your P_2O_5.

MODERATOR SAUCHELLI: Dr. Ewell.

DR. EWELL: Mr. Darden, from your vast knowledge of this subject, could you make an offhand guess as to what price, say, a Florida company might be willing to deliver phosphorus in India?

MR. DARDEN: No, I couldn't. I do know it is being shipped from the East Coast out into West Texas by rail and converted into fertilizers and I think that price was somewhere around, oh, between $300 and $350 a ton, depending on the time of the year and the market for phosphorus.

DR. EWELL: I have a figure quoted to me within the past two weeks by somebody concerned with India that some company in the United States had offered to deliver phosphorus in India for $130 a ton. I almost fell out of my chair but he insisted this was a firm figure.

MR. DARDEN: I think that's quite a bit too low. I think it may have been on a P_2O_5 basis, not per ton of phosphorus basis.

DR. EWELL: That may be the source of the discrepancy but this particular individual thought it was phosphorus.

MR. DARDEN: It sounds more like the cost per ton of P_2O_5 than the cost per ton of phosphorus.

MR. ALLEN LONGACRE, Fluor Corporation: You mentioned earlier about the possibility of alleviating air pollution at the point of manufacture of fertilizer products from elemental phosphorus. But how about the point of manufacture of the elemental phosphorus and what might be done about air pollution at that point?

MR. DARDEN: You still have the air pollution problem at the point of manufacture of phosphorus but at your conversion points, no.

MODERATOR SAUCHELLI: Thank you, Taylor. A very interesting paper. I am sure we are going to hear more about phosphorus in the future.

MODERATOR SAUCHELLI: A subject which the chemical process industry never tires of promoting is safety for the worker in the plant. Although humanitarian reasons come first, it is also pertinent to point out that accident prevention also pays well in dollars saved in insurance rates and indirect costs from accidents. The subject is of direct interest to most of this audience.

We have John Mark here from

the National Safety Council to tell us about the importance of accident prevention in the fertilizer plant. John needs no extended introduction to this audience. He has been here before. John, please.

Safety in the Fertilizer Plant Another Tool for Efficient Operations

John Mark

All too often we look at safety as a "tack-on" activity in plant operations. A necessary activity to keep employees from getting hurt. Something that is attended to when we are not too busy trying to meet production schedules. Perhaps it is the word "safety" that brings about this attitude. As we use the word safety, it implies that its use is for the welfare of the employee only. In recent years safety people have tended to use the definition accident prevention more and more to define this field of activity. Even this term doesn't completely clear up the confusion.

When we talk about safety in the fertilizer plant we get involved in many activities, which, if followed and carried out, results in not only an efficient plant, but a safe plant. Many of the things you do to insure an efficient plant, automatically results in a safe plant. The functions are interrelated.

Let's look at some of these functions. Management is responsible for efficient plant operations. Safety programs are also a management function and responsibility. Supervisors carry out efficient production programs. They also implement company safety programs. Safety is not a responsibility of the safety department or safety man. The safety department provides the technical know-how, the safety programs, the tools for operation of a safety plant. Because safety is his job, he helps and keeps everybody alert to hazards and how to correct them. If the organization does not have a separate safety department, then management and line supervisors must develop and implement the safety program.

What are some of the tools we use to insure an efficient operation which also results in a safe plant? We will discuss a few.

Good Plant Design and Lay-out

When a new plant is built this should get close attention. The safety department should be brought in to point out possible built-in hazards or trouble spots in design. Close attention to design and lay-out promotes good production flow resulting in an efficient operation and safe operation. In an old plant where this cannot be done, modification and study of existing lay-out will improve production and safety.

Purchase of Equipment to Do the Job

Good equipment designed for the job and placed in production flow sequence most certainly results in an efficient and safe operation. Bottlenecks impede production and usually present a hazard in some form to employees.

Training of Supervisors

Before a supervisor can handle production efficiently, he must know the operation from one end to another. He needs this knowledge to be able to train the people under his supervision. Management should provide the programs to make this possible. A supervisor who knows the jobs in the department, also knows the hazards and how to work around them.

Training of Employees

Training of new employees and guidance and retraining of regular employees is a very necessary operation today, if a plant is to be efficient and competitive. Training employees to perform a task according to a predetermined method results in an efficient production line and safe working habits. If you let the man teach himself, he may learn to do the job inefficiently and usually unsafely. The buddy system of training is alright, if the buddy knows the job plan and works closely with the supervisor.

Effective Production Planning

Plant management and line supervision should plan schedules well ahead, so everybody knows what is to be done. Advance knowledge of the job to be done results in initiation of the work with a minimum of confusion. Confusion causes inefficiency in plant operations and sets the stage for unsafe practices and possible accidents.

Good Housekeeping

Good housekeeping is usually a sign of efficient operations. Keeping the plant cleaned up, having a place for tools and equipment indicates an orderly and well thought out, planned procedure for plant operations.

Emphasis on housekeeping instills in the minds of employees the importance of orderly procedures necessary for an efficient operation. It develops an attitude of carefulness and pride in work. This contributes to a safe operation.

* * * * * *

Now, the above functions do not take care of all the things that should be done to insure a safe operation. But they do give you a good start and accomplish most of the work. Our point so far is to establish that doing things necessary to operate an efficient plant, also takes care of many hazards and promotes a safe working atmosphere.

To finish the job of maintaining a safe operation you need:

1. Safety equipment as needed.
2. Safety promotion plans.
3. Safety meetings.
4. Safety incentives.
5. Guarding of equipment.
6. Safety inspections.
7. A medical program.

These things are handled by the managers and supervisors with the help of the safety department.

There are many examples of successful safety programs in the fertilizer industry. The frequency rate for 1967 among reporters in the National Safety Council for the Fertilizer Section was 6.03. This is the first time the fertilizer industry was above the industry average. The industry average in 1967 was 7.22. The frequency of 6.03 in 1967 is about one-third of what it was in the early 50's. Excellent progress has been made since 1965. The frequency rate for that year was 9.91. The frequency rate through August of this year is 5.20.

Another interesting fact—146 plants participated in the contest. Of these 68 reported perfect records.

A plant in Jacksonville, Florida recently marked 10 years without a lost time accident. Many plants are reporting 1,000,000 manhours without a lost time accident. Operating a safe as well as an efficient plant is becoming an accepted way of doing things.

An inefficient plant operation indicates a higher unit cost of production. An inefficient plant operation is usually an unsafe operation. They usually have more first-aid cases and lost time injuries. Both conditions result in higher costs of production. They may not be set out separately to be seen, but they are there. Every accident has a charge which is not taken care of by insurance. These are the "out of pocket" costs. Some of these costs are loss of production time, removal of the injured, treatment of the injured, repairing the machine, the let-down that persists for awhile after an accident, the loss of the employee's services, the cost of training a new employee. These charges are measurable if the time is taken to figure them. A high frequency rate eventually results in a higher compensation rate.

An efficient plant operation, high production, good safety record go hand in hand. Whether we recognize it or not management and supervision is always involved in safety to a great extent. We just need to take one more step and make it a total part of management.

Yes, safety in the fertilizer plant is a necessary tool for efficient operations. Its benefits are readily measurable. Some of the benefits are, efficient production, low costs, good morale, good public image.

The fertilizer industry is to be congratulated on the fine record it has turned in, in accident prevention. But we can't stop there. Safety like every other phase of good management requires continuous attention. Let it take its regular place in your overall planning.

MODERATOR SAUCHELLI: Thank you, John. We are running short on time and we want to resume at one-thirty, so we stand adjourned until that —

VOICES: Two o'clock.

CHAIRMAN SAUCHELLI: Two o'clock?

Thursday Afternoon Session, Nov. 14, 1968

The Round Table Meeting Reconvened at 2:00 o'clock P. M.
Vincent Sauchelli and Robert R. Heck, Moderators

MODERATOR SAUCHELLI: The trend in American farm production methods since the 1940's has been toward intensification in all phases. We have new cropland varieties with greater capacity to produce more per acre, fertilizer compounds with substantially higher nutrient content and so on.

This intensification in production practices has led in many farm areas to the rapid depletion of native soil fertility elements and particularly of the trace elements.

Interest in these elements is growing throughout the industry which now is studying ways and means of replenishing them in deficient soils in a practical and efficient manner. Because of this interest, we considered it desirable to include on the program two talks on this subject. The Ferro Corporation has devoted much research and expense in developing one type of material to meet the situation, the fritted micronutrients, which are designed to release the contained nutrient element at a controlled rate.

Mr. Gene L. Bruton, Manager, Agricultural Chemicals, is here to describe the material and its function. He has been associated with this development from its inception and deserves a lot of credit for the manner in which he carried it through to the commercial stage. I have been in touch with this development from the start. I have been following Mr. Bruton's experiences and progress and I am certainly delighted to give him the credit for this fine work. Gene, please:

Development and Manufacturing of Fritted Micronutrients

G. L. Bruton

A few years ago, when it would have been highly unusual for a girdle manufacturer to merge with a soft drink company, we were often asked why Ferro Corporation was entering the fertilizer field. At that time, there had to be a logical reason for a corporation to stray so far afield in its diversification program.

We would like to explain the logic behind our development of fritted micronutrients and to show why FTE is an extension of Ferro's capabilities both in research and development and in the manufacture of the product.

Ferro is a highly diversified company but, if there is any one capability that is predominate, it is in the development of specialty glasses designed to fit stringent physical and chemical specifications. In the porcelain enamel field, the finish must meet many rigid tests. If it is used on a washing machine tub, then it must be resistant to alkalis. If it is applied to a range top or refrigerator innerliner, then it must have properties of acid resistance. If your wife spills tomato juice inside the refrigerator this is a severe test. If she spills it on the top of a hot range, the porcelain enamel must withstand not only the acid resistance test but also heat shock. Hot water tanks formerly failed in a very short time in some areas due to hot water attack. Now we have a porcelain enamel finish that resists this attack very effectively.

In the glaze field, the coefficient of expansion of the glass is most important in preventing crazing or spalling on bathroom ceramic tile or your lamp base.

We mention these examples to point up the many variables and requirements of a physical and chemical nature that have faced the Ferro research department for the last 35 years in helping to produce better products for your home.

We could add literally hundreds of additional qualities necessary in a glass to meet the manufacturing needs of the users of Ferro porcelain enamel or glazes. We have cited the above examples to substantiate the claim that Ferro has the technical ability to develop a glass product properly formulated to release nutrients to the plant at a predetermined controlled rate.

Of a secondary, but very important consideration is the fact that material of this nature can be manufactured with production equipment which is used in the manufacture of other frit products.

The product development of fritted micronutrients passed through several distinct phases since the original idea was conceived by Ferro's research department early in 1948. The original concept concerned the development and manufacture of controlled release of two glass forming major elements P_2O_5 and K_2O. Such a glass was made but due to obvious economic restrictions, there was really not much to inspire a development and marketing pro-program.

On consultation with experts in the field, it was pointed out that problems of toxicity, leaching and effects of soil environment were more prevalent in the field of micronutrients and the economic problems were not nearly as severe as those in the major element field.

The original and most important question to be answered was whether a plant could take up micronutrients from a glass matrix. To prove this, glasses containing single elements of iron and manganese were developed in our research department. A grant-in-aid was supported at Michigan State University under the direction of Dr. F. L. Wynd to make these basic research studies.

Dr. Wynd carried on his experiments in iron-free and manganese-free environments and established that both iron and manganese could be utilized by a plant when these elements were contained in a slowly soluble glass matrix.

After this fact had been established, Ferro research started in earnest to develop and test glasses containing all of the recognized trace elements. An agronomist and a ceramic engineer were assigned to the project to make composition studies.

During this phase of the development program, the objective was to study a range of release rates and develop an empirical chemical test to measure the rate of release. A chemist was added to the task force to develop the empirical test.

The first compositions contained six micronutrients; namely, boron, copper, iron, manganese, molybdenum and zinc. The agronomist in charge established the ratios of the elements, and glass compositions of varying theoretical solubilities were manufactured for test.

For the next two years these compositions were studied in greenhouse sand culture under the direction of the agronomist. Since growth was observed in sand culture, with the other elements added as chemically pure solutions, the only variables were rates of application of trace elements and the solubility of the glass matrix. Control plants used in these tests were beans, highly susceptible to boron toxicity, and turnips, which have a high need for boron. Check replicates were, no trace elements on one end and mixtures of soluble salts on the other end of the spectrum. It is interesting to note in passing that our agronomist saw evidence of interference or influence of one trace element on another when the rates of application of the soluble salts were increased to high levels. No evidence of these induced deficiencies were noted in the glass replicates even at extremely high rates of application. However, as we moved into softer compositions of glass we began to see evidence of induced deficiencies in the high rates of application of the glasses. This was our first indication of the advantage of controlled release of trace elements to plants. The absence of luxury quantities of available plant nutrients apparently reduces the effect of one trace element in over-supply on the uptake of another trace element. This was before we started leaf analysis, and these conclusions were reached by our agronomist through observation on leaf color in the growing plant. It can be said however, that these variations were so extreme that they could be seen by any casual observer.

During this period the chemist member of the Ferro research team began to compare the crop response with the release rate of micronutrients from the glasses in acetic acid buffered by ammonium hydroxide to pH_4, pH_5, pH_6, and pH_7. Briefly stated, in this test a standard fineness fraction of the glass is agitated for 16 hours in ammonium acetate at the four levels of pH mentioned. The amount of the various micronutrients released to this solution during the sixteen hours is taken as a measure of the release rate of the micronutrients from the glass.

The test, developed during this phase of our program, to determine the release rates of micronutrients from glass is still used today to guide us in the development of new FTE compositions.

Concurrent with the multiple trace element developments, we cooperated in a similar investigation with the U. S. Borax & Chemical Corporation for a study of glasses containing the single element boron. From these studies, we not only developed a satisfactory, slowly soluble boron frit, but also developed valuable information to guide us in our general development program.

At this point, we turned to the agricultural colleges and experimental stations to guide us in the development of a product to answer the needs of the fertilizer industry.

It would be impossible to cover here or to acknowledge all of the help that we have received from technical people in land-grant colleges over the past 14 years in the development of fritted micronutrients. Literally hundreds of investigators tested our products. Consequently, we must necessarily stress the high points in these investigations and confine direct reference to the development of FTE to the stage of becoming a commercially usable product.

Some of the earliest grants-in-aid were established at Clemson, Rutgers and the University of Florida.

Again, time will not permit us to go into detail on the work that was done between 1953 and 1961 in the three institutions mentioned and the U. S. Department of Agriculture. We will instead, report to you only on the aspects of these tests which we feel led to the establishment of a definite difference between FTE and other sources of micronutrients.

At Clemson, under the direction of Dr. N. R. Page, both laboratory and field studies helped us to determine a release rate that was most efficient from an economic standpoint and still maintain limits of toxicity most adaptable to use on a wide range of crops and soils. During these investigations, field test plots on beans were studied in relation to the rate of release of boron. We did in fact, increase the release rate of boron in some of the glasses to the extent that it was no longer safe to add what can be considered reasonable doses without fear of the toxic effects.

When rates of release were considered satisfactory, then the oposite effect; namely, soil build-up was studied over a period of four years with a product that we considered to be marketable. Repeated high applications were made to plots over the four years with no apparent indications of soil build-up.

During this time carefuly controlled leaching tests in lysimeters indicated the boron content of the glass was released over a period of approximately one year.

Since it was felt that cotton in South Carolina would respond to manganese and boron, a manganese-boron frit was developed for field testing. In two tests in each county of South Carolina, one acre plots of cotton compared fritted micronutrients with the soluble salts of manganese and boron. Average results throughout the state showed both frit and soluble salts increased the yield of lint cotton in South Carolina by 31 pounds per acre.

After four years of work, Dr. Page had investigated fritted micronutrients to the extent that he made the following statement in the publication, *What's New in Crops and Soils,* June-July, 1957, "Slowly-soluble minor element 'frits' offer a means of minimizing some of the problems associated with soluble minor element compounds.

Because they release the elements at slower rates, frits reduce seasonal fluctuations in the supply of available minor elements. They thereby reduce the danger of toxicity on the one hand while at the same time providing a more uniform and continuous supply throughout the entire growing season.

Thus, there is more efficient utilization of the applied minor elements and it is reflected in more consistent yield response. With less danger of toxicity, special fertilizers for specific crops are not necessary and minor elements may be included in general crop fertilizers."

At this time, this opinion was reflected in the South Carolina recommendations for cotton fertilizers in which they sanctioned either the use of colemanite and manganese sulphate or frits. There was a qualification however which stipulated that, fertilizers containing the soluble materials should be used on cotton only, but that fertilizers containing the recommended amount of frits could be used on any crop.

Concurrent with the work done at Clemson, the horticultural department of Rutgers University, under the direction of Dr. Norman L. Childers, investigated fritted micronutrients in plot tests, greenhouse studies and field trials on commercial vegetable crops in the South New Jersey area.

In carefully controlled greenhouse studies, Mr. Abdul R. Kamali, in conjunction with Dr. Childers, studied the micronutrient uptake by orange seedlings from a fritted form of trace elements. Although this was one of our earlier compositions, results as reported in the publication of the American Society of Horticultural Science, Volume 72, 1958 established the fact that all trace elements including boron, copper, iron, manganese, molybdenum and zinc were taken up by the plants in quantities showing an increase in uptake from low to high rates of application. Thus we substantiated earlier studies at Michigan State regarding the ability of plants to take up minor elements from a glass matrix.

After several years of study, research and continued development, including the yield tests mentioned above, Dr. Childers reported in *New Jersey Farm and Garden,* in March, 1957 in an article titled a "Progress Report on Minor Elements", that the tendency to produce fertilizers containing insurance quantities of minor elements was growing in popularity. In this article he states, "Many fertilizer companies, who typically look at the over-all problem from a practical standpoint, have devised fertilizer mixes that will supply, in addition to major nutrients, modest amounts of trace elements, These are referred to as "Premium Grades". By this "shotgun" or "short-cut" approach, the grower can pay $5 to $10 more a ton for these grades. He more or less considers them "insurance" against trace element deficiencies. The increased fertilizer cost is considered nominal as compared with cost of, for example, spray materials for apples on an acre basis."

In work done under grants-in-aid by Ferro at the University of Florida in Gainsville, Florida during the period of 1954 to 1960, Dr. J. G. A. Fiskell and Mr. H. W. Winsor directed projects which substantiated the claims to low toxicity hazards and long lasting effect of fritted micronutrients.

In an article printed in the *Florida Grower and Rancher,* January, 1960, Mr. H. W. Winsor demonstrated that fritted micronutrients go to work immediately after it is applied. He stated, "Frit has been designed as a persistent material. But it also appears (see lysimeters of turnips on page 9) to furnish an adequate early-season supply of nutrients. In the case of the turnips, the fritted plants began to show superior growth and vigor within four days from seedling emergence." This result found by Mr. Winsor is an effective rebuttal to some arguments that frit should not be used where early response is needed on fast growing crops.

The long lasting effect or persistency of micronutrients from a fritted source is attested to in work done by Dr. J. G. A. Fiskell and the Beef Research Unit Range Cattle Station on the maintenance of clover forage throughout the season in Florida. In his article, printed in the October, 1958 issue of the *Florida Cattlemen,* he stated: "Few cattle or dairy herds have a diet of good clover grass twelve months a year. Proper soil fertility can keep clover growing from season to season. Lime, fertilizer and minor elements must be supplied." In this study he proved that fritted micronutrients performed their part of this requirement by staying in an available form throughout the growing season. They furnished minor nutrients when they were most needed to maintain the clover growth.

Dr. E. R. Holden, of the U. S. Department of Agriculture made some very thorough investigations of agricultural frits. Over a period of several years he studied the release rates of boron from single element boron frits. He studied the effects of fineness of grinding as well as composition on the uptake of boron versus a soluble source. He used alfalfa, a highly tolerant crop to boron, as his control plant. Only a thorough study of the reports of Dr. Holden and his associates in *Agricultural and Food Chemistry,* and the summary included in the Micronutrients Symposium in May-June, 1962, can do justice to Dr. Holden's thorough investigation.

Here we can only quote a statement made in the article, "Properties and Uses of Micronutrient Glasses in Crop Production," by Dr. E. R. Holden, Soil and Water Conservation Research Division, Agricultural Research Service, U. S. Department of Agriculture; Dr. N. R. Page, Department of Agronomy and Soils, Clemson Agricultural College and Dr. J. I. Wear, Department of Agronomy and Soils, Auburn University; which stated, "Response to the glass, though initially lower, becomes greater than that to borax in late growth. Only about one half as much boron was needed to keep boron content of the crop from falling below the lowest level occurring with borax. Broadly, the effect of the glass is to minimize seasonal variation in crop boron (25) as indicated in Figure 3."

This then is the basic story of the research and development in fritted micronutrients. Our reliance on the technical agronomist in the land-grant colleges and the U. S. Department of Agriculture is obvious. Ferro as a corporation is strong in its knowledge and the basic concept of the manufacture of glasses. We have relied on the technical ability of college personnel to furnish agronomic advice and guidance.

Since early experience indicated that a product with our qualities was in demand in the insurance type trace element field, we naturally gravitated in that direction. Fritted micronutrients have found a receptive market. The safety and over-all predictability fit this type of use.

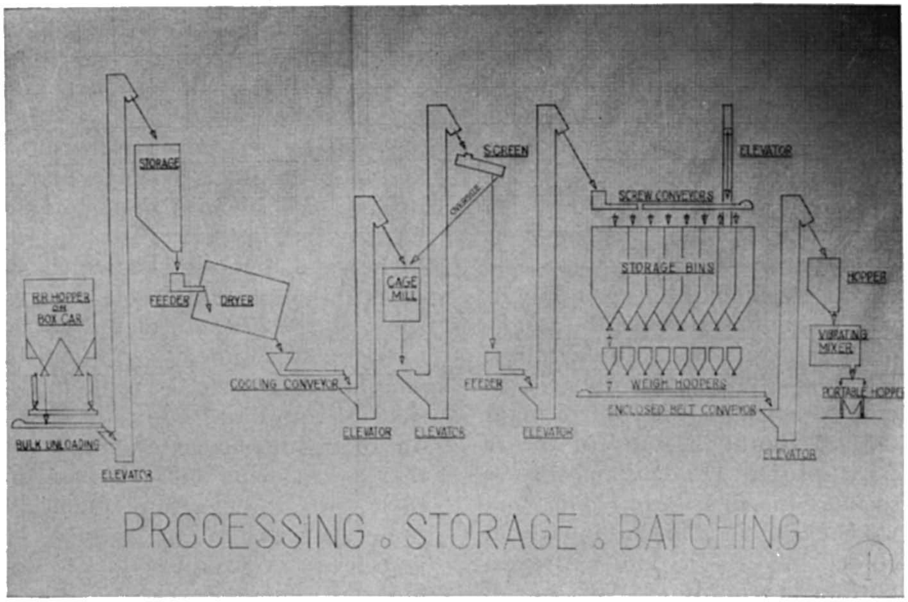
In the past few years, more and more emphasis has been placed on the use of micronutrients in fertilizers. The grower is going for higher and higher yields which increases the possibility of running short of one or more of the micronutrients. Trained agronomists, who know crop needs, want to design micronutrient additions based on their knowledge of the crops they are growing and the needs in their area. They want materials they feel will give the farmer the best fertilizer product their training and experience can furnish.

Now after this time of development and agronomic proof of the value of fritted micronutrients from the users standpoint, we must turn to the practical handling of this product in the fertilizer manufacturing plant.

FTE, in its normal state, is a very fine powdered material approximately 90 to 95% minus 200 mesh. It is relatively inert, being soluble in water at a rate measured in parts per million. If we mix it with powdered fertilizer material, which is rather unusual today, we have no particular problems and have the advantage of the inert nature of the material to do away with picking up moisture and causing setting-up of the fertilizer.

In the past 10 to 15 years, probably 90% of the FTE sold has been added as a part of the dry raw mix in the manufacture of chemical fertilizers. It became a part of the powdered mixture that subsequently went through ammoniation, phosphoric acid addition and on through the regular granulation processes.

Here again, the inert nature of the material practically nullified the possibility of interaction with other chemicals in the process. During the short period in the process there may have been some slight reaction during the time that the material was on the acid side. In general most of the material went through the process without any physical or chemical change. The heat certainly would not affect any changes, as it reportedly does in certain of the organic materials,



Slide 1

since we originally manufactured this material at 2350 degrees F.

We could here refer back to Dr. Page's conclusion, that with less danger of toxicity, special fertilizers for specific crops are not necessary and minor elements may be included in general crop fertilizers. Certainly a lesser number of the specialty grades is of interest to the fertilizer manufacturer.

If we have developed inherent good qualities that fit certain of our fertilizer manufacturing processes, we also have seen other problems develop as the industry needs change that must necessarily be answered if manufacturing problems are to be minimized.

The increased popularity of the suspension type fluid fertilizer has created problems that must be answered. It is easy to say that insoluble micronutrients can be used in suspensions but certainly there are many problems in handling and perhaps even particle size that are going to have to be studied in order to ease your problems in the manufacturing process and in the field.

Ferro has started a program of research and development to study these problems in the laboratory and it is our hope that in the future we will be able to help you simplify the manufacturing and control problems of micronutrients in suspension fertilizers.

The increased popularity of granular blending in relation to the use of micronutrients has created problems both of distribution and segregation.

To answer the changes and varying needs of the fertilizer industry it became apparent that a new plant designed for more flexibility was needed.

Since we had outgrown the available area surrounding the Cleveland Plant, a survey showed that the more centrally located Nashville plant area was the proper place to build a micronutrient center to serve the fertilizer industry.

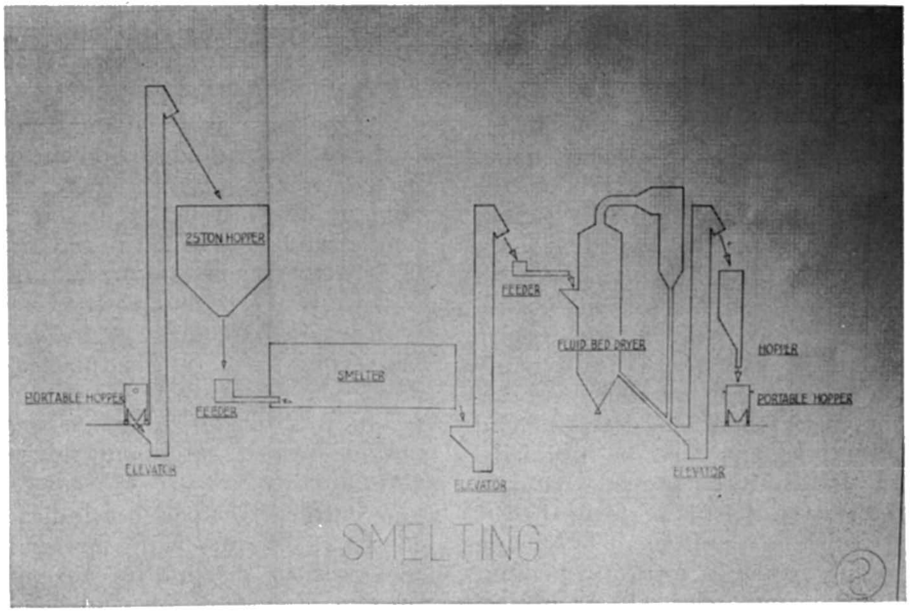
This meeting is somewhat ahead of our construction program in Nashville and consequently I will use a flow sheet type of illustration to describe our capability of production. We will also show you some slides of actual construction of this unit. Certain units necessary to furnish granular products are already in operation and it is estimated that we will be in full plant production by December 15th.

Slide number one, shows our bulk storage for raw material. This includes twelve bins each having a 3000 cubic foot capacity, roughly $2\frac{1}{2}$ cars of average raw material. In addition, there are three bins on the in-going end for processed raw materials. Each has a 1500 cubic foot capacity and can be serviced for our daily requirements either from bunker storage or from railroad car. All materials going to these three bins will have gone through a processing operation which includes drying and/or grinding.

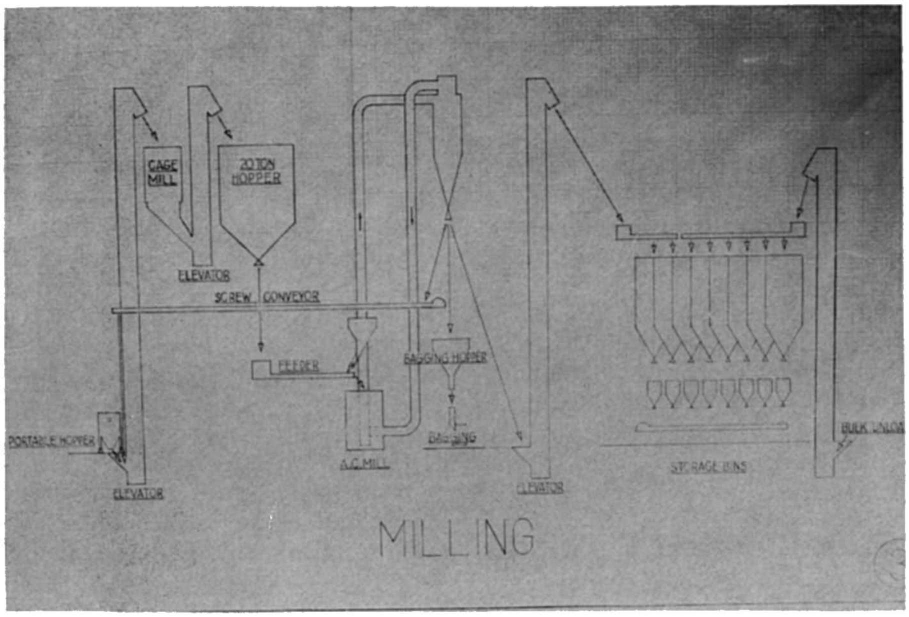
Also there are three bins of this same capacity (1500 cubic feet each) for use in holding materials consisting of powdered FTE or granulating additives for the compacting section.

Batch weighing is done under each overhead storage hopper using Howe-Richardson hopper scales with $\frac{1}{2}$ ton ingredient capacity each. Each scale beam serves two overhead storage hoppers. Weighed raw materials are dropped on an enclosed Link Belt slide conveyor to the batch storage hopper above a Carrier Swirl-a-Flow mixer.

From the batch mixer the ma-



Slide 2



Slide 3

terial is dropped into a portable batch hopper which may either go to the compacting section or the smelting department.

Slide number two, shows the smelting operation. This is one operation that is unusual in the fertilizer industry. Raw batches containing all of the trace elements and other raw materials necessary to form the glass matrix are transported in the portable batch hopper to a 25 ton batch hopper feeding the smelter.

This smelter is the largest we have ever built in our own operation and is capable of melting special glasses at the rate of 2½ tons per hour. The smelting takes place at approximately 2350-2500 degrees F. The product, a homogeneous glass containing all the trace elements to be claimed, runs from the smelter into water. This quenching action shatters the glass into fine particles which drop to the bottom of the quench tank. A bucket elevator, perforated to release the water, elevates the wet frit to a Barber Greene fluid bed dryer. This dryer is an innovation in our industry as well as yours.

From the dryer, we again go into a portable batch hopper at which point production is check weighed.

Slide number three, shows the milling section. The portable batch hopper is delivered from the smelter to an elevator which carries the dry frit to a surge hopper serving a Stedman cage mill pre-crusher.

The pre-crushed material goes to a 20 ton milling storage hopper serving an Allis Chalmers vibrating steel ball mill.

The fineness of the finished product is controlled by a Hardinge air swept fineness classifying system.

Course materials are returned to the Allis Chalmers mill feeder and the end product goes to a Black Diamond bagger system or, if it is to be compacted, directly back to one of the previously described 1500 cubic foot storage bins serving the weighing and batching process.

Slide number four shows the compacting unit. Material to be compacted, including ground FTE, is weighed on the batch weighing unit, mixed in the Swirl-a-Flow mixer and discharged to the portable batch hopper. This batch hopper transports the mix for compacting to a 20 ton storage hopper over the compactor.

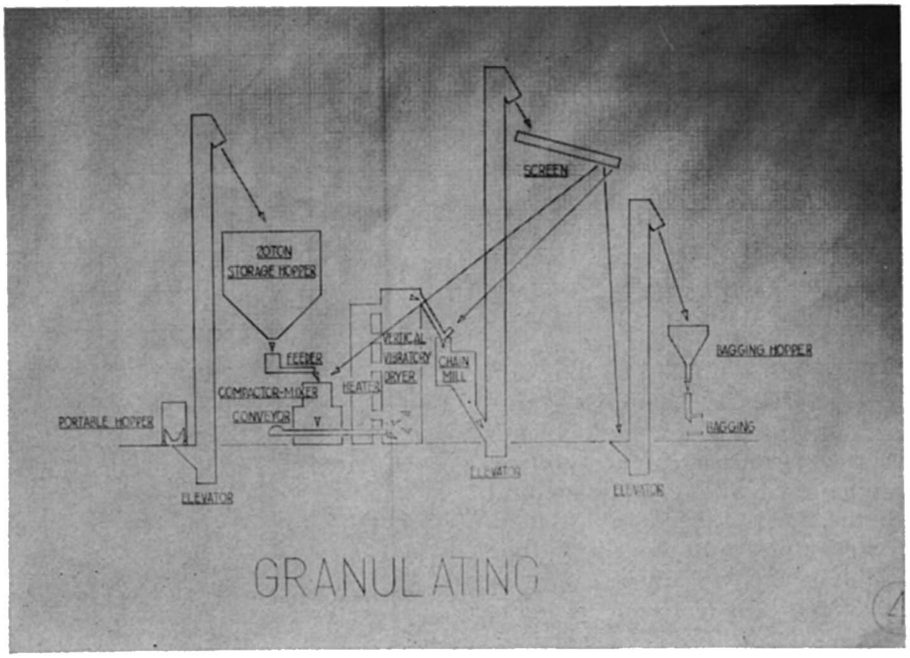
The batch to be compacted is fed through the Komarek-Greaves pre-mix for water addition and from there is fed through the corrugated Komarek-Greaves compacting rolls.

The compacted material is discharged on a vibrating conveyor which screens out the wet fines which are returned to the mixer. The compacted material goes through a vibrating vertical dryer and through a chain mill where the compacted material is broken up. The material then passes through a vibrating sizing screen which follows the chain mill.

Properly sized product goes to the bagging station, over-size is recycled through the mill and fines go back to the compacting operation.

Compacted product of the correct size goes to surge storage serving a Black Diamond pressurized bagging unit.

We will now show you a few slides of the equipment that I have



Slide 4

been describing. This will give you some idea of the type of equipment we use and illustrate the flexibility of the installation and its ability to serve the fertilizer industry.

MODERATOR SAUCHELLI: Thank you, Gene.

We will go to the next paper because it deals with a similar subject and then we will have time for questions.

The next speaker has chosen for his subject Coating Micronutrients On Blended Fertilizers. You will notice the semantics, these materials are referred to as minor elements, trace elements, micronutrients. It all depends on with whom you are talking. The agronomists like micronutrients. Generally throughout the world it is trace elements and minor elements is going into discard. But trace elements and micronutrients are the proper terms.

The next speaker Mr. R. L. Gilbert represents the American Cyanamid Company, a company that has been very prominent in this field.

Coating Micronutrients on Bulk Blended Fertilizer

R. L. Gilbert, H. H. Nau and T. R. Cox

Introduction

In the past several years the need for micronutrients in high yield fertilization programs has become increasingly apparent, with responses commonly being obtained from zinc, manganese, molybdenum, and boron on a number of field crops. The need for specific elements varies widely among different crops and soils. It thus becomes important to develop a flexible system whereby any one or a combination of the micronutrients can be added on a prescription basis to fertilizers required for specific fields.

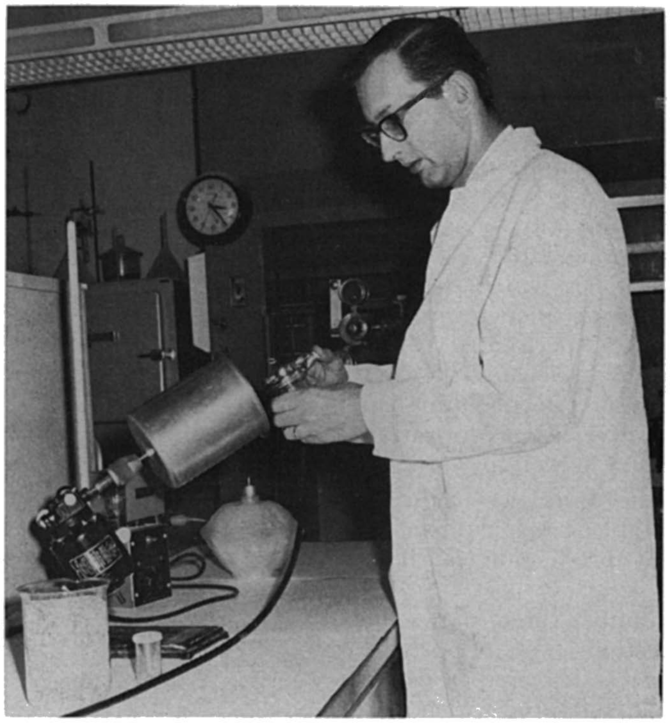
The type of micronutrient source used to supply the deficient element depends upon the type of fertilizer into which the micronutrient is to be incorporated. Liquid fertilizers require the use of soluble salts, and the amount of micronutrient which can be added depends on solubility in the liquid fertilizer. With suspension fertilizers or chemically granulated goods, either soluble or insoluble micronutrient sources may be used. Finely divided materials are required for use in suspensions and are desirable for chemically granulated fertilizers. In bulk blends granular micronutrient sources may be used when a large amount of the micronutrient is needed. For example, granular zinc sulfate might be used to add 4% zinc to an 8-32-16 for corn in an area where extreme zinc deficiency occurs. For most soils, however, where only insurance levels are desired, such large amounts of micronutrient are not needed and uniform distribution in the soil could not be assured if granular sources were used. The problem we set out to solve, then, was uniform distribution of relatively small amounts of finely divided micronutrient sources in bulk blended granular fertilizers. In addition to uniformity of distribution, it was required that a high degree of adhesion of the powder to the fertilizer granules be obtained, and that any additive used should not cause caking nor sensitize the ammonium nitrate in the blend.

Others were also making efforts to solve these problems at about the same time. Our friends at TVA were using water, diesel oil, or used motor oil as a binder for micronutrient dusts.[1] In their work they had pre-mixed the dust with granular fertilizer, and then added the binder, 1 to 3% by weight, either as a spray or through a perforated sparger. When water was used there was a tendency for caking, especially if the product were bagged. Oil did not cause caking but was smelly, tended to bleed through bags, and could sensitize ammonium nitrate contained in blends.

Experimental

We originally considered spraying a solution of soluble micronutrient, or a slurry of insoluble micronutrient onto the granular fertilizer. Neither of these ideas was practical because they required excessive amounts of water. We decided therefore to try to stick micronutrient dust on granular fertilizers with a binder.

Our laboratory work was done with very simple equipment, as shown in the first slide. A rolling bed of granular fertilizer was maintained in either a stainless steel



Slide 1

beaker or a polyethylene tumbler, rotated by a laboratory stirring motor. Liquid was sprayed with a standard medical atomizer.

The use of oily materials as binders was not considered, because problems associated with them seemed insurmountable. With aqueous binders the problem appeared to be a very specialized type of granulation, in which we needed a maximum of solution phase with a minimum amount of water. With very small amounts of water, we expected caking of the product could be avoided. Solutions of very soluble materials met these requirements for binders. Among the solutions we tested as binders were fertilizer materials such as (ammonium nitrate, urea, and nonpressure nitrogen solutions) ; sugars (dextrose, and by-products of dextrose refining) ; and lignin sulfonate products.

The micronutrient materials which we used were, for the most part, zinc, cuprous, and manganous oxides and sodium borates; and mixtures of these materials. We also did some work with sulfates and frits.

To prepare a test sample, fine micronutrient dust, preferably 90-95% through a 200 mesh screen, was mixed with the blended fertilizer, and then binder solution was sprayed onto the mixture.

We tested samples for adhesion of micronutrient by screening on 60 mesh vibrated by Ro-Tap for one minute. The −60 mesh material was considered to be all micronutrient. A period of 24 hours was allowed to elapse between preparation of the sample and testing for adhesion. We tested for caking by sealing samples into small polyethylene bags and weighting them with 3.5-4 psi for 3 days. The degree of caking under this pressure was estimated qualitatively.

Slide 2
Laboratory Formulation Micro Charger® on 6-24-24

Binder	Adhesion %	Caking in 24 hrs
Ammonium Nitrate	85	None
Ammonium Nitrate	87	None
NA Lignin Sulfonate	92	Slight
Dextrose	92	Slight

Slide 3
Laboratory Formulations of Micro Charger®

Binder Type	%	Micronutrient Type	Micronutrient % by wt. Element
AN Soln, 64%	7.4	$ZnSO_4$	20.4
		ZnO	1.2
AN Soln, 64%	10.4	$ZnSO_4$	18.0
		ZnO	2.0
Enzose	2.1	ZnO	14.0
AN Soln, 64%	1.0	$Na_2B_4O_7$	1.0

Some typical results of the laboratory work are shown in Slides 2 and 3.

The 6-24-24 used as substrate in these tests was made from DAP, TSP, and Potash. The micronutrient dust was a mixture of zinc and manganese oxides and sodium borate, added to give 0.25% each of Zn and Mn, and 0.06% B. The amount of binder used was 1%. All binder solutions contained 50% solids.

Three types of substrates were used in this work to make blends having nutrient ratio 5-4-0. The substrates were AN + TSP, DAP + TSP, and Ammonium Sulfate + TSP. In all cases adhesion of micronutrient dust was over 97%, with little or no caking.

Our work, involving the use of liquid fertilizers as a binder, was subsequently granted a patent[2] on November 21, 1967.

Adaptation of the laboratory procedure to our bulk blending plants required additional development work. Through numerous "in plant" tests, we gradually developed procedures and equipment which now do an excellent job of coating and sticking various micronutrients in a wide range of quantities on blended fertilizer.

Slide 4
Composition of 6-24-24 Batches

Material	Wt., Lb.
DAP	377
AN	156
TSP	667
Potash	800
ZnO	6.5
MnO	8.7
$Na_4B_2O_7$	5.2
Nitrogen Soln (28%) or 50% AN Soln	20

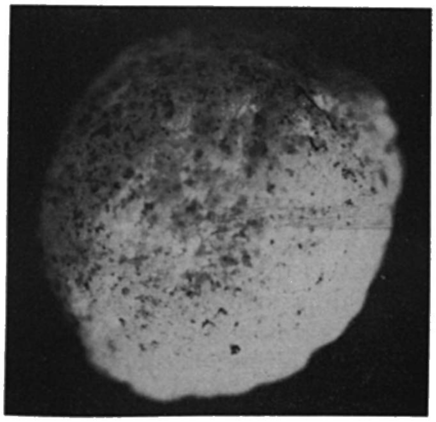
Slide 5
Analyses of 6-24-24 Batches

Batch #	Calculated Analysis	% 1	2	3
Zn				
Range		.20-.23	.22-.27	.23-.30
Average	0.25	.21	.25	.29
Mn				
Range		.17-.20	.22-.24	.24-.28
Average	0.25	.19	.23	.25
B Range		.04-.05	.05	.04-.05
Average	0.06	.045	.05	.04

Results of some tests of the equipment are shown in Slides 4 and 5. Batches of 6-24-24 were mixed by the standard procedure, and samples were taken at intervals from the stream as the mixer discharged. Slide 4 shows the composition of the batches; slide 5 the analyses for micronutrients.

Cyanamid has trade named this coating process "Micro-Charger." Customer acceptance has been very good, primarily because of the wide range of micronutrient materials and quantities which can be applied and because the customer can see the amount and distribution of micronutrients on the surface of each granule. Shown here is a blow-up of a typical "Micro-Charged" fertilizer particle showing the micronutrients on the surface.

Development work will continue toward further improving the process, speeding the thru-put, and increasing the quantity of micronutrients which can be applied in a single pass.



Slide 6

In summary, we believe that the micronutrient coating process developed and patented by Cyanamid will greatly increase the flexibility of our Farm Service Centers to provide farmers with prescription applied micronutrients on prescription blended primary and secondary fertilizer materials.

References

1. TVA: New Developments in Fertilizer Technology, Oct. 1964.
2. U. S. 3,353,949, H. H. Nau to American Cyanamid Co.

MODERATOR SAUCHELLI: Thank you, Mr. Gilbert. I am sure that was of interest to our operations men because they are going to face that problem more and more in the future.

We are pressed for time and have time only for one or two brief questions. Are there any questions?

A MEMBER: Do you feel you are getting value for your micronutrients in the sales of your fertilizers in the marketplace? Can you get the money out of your process in addition?

MR. GILBERT: Oh, I think so.

MODERATOR SAUCHELLI: I now turn the meeting over to Mr. Robert Heck who will moderate the remaining part of this session.

MODERATOR MR. ROBERT R. HECK: Thank you, Vince.

When the Round Table first started in 1951 I think the most immediate objective it set for itself was to provide a means of helping people in the fertilizer industry solve problems. I think the agenda that we have had today and the one we have had for the past 15 or 16 years has indicated our interest still remains in the ability to solve problems.

This afternoon we are very fortunate to have Dr. John Connor, Chemical Construction Company, with us and in line with what I have just said about problem solving, Dr. Connor will discuss Sulfuric and Nitric Acid Plant Operation Problems. Dr. Connor, please.

Operating Problems in Small Sulfuric and Nitric Acid Plants with Special Reference to Effluent Difficulties

John M. Connor

Introduction

Apart from the fact that the products are the two most important mineral acids, sulfuric and nitric acid processes and the plants used for them bear little resemblance to each other. However, they have some common features which lead to common problems and it may be well to deal with these first.

1. *Waste Heat Recovery*

Both processes are exothermic overall and the initial reaction in both cases takes place at a relatively high temperature. Plant development for both processes has passed through the same stages for dealing with this surplus heat; initially simple heat wastage to the atmosphere or cooling water followed by heat recovery as low pressure steam for process heating purposes in other plants (as well as for sulfur melting in sulfuric acid plants). Heat recovery as high pressure superheated steam to give power for plant drives and power production for export is the most recent development.

In most modern nitric acid plants there is some heat recovery for direct use in gas expanders, a development which has not yet arrived in the sulfuric acid plant, but may yet come.

Boilers vary a great deal in sophistication but because in both cases the process gas becomes corrosive if cooled too far they are normally designed for pressures of 200 psig or over. Although no great expertise is required to operate a 250 psig fire tube boiler, as the highest pressure unit in the plant it merits some special care and if a natural or forced circulation water tube boiler is used more operating care is required. Some degree of water treatment and dosing is always desirable and many boiler troubles can be traced to improper operation of this equipment. In fact overzealous dosing with sodium sulfite and phosphate leading to build up of deposits on or in tubes is in my experience the most common cause of boiler failure.

Boiler failure itself can cause secondary problems, as the injection of water into the gas results in severely corrosive conditions in the rest of the plant. This may be less of a problem in nitric acid than sulfuric acid plants because of the lower heat capacity of the plant and the fact that much of it is constructed of stainless steel. In sulfuric acid plants a series of mishaps with the boiler will almost certainly lead to corrosion problems in the later stages of the plant, particularly if a feed water economizer is included. These problems may not show up until much later in the life of the plant but the effect is sumulative. It is important to establish proper procedures for shutting down the plant in the event of an actual or suspected boiler failure to reduce this danger of further damage. As in both cases the plants can be substantial steam exporters other plants may be put in difficulties by a sudden shutdown and their problems must be considered also.

2. *Mechanical Equipment*

Another common feature of the processes is that although the smaller pumps are usually provided with installed or stored spares, both plants rely on a single centrifugal blower or compressor to provide the motive force to drive the gas through the plant. In the case of many nitric acid plants this is a complex unit including a letdown recovery gas turbine drive as well as steam turbine or electric motor. Proper care in the maintenance of these units is an obvious requirement and there is little need to say anything else. On the whole they are reliable pieces of machinery which cause little trouble, although the greater complexity of the nitric acid unit may mean more initial problems, particularly as plants are getting larger and the compressor-turbine units themselves are often to some extent prototype machines.

3. *Corrosion*

Where acids are made, corrosion is an ever-present problem although in neither of these cases is it a particularly serious one. For this aspect it will be simpler if we look at the two plants separately.

The resistance of cast iron and steel to corrosion by strong sulfuric acid means that in the strong acid section of the plant corrosion will cause little trouble and although leaking pump or valve packing may give the appearance of serious corrosion there is usually little damage to the plant. A common cause of trouble in this section is overheating of acid due to the gas or acid coolers being too small or fouled. Where sulfuric acid exceeds 200°F there may be relatively rapid corrosion of cast iron. The best remedy is to keep the acid cool. Corrosion resulting from boiler failure has already been mentioned.

Where acid is produced from pyrites, hydrogen sulfide, or other material requiring a wet purification section, there may be more trouble from corrosion. In this case the purification tower will be using recirculated acid liquor which, depending on circumstances, may vary from about 1% to 60% in concentration at relatively high temperatures. The main units of equipment will be lead or lead and brick lined, but valves and spray nozzles as well as pumps cannot be protected in this way. Lead, rubber in one or other forms, and various plastics are probably the most resistant common materials and the use of lined diaphragm valves of the Saunders type has solved a lot of problems. Carbon or graphite has proved a sound material for heat exchange equipment even though expensive. Where machineable metal must be used one of the "20" alloy group of stainless steels is probably best although Type 316 is often adequate and the higher nickel alloys are sometimes used.

Problems arise in both sulfuric and nitric acid plants because gas containing sulfur or nitrogen oxides, though relatively noncorrosive when above the dewpoint becomes corrosive once cooled below it. In sulfuric acid plants this stage is usually passed through very quickly in the quench section of the purification plant where special materials resistant to both heat and weak acid are used. In the nitric acid plant cooling the gas through the dewpoint is an essential part of the heat recovery process and condensation always occurs. Difficulties arise when the position in the plant where the gas reaches the dewpoint varies with plant operating conditions so that sections may be subjected alternately to condensing and boiling. This may occur, often with disastrous results where the layout of piping or equipment is such that condensate produced by cooling the gas can travel upstream by gravity to a point at a higher temperature where it can evaporate. It can also happen at tube plates of feedwater heaters or condensers where the tube plate and the part of the tube rolled into it is cold enough for condensation but the body of the gas does not reach this temperature until some distance along the tube. In most modern plants this problem can be overcome by arranging that the gas passes through its dewpoint in a unit where the metal temperature is low so that corrosion is reduced. Arrangements for easy replacement of this section are also an advantage.

4. *Pollution Problems*

Both types of plants can and do cause considerable air pollution and now that serious attention is being given to environmental problems operators must consider how best to reduce the pollution they cause. As in the two plants the solutions are quite different I propose to deal with these separately. It is as well to point out, however, that in neither plant can an economic case be made out for better pollution control if the economics of acid production only are considered and although there normally is some return to the capital invested it is generally a poor one.

It is also interesting to note that while practically all systems for reducing pollution from sulfuric acid plants result in some recovery of additional product or its equivalent, in nitric acid plants the emphasis has usually been on destruction of the nitrogen oxides present.

a. *Nitric Acid*

Apart from the obvious desirability of building into the nitric acid design sufficient absorption equipment to recover the bulk of the nitrogen oxides produced, the only practical method now available for reducing contaminants in the stack gas is to destroy them by heat with the aid of a catalyst. The most usual method is to preheat the stack gas to about 900°F, add a combustible gas or vapor and pass the resulting mixture over a catalyst. Provided sufficient fuel is present to heat the gas to about 1100°F any NO_2 or N_2O_4 present will be reduced to NO. This, of course, merely means that the gas is colorless as it leaves the plant and usually by the time the NO is re-oxidized the stack gas is sufficiently dispersed so that it is not noticeably colored (about 200 ppm of NO_2 is visible). Although the logic of this process is somewhat difficult to defend it is quite widely practiced. In Europe it has been common to arrange to dilute the stack gas with air either by an induction effect in the stack or by a separate blower, a practice which seems even less defensible.

Complete reduction of the oxides to nitrogen can be effected if sufficient fuel is burnt to remove all the excess oxygen and if the right fuel is used. Many plants currently being built are provided with equipment for this purpose but the available experience is limited. The plant must be designed so that all the oxygen is removed within the limits of the temperature stability of the catalyst. The method used will depend on the catalyst and the fuel used. Where hydrogen is available the lower ignition temperature will permit the elimination of oxygen at lower temperatures than with methane.

Using a two stage reactor with intermediate quench maximum temperatures can be limited to 1250°F even using methane and at this temperature the gas can be used directly in expanders and give increased power generation. Single stage reactors using methane will give temperature of 1500°F and complete reduction to nitrogen but the gas must then be cooled in a boiler before being used in an expander. Expanders designed for this temperature are becoming available.

Both pelletted and Honeycomb type catalysts are being used. Pelletted catalysts are more rugged but take a higher pressure drop. There have been problems in obtaining reproducible results with the Honeycomb type but development is proceeding and eventually it will probably be the preferred type.

If either type of tail gas combustion equipment is built into the plant during design advantage may be taken of the high temperatures produced to recover some of the fuel energy in a gas turbine driving the compressor. In this way better thermodynamic use of the energy is obtained and the increased quantities of steam made available may exceed that which would be produced by the combustion of the fuel in boiler equipment. Where steam is credited at a sufficiently high price this aspect may be sufficient justification for the tail gas reduction equipment and the stack improvement is a bonus. Where stack gas reduction equipment is added to the plant after construction boilers or economizers may be installed to recover the heat as steam.

Although catalytic reduction is the most popular method of dealing with the nitrogen oxides other processes are being investigated. It is reported from Austria that a process for scrubbing the stack gases with an aqueous suspension of magnesium oxide is being tested on an industrial scale. This process produces magnesium nitrate from which both the nitrogen oxide and the magnesium can be recovered by heating to 280-300°F the NO being produced at a high concentration which can be readily recycled to the plant.

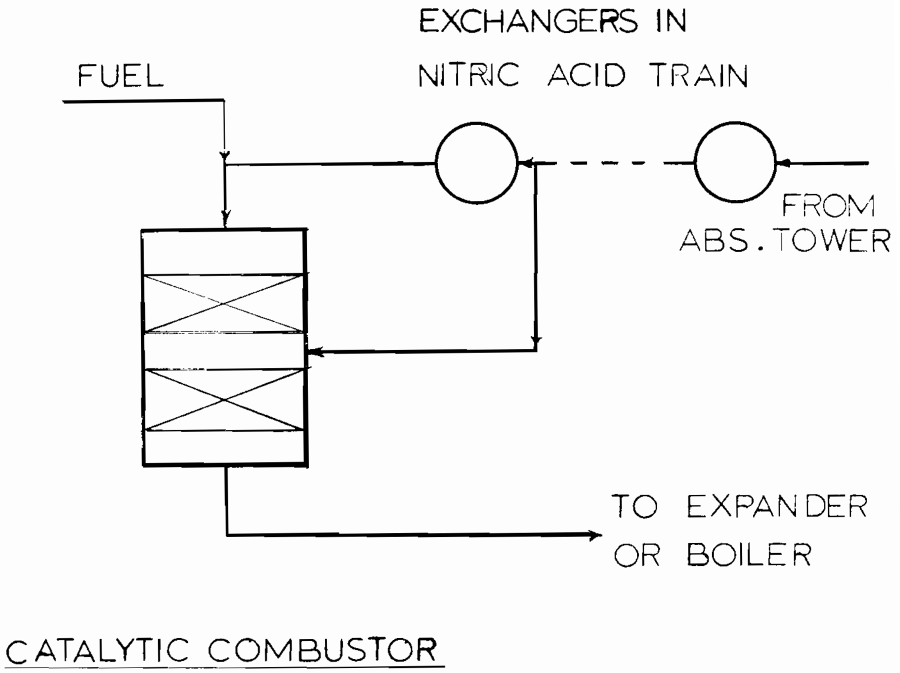
Processes using sulfuric acid to produce nitrosyl sulfuric acid are also being considered in Europe. There are in progress studies of various adsorbents but as yet none have been so economical as the reduction process.

b. *Sulfuric Acid*

Stack gases from sulfuric acid plants contain SO_2, SO_3, and sulfuric acid mist as pollutants. Of these SO_2 is present in by far the greatest quantity but SO_3 and acid mist are often the most troublesome and are considered by many the most dangerous. They are also the most obvious from an outside viewpoint. Although these more visible pollutants are not a serious problem in modern plants they may be in older plants running at overload conditions. In the last few years several filters of knitted stainless steel wire, glass fiber, teflon or mixtures of these materials have been developed which will successfully remove acid mist. It is important to note that the mist particles which constitute acid mist vary greatly in size and a filter which may be quite adequate for one plant may be useless on another. Particular care in the choice of a filter is necessary in plants where Oleum is produced.

It is, however, the much larger quantity of the invisible pollutant SO_2 which is causing concern to the public and, therefore, to the acid manufacturer. On the whole the movement towards higher conversion of SO_2 to SO_3 has been slower in the U.S. than in Europe where very few plants have been built since 1945 with guaranteed conversion of less than 98% for plants based on sulfur or less than 97% for other materials (corresponding to about 1700 and 2300 ppm respectively). Now there is another move underway, started in the German Ruhr Valley at one time notorious for its pollution problems, to increase conversion to 99% or more by using an absorption stage between stages of conversion. It seems probable that as new pollution control legislation comes into force plants of this type will be built here also.

This comparatively late but rapid change in the U.S. attitude to air pollution has resulted in there being a number of plants in operation designed for lower conversion and still with a comparatively long useful life. To meet new regulations some modification of these plants will be necessary either to absorb the SO_2 from the stack gas or to convert it to SO_3 by an improved conversion system. To convert the plant to a two stage absorption system in the accepted sense of the term requires drastic modification to equipment. To avoid this a scheme has been developed whereby a second conversion and absorption stage can be added to an existing plant with a minimum interference with the plant operation. The additional equipment required consists of two stage converter, and associated heat exchangers, an absorption tower and an auxiliary blower. However, the additional heat for the system instead of being obtained by heat exchange with the burner gas is obtained by directly injecting the burner gas into the preheated tail gas stream. This is not, of course, as effective as a properly designed two stage absorption-conversion system since some of the SO_2 bypasses the first converter en-



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tirely, but in spite of this we estimate that a plant at present operating at 95% conversion could be brought up to about 99% overall by this method. Because with this modification some part of the burner gas passes directly from the sulfur furnace to the second converter and so bypasses the boiler of the main plant this may be used to add to the production of the plant. We estimate that with this above condition, the plant production might be increased by 20% by this method provided adequate blower capacity is available.

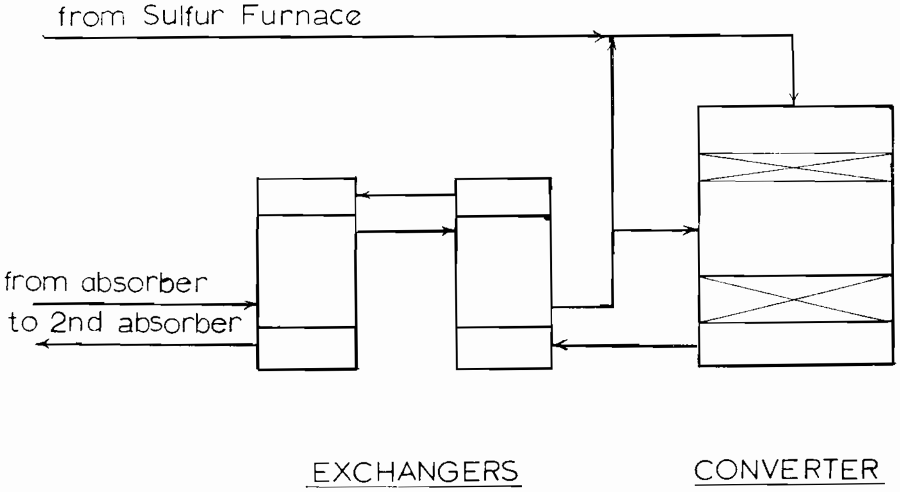
Another method currently being put through pilot plant tests is to scrub the tail gas with a suspension of magnesium oxide. A wet SO_2 recovery scrubbing process of this type has been developed and is now being offered by Chemico's Pollution Control Division. The scrubber used is a low energy wet approach Venturi requiring a pressure drop of about 6 inches W.G. The scrubbing liquor is a slurry of magnesium oxide with magnesium sulfate and sulfite crystals. The characteristics of the system are such that the SO_2 absorbed into the alkaline solution crystallizes as magnesium salts. A bleed from the circulating system is taken to a centrifuge or filter and dewatered. The mixed magnesium salt crystals are then dried and calcined to produce SO_2 and MgO. The SO_2 is recycled to the acid plant—either to the scrubbing system of a wet gas plant or to the drying tower of a sulfur burning plant. The MgO, is of course, recycled to the scrubbing liquor.

The cost of the scrubbing equipment will depend on the volume of gas to be handled and the cost of the calcining equipment on the quantity of SO_2 recovered. It is estimated that on a plant operating at 95% conversion recovering 90% of the SO_2 in the stack (i.e. giving an equivalent of 99.5% recovery) a scrubbing plant of this type would, after allowing for depreciation, show a small return on the investment. Of course, there have been for a long time other methods for reducing acid gas content of the stack gas by scrubbing with alkali solutions. Ammonia has been most commonly used particularly in plants built in the 1930's and 1940's and especially in plants where ammonium sulfate was the final product. This proved an easy way of solving the pollution problem and increasing production by 2 or 3% at the same time. However, with the falling price of ammonium sulfate this scheme has lost its interest.

MODERATOR HECK: Thank you, Dr. Connor.

We will take a few minutes to open the floor for questions. We would like to ask, though, that you make sure that the question you ask is of a general nature to the audience here because of our time limits. Do we have a question?

I wish I had about two hours of Dr. Connor's time, I've got a lot of questions. During the past two years we have seen quite a significant change take place in the sulfur consumption throughout the world. We have had indications that at the rate sulfur was being consumed there would be serious shortages of material. I am sure this and many other things led to an interest again in recovering sulfur from gypsum, either natural



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gypsum or byproduct gypsum from phosphoric acid plant operations.

Those of you who have been in Florida and have seen the gypsum dams and the gypsum mines there, I think if we continue mining in Florida at the rate we are consuming there, we will be able to cover up the State of Florida with gypsum in the very near future.

This afternoon we have with us Dr. Derek S. Ashburner with the Power-Gas Corporation of America. He is a process development engineer. He has served some time in Europe, I believe, with Batelle. He is a graduate of the University of Cambridge. Dr. Ashburner will discuss Cement and Sulfuric Acid from Calcium Sulfate.

The Production of Cement & Sulphuric Acid by the Marchon Process

D. S. Ashburner

Gentlemen, I am very pleased to have been invited to give this paper on the production of sulphuric acid and cement from calcium sulphate. It is indeed pertinent to present this paper at this time as Power-Gas has found much more world-wide interest expressed in this process in the past year or so than had been expected at the time Power-Gas licensed the Marchon technology. In fact, Power-Gas has a letter of intent from Chemoleum for a cement and sulphuric acid plant from by-product gypsum for a South American project and are doing a feasibility study for United Gypsum Corporation Ltd., in Canada. A number of similar studies are being carried out in other parts of the world.

The basic process of making sulphuric acid from calcium sulphate was developed about the time of the First World War in Germany when the import of pyrites began to be severely restricted. Over a considerable period of time W. S. Müller and H. H. Kühne of I. G. Farben carried out a good deal of laboratory research on the decomposition of calcium sulphate; following this work a small plant was set up at Leverkusen and operated until 1931. Later a similar but larger plant was built at Billingham in England with some assistance from the people at Leverkusen in the early stages of operation. Initially there was one kiln and with a later additional kiln production at the time was around 300 tons/day each of clinker and sulphuric acid. The Billingham plant is located on an area of anhydrite covering the whole of the plant site at a depth of a few hundred feet, and is therefore in a good position for mining the anhydrite cheaply. These early plants quite naturally experienced a great deal of difficulty with kiln linings and with raw material control; Dr. Kühne in a paper published in Chemie-Ingenieur-Technik (1949) refers to the meter thick sausage like masses several meters in length which were often produced in the kiln. Occasionally a completely molten mass ran out and choked the clinker cooler. The brickwork in the kiln at Leverkusen had to be replaced about 20 times in 18 months and it was not until magnesite bricks became available in the 1930's that the lining problem was vastly improved. One has only to read this article to realize how very important is close raw material control and it is a measure of their success in this that Marchon are able to operate their kilns for about 2 years before shutdown for relining.

The Germans built a large plant at Wolfen, the details of which were described in a BIOS publication. 2 kilns and 4 contact systems were built in 1938 with a further 2 kilns and 4 contact systems in 1942. The raw material at Wolfen was 98% calcium sulphate which is a fairly pure material and the other raw materials were clay, sand, pyrites and coke breeze.

Marchon Products Limited was established in the years before the war on a small scale to manufacture detergents and it was at the beginning of the Second World War that the company was moved from the London area up to Cumberland and became established near Whitehaven in one of the more remote parts of the country. In 10 or 11 years the Company had grown into an important chemical industry employing some 700 people with an extensive domestic and export trade in detergents and detergent raw materials. A few years after the war had ended Marchon Products decided to become more self sufficient in sulphuric acid and applied for permission to construct a sulphuric acid plant using pyrites as the raw material. This the UK Board of Trade refused on the grounds that a large number of similar plants were already under construction at that time. Marchon then realized that the plant was located over one of the largest deposits of anhydrite in England; this reserve has since proven to be even larger than originally estimated. They therefore established a subsidiary company called Solway Chemicals Limited to erect and operate a sulphuric acid plant which used anhydrite as the main sulphur source. The construction of the plant began in 1952 and cement and sulphuric acid were being produced by 1955. These two kilns are still operating well above the original design capacity. A third kiln of similar capacity was erected a few years later and then in 1965 the capacity of the plant was doubled by the addition of 2 further kilns making a total of 5 kilns producing 440,000 short tons of sulphuric acid and cement clinker per annum. A substantial part of this sulphuric acid is used for making phosphoric acid which is in turn used for making polyphosphates for detergents. Some cement clinker is sold without further processing but a substantial part is ground to make Portland cement which is then bagged and marketed through the marketing organization of APCM in the UK. Indicative of the quality of the product produced and the economic viability of the process is the fact that Marchon doubled their plant capacity in 1965. These recent kilns incorporate all of

Marchon's latest thinking developed from their experience in operating kilns over the preceding decade. The two newest kilns are operating above design capacity and the kiln linings of these kilns and of the older ones work for 2 years before re-lining becomes necessary.

Process Description

In a conventional cement plant some form of calcium carbonate is heated with other raw materials containing silica and alumina and iron in a rotary cement kiln. Carbon dioxide is first driven off and then in a hotter part of the kiln the lime remaining after the carbon dioxide has been evolved combines with the other raw materials present to form cement clinker. In the Müller-Kühne process, calcium carbonate is replaced by calcium sulphate. This material however does not decompose into lime and sulphur dioxide until a temperature appreciably above the decomposition temperature of limestone. It was this problem which the early work of Müller and Clingestein overcame by the discovery that a small addition of powdered coke lowered the temperature at which this decomposition appeared to take place. One of the difficulties in the early work arose because too much coke was added, Müller having assumed that one mole of carbon was needed per mole of calcium sulphate. In fact the main reactions which are believed to take place are:—

1. *A reduction step.* Carbon in the coke reacts with one quarter of the calcium sulphate to form calcium sulphide. $CaSO_4 + 2C = CaS + 2CO_2$.

2. *Decomposition.* The calcium sulphide previously formed now reacts with the rest of the calcium sulphate at a somewhat higher temperature to form sulphur dioxide and calcium oxide.
$CaS + 3CaSO_4 = 4CaO + 4SO_2$

3. *Clinker Reaction.* The calcium oxide combines with silica, alumina and iron oxide present in the other raw materials to form the compounds which make up ordinary Portland cement (e.g. tricalcium silicate, dicalcium silicate, tricalicium aluminate and ferrite compounds etc). The main differences between this process and conventional cement technology lie in the closer control that is needed at each stage of the process. The raw material mixture has to be accurately proportioned and the temperature and firing conditions in the kiln have to be closely controlled. For instance if the temperature in the firing zone becomes just that bit too high the material will melt causing "flushes" and consequent damage to the kiln lining. Excess CaS can also result which produces a poor cement clinker. If the atmosphere in the kiln becomes reducing, quantities of sulphur can be deposited in the gas cleaning equipment causing serious operating and maintenance problems in those areas.

The main raw materials at Whitehaven are anhydrite, (natural anhydrous calcium sulphate) shale, and coke, a small amount of sand being added to control accurately the silica content of the raw meal. The anhydrite deposit at Whitehaven lies a few hundred feet below ground and is mined by conventional room and pillar techniques. Primary crushing takes place in the mine and secondary crushing and screening is carried out at the mine head. Coke and sand are brought to the plant by road and rail and shale is quarried from a hillside close to the plant. The shale is crushed and conveyed to intermediate raw material storage before being dried. The shale does vary slightly in analysis but a typical analysis would be:—

SiO_2	60%
Al_2O_3	18%
Fe_2O_3	6%
CaO	4%
Alkalies	2-7%

The materials used by Marchon at Whitehaven are not of course the only ones which could be used. There is a wide variety of shales and clays and sand which could be employed to supply the silica, alumina and iron. Part of the know-how in this technology lies in knowing and understanding the limits between which the silica and alumina concentrations can vary whilst maintaining successful operation of the process.

From intermediate storage the wet materials are conveyed to hoppers feeding rotary oil fired dryers. The anhydrite is not normally dried because this comes dry from the mine. Water content of coke, shale and sand is normally reduced to about 1% and the materials are then ready for proportioning.

From small intermediate storage following the dryers, the various raw materials are proportioned on automatic weigh feeders together with the anhydrite and this mixture then passes from feed hoppers into the ball mills. These mills are fairly conventional rotary ball mills containing a number of diaphragms. The raw materials are ground together with a certain amount of recycle dust to a fine meal. The raw meal is then stored in one of a number of silos, the storage being so arranged that any variations in raw material composition over a comparatively short time are evened out. These variations are monitored by taking regular samples of all the materials and analysing by X-ray spectrographic methods. Any variations can then be compensated by adjusting the weigh feeder settings. At this stage the raw meal consists of ground anhydrite, coke, shale, sand, and recycled dust.

The raw meal is then pelletised on rotating pan pelletisers by mixing with a small quantity of water. Briefly the main advantage of pelletising is to stop the carry-over of very large quantities of dust from the cement kiln. The nodules fall into the kiln where the reactions previously described take place. The kiln itself is, of course, a very important part of the process and the temperature and composition of the kiln atmosphere must be very closely controlled, in the first case to prevent melting of the charge and in the second place to prevent production of sulphur and H_2S in the kiln gases.

The kilns operated by Marchon are now all fired by heavy fuel oil although for many years Marchon used coal firing, and could indeed again return to coal firing if oil prices were to rise to very high levels. The Company is set up to change from oil to natural gas should this become available

Figure 1-A
5 kilns at Marchon's Whitehaven Plant

in the near future. Power-Gas is, therefore, able to offer designs based on coal, oil or natural gas firing. In some ways the kilns are very similar to conventional dry process limestone cement kilns, but the main difference is that these kilns have ceramic heat exchange devices built into them in order to control the rate of flow of material through the kiln, to shorten the length of kiln required, and to increase the rate of heat exchange between the walls and the solid materials. The exact design of the dams used in the Marchon kilns is proprietary information. These ceramic dams obviously increase the weight of the kiln and for this reason the shell of the kiln tends to be rather heavier than conventional cement kilns of the same size. This results in an extra tyre or two over what the conventional cement plant producer might have expected. Since the operation of the kilns is quite complex and must be closely controlled, Marchon and Power-Gas are studying the application of a computer to this system. Air is introduced into the kilns, mainly through the rotary clinker coolers and thence to the kiln, a lesser amount as primary and fuel atomising air and also as a small amount of tertiary air supplied to the back end of the kiln through the shell. This tertiary air is used to maintain the critical slightly oxidising kiln atmosphere.

As a rough guide to capacity these kilns produce something like 60% of the clinker that could be produced from a kiln of similar size using a conventional cement process. The largest kilns which are at present operating at Marchon and in other plants are of about 100,000 tons/year capacity. Marchon are the only people to have any experience of recent construction of these kilns having constructed 2 in 1966. There is no major mechanical problem, however, in building a much larger kiln certainly up to 500 and possibly a 1,000 tons/day, except that these kilns would be very much beyond present established experience.

There are several references in the literature to the formation of rings in the cement kilns and it is worth saying at this stage that Marchon has no trouble at all with the formation of cement rings in their kilns. The formation of rings is caused by two factors, poor raw material control, and poor temperature and firing control of the kiln. The composition of cement is quite often defined in terms of the lime factor, the silica ratio, and the alumina ratio:—

$$\text{Lime factor} = \frac{CaO}{2.8\,SiO_2 + 1.2\,Al_2O_3 + 0.65\,Fe_2O_3}$$

$$\text{Silica Ratio} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$\text{Alumina Ratio} = \frac{Al_2O_3}{Fe_2O_3}$$

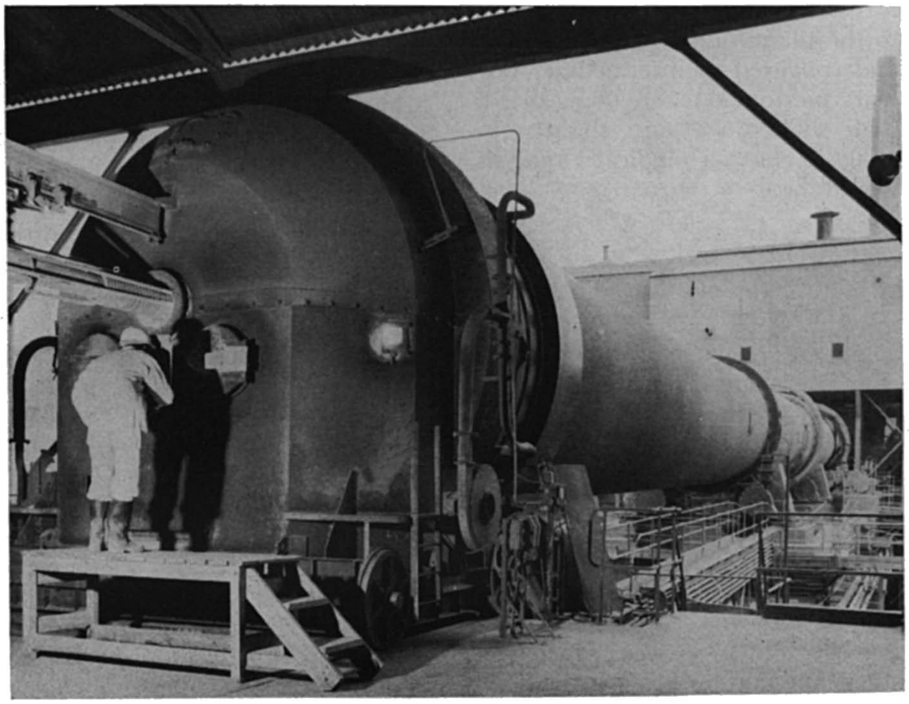


Figure 1-B
One of Marchon's two most recently erected kilns

and in the case of plants producing cement and sulphuric acid these ratios must be much more tightly controlled than would be the case with conventional cement plants. Thus in one particular article which appeared recently, the factors given are much too wide in range for successful operation. The actual factors which are used, of course, form part of the 'know-how' which is available under licence.

The hot clinker drops from the firing end of the kiln into a rotary cooler mounted underneath the kiln, and from here it passes through a squirrel cage screen and is conveyed to clinker storage. The clinker is then ground with a small addition of gypsum to produce Ordinary Portland Cement and is then either bagged or conveyed from the plant in bulk.

The gases which leave the end of the kiln consist of SO_2, O_2, CO_2, N_2 and carry a substantial burden of dust. Normally the SO_2 at this stage is about 9%. The gases are passed through a gas cleaning system consisting of cyclones, electrostatic precipitators, wash towers, indirect coolers and wet gas precipitators. Following the addition of air, in order to bring the oxygen content to the level required by the process, the gas which is passed to the converter system contains about 5.5% sulphur dioxide. The flow of gases through the plant is brought about by blowers downstream of the drying tower. The plant can be designed to produce either 96-98% solution or oleum.

Utilities

As has been explained already the raw materials which can be used other than the calcium sulphate source are quite wide in variety and their costs depend largely on the mining or quarrying techniques used and any transport from the mine or quarry to the plant site. The following utilities are based on the production of one short ton of 100% sulphuric acid and are, of course, approximate figures.

Item	
Anhydrite	1.6 to 1.7 tons
(or Gypsum	2.0 to 2.2 tons)
Shale	0.29 tons
Sand	0.06 tons
Coke	0.10 tons
Fuel	6 million Btu's Anhydrite (10 million Btu's Gypsum)
Cooling Water	14,000 gals. (Circulating)
Electricity	190 kwh up to clinker production 38 kwh for cement grinding

The question sometimes asked at this point concerns the steam credit which is available from normal sulphur burning plants. The plant is in steam balance except in very cold climates where steam may be required for fuel oil heating and tracing of pipework.

Capital Costs

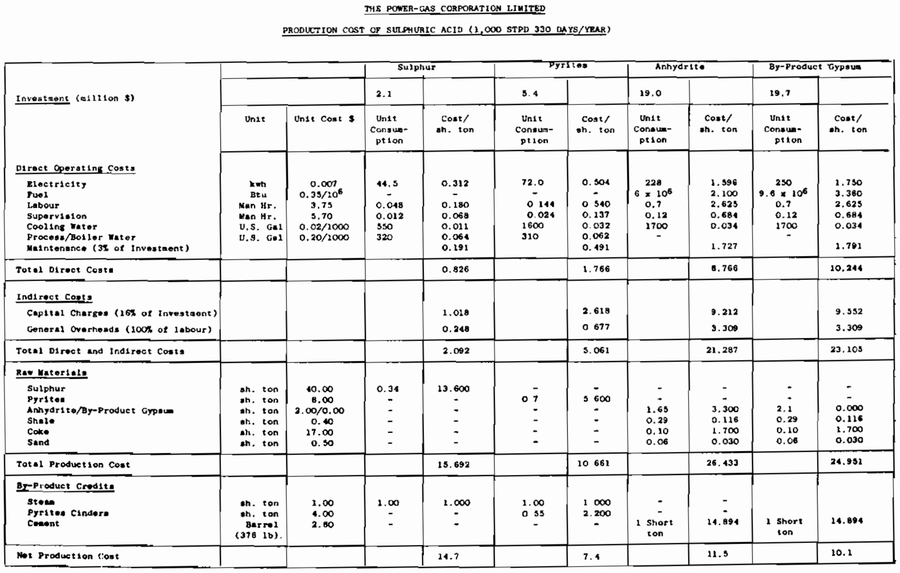
I would now like to turn to the interesting topic of the cost of these plants since I am sure many of you will be aware that the capital cost of a cement plant is very high when compared with many chemical plants of comparative capacities. In the following table we have given in round figures the capital cost of typical capacities of plants where the costs refer to ready to operate plants erected on so-called 'green field' sites. The plant begins with the reception of raw materials, in the case of anhydrite at the mine or quarry head, and finishes with the production of stored sulphuric acid and cement.

Capacity tons/year	No. of Kilns	No. of Acid Plants	Cost US Dollars
100,000	1	1	7,000,000
150,000	2	1	10,000,000
200,000	2	1	12,000,000
300,000	3	2	18,000,000
300,000	4	2	19,000,000

The capital costs indicated in these figures refer generally to Western European conditions in 1968, and include the cost of equipment, erection, starting up, civils, engineering, and license fees, and all utilities provided that power and demineralised water are available on site. The breakdown between these different items does vary from project to project, but typically the breakdown might be:—

Equipment	57%
Erection	15%
Civils	20%
Fees	8%

It does need to be emphasized,



THE POWER-GAS CORPORATION LIMITED

PRODUCTION COST OF SULPHURIC ACID (1,000 STPD 330 DAYS/YEAR)

			Sulphur		Pyrites		Anhydrite		By-Product Gypsum	
Investment (million $)			2.1		5.4		19.0		19.7	
	Unit	Unit Cost $	Unit Consumption	Cost/ sh. ton	Unit Consumption	Cost/ sh. ton	Unit Consumption	Cost/ sh. ton	Unit Consumption	Cost/ sh. ton
Direct Operating Costs										
Electricity	kwh	0.007	44.5	0.312	72.0	0.504	228	1.596	250	1.750
Fuel	Btu	$0.35/10^6$	-	-	-	-	6×10^6	2.100	9.6×10^6	3.360
Labour	Man Hr.	3.75	0.048	0.180	0 144	0 540	0.7	2.625	0.7	2.625
Supervision	Man Hr.	5.70	0.012	0.068	0.024	0.137	0.12	0.684	0.12	0.684
Cooling Water	U.S. Gal	0.02/1000	550	0.011	1600	0.032	1700	0.034	1700	0.034
Process/Boiler Water	U.S. Gal	0.20/1000	320	0.064	310	0.062	-		-	
Maintenance (3% of Investment)				0.191		0.491		1.727		1.791
Total Direct Costs				0.826		1.766		8.766		10.244
Indirect Costs										
Capital Charges (16% of Investment)				1.018		2.618		9.212		9.552
General Overheads (100% of labour)				0.248		0 677		3.309		3.309
Total Direct and Indirect Costs				2.092		5.061		21.287		23.105
Raw Materials										
Sulphur	sh. ton	40.00	0.34	13.600	-	-	-	-	-	-
Pyrites	sh. ton	8.00	-	-	0 7	5 600	-	-	-	-
Anhydrite/By-Product Gypsum	sh. ton	2.00/0.00	-	-	-	-	1.65	3.300	2.1	0.000
Shale	sh. ton	0.40	-	-	-	-	0.29	0.116	0.29	0.116
Coke	sh. ton	17.00	-	-	-	-	0.10	1.700	0.10	1.700
Sand	sh. ton	0.50	-	-	-	-	0.06	0.030	0.06	0.030
Total Production Cost				15.692		10 661		26.433		24.951
By-Product Credits										
Steam	sh. ton	1.00	1.00	1.000	1.00	1 000	-	-		
Pyrites Cinders	sh. ton	4.00	-	-	0 55	2.200	-	-		
Cement	Barrel (376 lb).	2.80	-	-	-	-	1 Short ton	14.894	1 Short ton	14.894
Net Production Cost				14.7		7.4		11.5		10.1

Chart 1

however, that these are only guidance figures and one needs to carry out a detailed evaluation of each individual project before knowing exactly what the capital cost is likely to be.

Operating Costs

I would now like to indicate the likely operating costs of this process in a typical location and to compare this with the production of sulphuric acid from sulphur and pyrites. Similar figures have also been published comparatively recently in 'Chemical Week' and 'Chimie Industrie' for March 1967. Chart 1, on page 75, gives our figures.

By-product Gypsum

In the newsletter that was circulated with the programme for this meeting it was indicated that I would probably have some remarks to make on the solution of profitably disposing of ever accumulating by-product calcium sulphate from phosphoric acid plants. In doing this I would like to make it clear that my remarks are somewhat restricted by pending Patent Applications and existing Secrecy Agreements, and I think it might be helpful, therefore, to indicate those areas where the use of by-product gypsum in place of natural materials leads to change in plant design. The difference in raw materials cost in substituting by-product gypsum for a natural material would be roughly 2.5 dollars/ton of acid assuming that the natural materials would have to be mined and that the waste gypsum was available at zero cost. It is, of course, quite conceivable that the gypsum would be available at a negative cost for some years in many of the locations. Set against this figure up to 4 million Btus/ton acid of fuel would probably be needed in the first instance for drying the by-product gypsum, and at 40 cents/million Btus this means an approximate net saving of one dollar/ton of acid produced.

The gypsum which is supplied as a feed for cement/acid plant can be obtained either directly from a filter or from the stockpiles which have been built up over many years around phosphoric acid plants. In the former case the feed to the plant could either be as a slurry or as the cake washed from the plant. There are occasions where it will be preferable to store gypsum direct from the filter on an intermediate stockpile. After a short time gypsum would then be reclaimed, water having by that time had the chance to drain and evaporate. Gypsum prepared in this way may then contain between 15 and 25% free moisture. It will be abrasive and corrosive and may cause caking at some points on the plant. The material will then be dried in an external dryer and added to the raw material mix. The use of gypsum as a direct feed to the kiln rather than dried gypsum would mean that more fuel was required in the kiln to dry the gypsum and the gases coming out of the kiln would contain that much more CO_2 and nitrogen so that the gas passing to the acid plant would be more dilute in sulphur dioxide than normally.

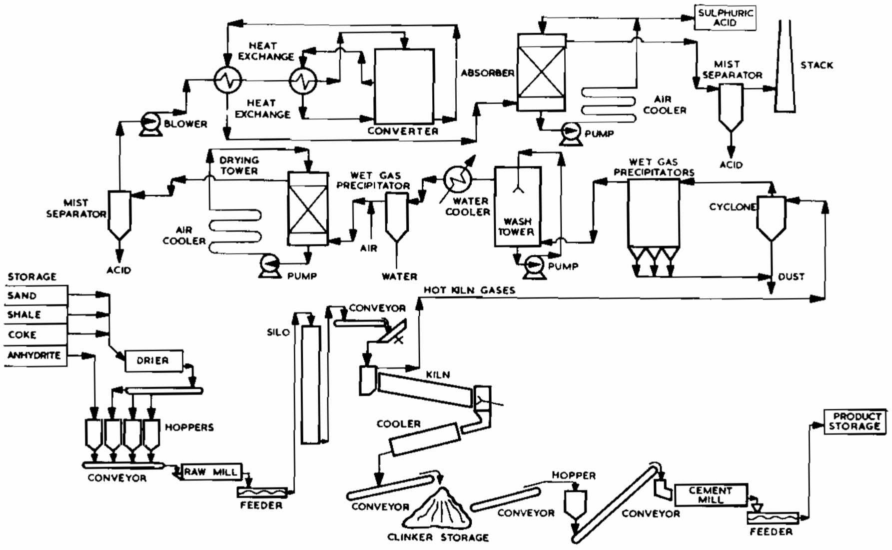
The design of a plant operating in by-product gypsum is, therefore, to some extent a balance between external drying and increased acid plant cost.

The raw materials handling would be slightly different in that since the dried gypsum is already fairly fine there is no need to mill this along with the other raw materials. This arrangement saves power and avoids the problems which can arise with blinding of the mill charge by powdered calcium sulphate. The feed to the kiln is prepared in the same way as before and only slight changes in the firing conditions have to be made.

By-product gypsum contains in addition to a large amount of water, a number of other chemicals which would affect the cement quality and acid plant performance if present in large amounts. These are briefly: phosphorus compounds, fluorine compounds, and one or two other materials such as magnesia and alumina which were present in the original phosphate rocks. The alumina is, of course, not detrimental but has to be allowed for in the raw material calculations; the magnesia on the other hand has to be restricted to fairly low levels for most cement standards. Phosphorus is normally present in typical by-product gypsum partly as soluble phosphoric acid but mostly as insoluble co-crystallised phosphates. If this phosphorus passes through the kiln and eventually reaches the cement clinker it will stabilise the dicalcium silicate phase in the cement clinker to the detriment of the tricalcium silicate phase. Since dicalcium silicate is slow setting and tricalcium silicate is fairly fast setting, the net effect is a reduction in early strength of the cement which, therefore, does not always meet appropriate cement standards. Laboratory work enables one to fix an upper limit to the amount of phosphorus which can be permitted. Power-Gas and Marchon have been doing some fairly extensive work on these topics but this must remain confidential. There is a certain amount of published information and in particular work which has been carried out at the Building Research Station at Garston, Hertfordshire, England under the Direction of Dr. Nurse. He was able to show for instance that cement clinker which contains more than 2.25% of P_2O_5 failed to meet the appropriate British Standards. In the long term we believe that there will be an increasing tendency to install cement/sulphuric acid plants together with phosphoric acids plants which produce high purity by-product calicum sulphate. There are several processes which of course now do this.

Fluorine is rather a different problem in that its presence in the kiln can lower the melting points of the materials in the kiln and may cause ring formation, and any fluorine which does manage to pass through to the converter will cause a shortening in the effective life of the catalyst. There are a number of other minor problems with fluorine evolved from driers and from kiln gases since most countries have very stringent fluorine effluent regulations which look like becoming more severe as time passes.

Well gentlemen, I am sure that this brief review of Marchon technology and present developments has left several questions in your minds, but I will endeavour to answer any questions which you may have. I would like to conclude my talk by showing you a few slides of the present Marchon installation which is situated on the Western side of the Lake District of England, one of the most beautiful parts of the Country where one can still spend a day walking without seeing another soul and where one can sail a boat on a lake without risking collision every five minutes.



SULPHURIC ACID / CEMENT PRODUCTION BY THE MARCHON PROCESS.

Chart 2

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Moderator Heck: Thank you Dr. Ashburner.

Mr. Strelzoff (Chemical Construction Company): I have only one question which was asked of me yesterday. Is there any plant operating a phosphorus-gypsum plant that you know about that has been really running, let's say, continuously over a one year period of time or just only a few days, if you know?

Mr. Ashburner: Mr. Strelzoff has asked two questions. The answer to the first is no. The answer to the second is yes, to my knowledge, I think in two cases, one other apart from our own plant for a few days.

Mr. Strelzoff: Thank you.

Moderator Heck: I think I have always felt at some time in the history of the Round Table if we had more than one speaker from the same company we would have a paradox and I think we have reached that point today.

Mr. Ashburner has told us how we can increase the production of sulfur in our country and in your country and now Mr. Dumain will deliver a paper on Save Sulfur Use Nitrophosphate. So he is going to tell us how to get rid of the sulfur and Mr. Ashburner has just told us how to make it.

Mr. Barrie A. Dumain is with the Power-Gas Company of America. He is a business development engineer and has a degree from the University of Durham in England and has, I believe, been with Power-Gas about 7 years now. He has had quite a bit of experience in the startup of ammonia plants of that type and he has done pilot plant granulation, fertilizer development work and processing engineering work. We are happy to have Mr. Dumain with us.

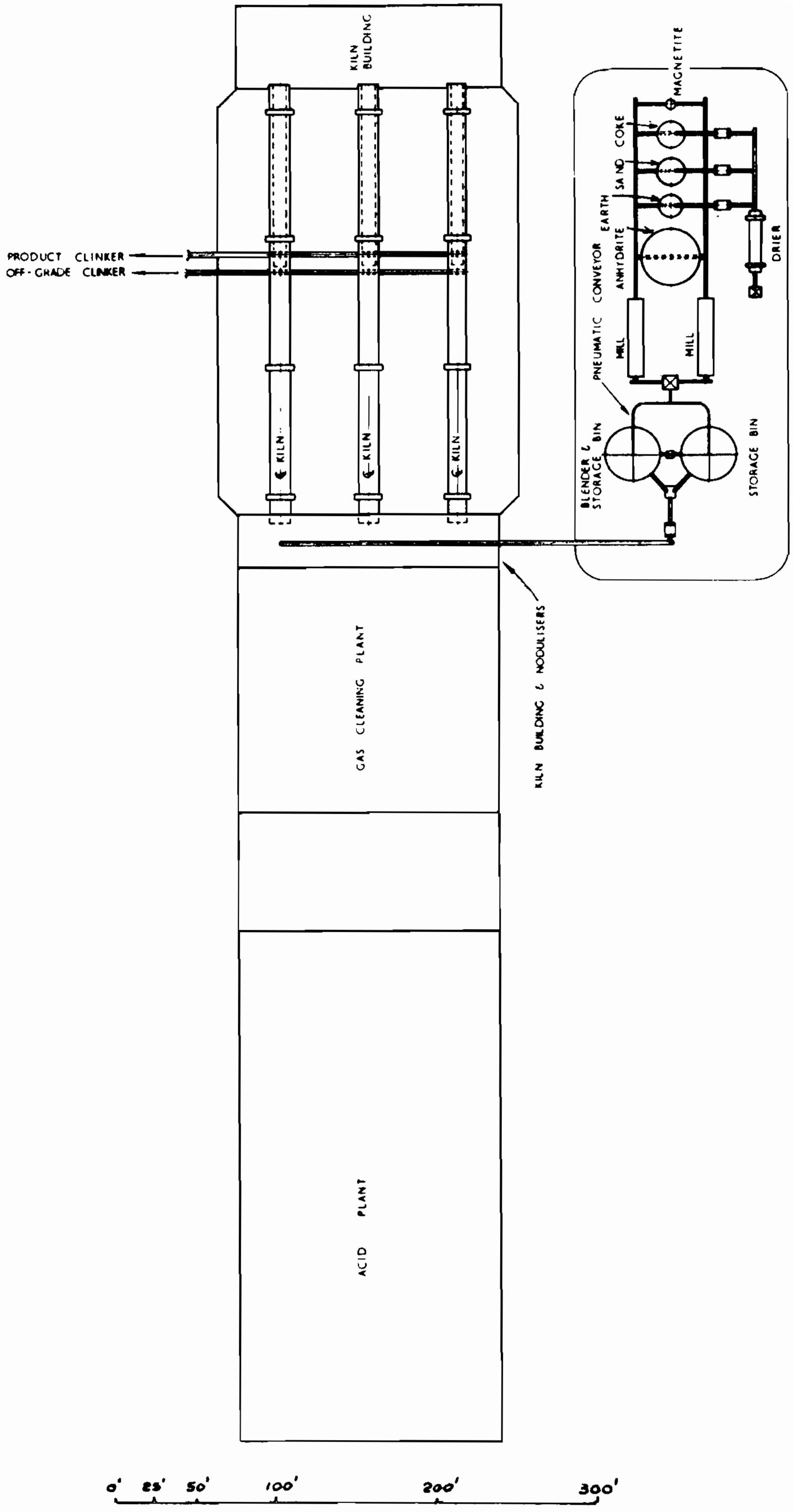
KILN BUILDING
MAGNETITE
COKE
SAND
EARTH
ANHYDRITE
DRIER
PNEUMATIC CONVEYOR
MILL
MILL
BLENDER & STORAGE BIN
STORAGE BIN
PRODUCT CLINKER
OFF-GRADE CLINKER
KILN
KILN
KILN
KILN BUILDING & NODULISERS
GAS CLEANING PLANT
ACID PLANT
0'
25'
50'
100'
200'
300'

Chart 3

Save Sulfur—Use Nitrophosphate

Barrie A. Dumain

That sulfur is important in meeting the world's fertilizer requirement is an undisputed fact. It will continue to be important, but with the price of elemental sulfur now up to the US $40 per ton region, and with future availability in doubt, it is reasonable for all concerned — from the agronomist to the farmer—to ask, "How can we supply the basic plant nutrients to the soil without facing regularly increasing fertilizer prices?". A considerable amount of research into this problem has been carried out, particularly in Europe where the manufacturer has never enjoyed the low sulfur prices encountered, until quite recently, in the United States.

The world's population is expanding at an alarming rate and each new mouth brings with it additional problems, both moral and technical. While theologians argue, the new mouths have to be fed and it is up to the manufacturer to provide cheap fertilizers for the farmer, wherever he is located and whatever his crop.

This paper presents the Dutch State Mines/Power-Gas process for making high water soluble P_2O_5 content compound fertilizers. Since this process depends upon nitric acidulation of phosphate rock it is independent of any future variations in the price of sulfur or sulfuric acid and in the vagaries of supply. It is hoped that this paper will show that the cost of P_2O_5 production via the nitric acid route is considerably cheaper than the corresponding process based on sulfur or sulfuric acid.

The accent in this article is on making high water soluble P_2O_5. All things being equal (particularly the cost per unit of P_2O_5 to the farmer) most farmers and agronomists opt for water soluble rather than citrate soluble phosphate in the final nitric phosphate fertilizer. This matter will be dealt with in greater length later. However, the nitric phosphate process described here will produce water soluble P_2O_5 content of up to 95% in the final high analysis NP/NPK products. These fertilizers can thus be directly substituted for many present day high water soluble P_2O_5 compounds based on sulfuric acid technology. This is not to say that low grade phosphate rocks (with P_2O_5 as low as 25%) cannot be economically utilised—the process will accept rocks with a high CaO/P_2O_5 ratio quite happily.

The Use of Sulfur and Sulfuric Acid in the Production of Modern Day Fertilizers

We have just to look at the following six equations to find out why sulfur is so important in the modern fertilizer industry:—

$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 \rightarrow H_2O \rightarrow H_2SO_4$ Sulfuric acid

$Ca_3 (PO_4)_2 + 2H_2SO_4 \rightarrow [2CaSO_4 + Ca (H_2PO_4)_2]$ Single superphoshate (SSP)

$Ca_3 (PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$ Phosphoric acid

$Ca_3 (PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca (H_2PO_4)_2$ Triple superphosphate (TSP)

$H_3PO_4 + NH_3 = NH_4H_2PO_4$ Mono-ammonium phosphate (MAP)

$NH_4H_2PO_4 + NH_3 = (NH_4)_2HPO_4$ Di-ammonium phosphate (DAP)

The formulae, I think, show the dominating position of sulfur in conventional P-fertilizer technology. We now come to a consideration of where the basic sulfur is obtained. Nearly two thirds of the world's brimstone production is from easily worked Frasch mines[1] of which the most important are in the United States and Mexico.

These figures apply to free world production, i.e. excluding the Communist bloc.

While brimstone production is increasing, and will continue to increase, it must be remembered that 91% of the world's supply of elemental sulfur is contributed by four countries. It could be said that 91% of the world's supply pects for "conventional" processes depend on the price rather than the availability of sulfur. The current prices, in the US $40 per ton region (with make-up "supplies of sulfuric acid" being sold at around 50 dollars per ton[3] of equivalent sulfur), are already making themselves felt by the American farmer and indeed by his counterparts throughout the world. Increases in the cost of food production impinge heavily on any country's economy and its external trade balances. Alternative ways of producing phosphatic fertilizers are available such as

a) Recovery of elemental sulfur from oil and natural gas (already extensive and increasing rapidly).
b) Pyrites (particularly in the Communist bloc).
c) Digestion of phosphate rock by hydrochloric acid[4].
d) Processes to produce sulfuric acid from anhydrite or gypsum[5].
e) Thermal processes based on hydroelectric[6] or nuclear power[7].
f) Nitric acid acidulation.

Nitric Acid Acidulation Processes

I do not propose to dwell here on the various processes and their merits[8]. This paper is intended to present one of the nitric acid processes available. I will consider here the DSM/Power-Gas process involving sulfate recycle. However, before pressing on to discuss the merits of this process in greater length I will reiterate the general chemistry of nitric attack on phosphate rock. The equations given below cover the various processes available pretty fully.

$$3[Ca_3(PO_4)_2] \quad CaF_2 + 20\ HNO_3$$

$$\downarrow \text{aqua}$$

$$6\ H_3PO_4 + 10\ Ca (NO_3)_2 + 2HF$$

Ammoniation of this intermediate product yields:—

$$\downarrow 8\ NH_3$$

$$[3Ca (H_2PO_4)_2 + 6\ Ca (NO_3)_2 + 8\ NH_4\ NO_3 + CaF_2]$$

$$\downarrow 6\ NH_3$$

$$6\ Ca\ HPO_4 + 3\ Ca (NO_3)_2 + 14\ NH_4NO_3 + CaF$$

Table I
World sulfur production 1966[2]

Source of Sulfur	Brimstone %	Sulfur—other forms %	Total %
Frasch	35.0	0.1	35.1
Other	2.0	1.2	3.2
Pyrites	0.2	25.3	25.5
Sulfides	—	9.0	9.0
Oil and Gas	20.2	1.0	21.2
Anhydrite	—	3.9	3.9
Coal	0.1	0.4	0.5
Waste products	—	1.6	1.6
Total percentage	57.5	42.5	100.0
Million tons of sulfur	15.8	11.7	27.5

Calcium nitrate is not a desirable constituent of NP/NPK compound fertilizer. It is hygroscopic and imparts poor physical properties to the final solid fertilizer product. The calcium ion can be removed in various ways. One of these is the "freeze out" method. One of the problems of calcium nitrate freeze out is the expensive equipment required to handle the small crystals of calcium nitrate produced. Not all of the calcium nitrate can be removed and a major difficulty involved in further ammoniation is that apatite, which is both water and citrate insoluble, can be produced.

Over many years a number of processes to precipitate calcium ions as carbonate, sulfate or phosphate have been developed but all have the major disadvantage of leaving the original calcium of the rock in the end product fertilizers. The product tends to be of low grade and usually contains only 25% to 40% water soluble P_2O_5. In this paper I have used the term nitricphosphate as meaning those end products with over 60% water soluble P_2O_5 content.

Two basic nitricphosphate process have been exploited; "freeze out" and "sulfate recycle".[9,10]

The "Freeze Out" Processes

The "freeze out" process (original Odda process) was first proposed in 1928 by Erling Johnson[11] of Norway. As the name implies it involves crystallisation of the undesirable calcium nitrate and its subsequent removal by filtration or centrifuging. Dependent on the calcium nitrate left in the filtrate will be the water-soluble P_2O_5 content of the final ammoniated fertilizer product. Various degrees of cooling have been attempted and some are quite successful. It is reported by Tennessee Valley Authority[12] that up to 88% of the calcium can be removed at temperatures around 32°F.

In all modifications of the Odda process the calcium nitrate crystals have to be removed from the mother liquor and this is not an easy procedure because of the viscosities encountred. Excess nitric acid has usually to be used to facilitate this removal. Some "free" acid adheres to the surface of the calcium nitrate crystals. This can be washed off and recycled. In terms of total $N + P_2O_5$ the overall N/P_2O_5 ratio of all the fertilizers produced in this type of plant is high, around 1.5–2.2:1. The ratio, of course, depends on water soluble P_2O_5 production.

The calcium nitrate crystals can be washed and then processed to produce straight N-fertilizers in a number of ways, such as:—

a) Melting with ammonium nitrate to form a double salt. The product is of low grade, approximately 15.5:0:0.
b) Reacted with ammonium carbonate solution to form an ammonium nitrate/chalk slurry. The calcium ammonium nitrate product can be up-graded if required by the addition of ammonium nitrate. CAN products usually analyze at around 21 to 24% nitrogen.
c) Reacted with ammonium carbonate to produce ammonium nitrate which can be separated by having the chalk filtered off and then concentrated to give a 33.5–34:0:0 product.

If the calcium nitrate of calcium ammonium nitrate market is depressed, or if government safety regulations preclude the distribution of ammonium nitrate, then the manufacturer using the freeze-out type of process has serious problems to face.

The second basic nitricphosphate process was proposed as far back as 1930 by F. G. Liljenroth[13] of Sweden. This is the nitricphosphate/ammonium sulfate recycle process which has been further developed by DSM and Power-Gas and with which this paper is primarily concerned. For ease I have designated this the NP/ASU process. Before going on to a discussion of the merits of this process it is worth saying a word or two on what kinds of fertilizers are currently being used and what is desirable.

What type of fertilizer is most acceptable?

Whatever the source, water soluble phosphate has the same high value to the crop. In the U.K. it is recommended that water soluble P_2O_5 be used to give a crop a quick start, or when the fertilizer is drilled in bands with or near the seed. If the fertilizer can be applied well before growth starts, or when rapid action is not necessary then citrate soluble phosphate is acceptable. Insoluble phosphate in NPK's should not be valued too highly as it acts very slowly and is only fully effective on acid soils. While these three types of phosphoric fertilizers have markedly different immediate effects, the long term effect of a given quantity of P_2O_5 tends to be the same for all of these in succeeding years. The question of whether to use citrate soluble or water soluble P_2O_5 is still a matter for discussion. Although citrate soluble P_2O_5 has been found cheaper to produce in Europe, most agronomists argue that citrate soluble P_2O_5 is nearly as good as water soluble P_2O_5—rarely that it is better. Russian agronomists have expressed a preference to move all the way up to 90% water soluble P_2O_5 from the 50% currently in use in the Soviet Union.[15]

The table given below shows compound fertilizers of the NPK type currently in use in the United Kingdom.

Most British and European farmers depend on the cheaper single superphosphate, triple superphosphate and finely ground basic slag (0:15;–16:0) for satisfying high phosphate requirements, rather than high phosphate NPK compounds. MAP and DAP production is almost wholly absorbed as intermediates used by blenders.

This point is brought home particularly in the knowledge that Americans, and indeed many of the world's phosphatic fertilizer producers, make 12:52:0 and 18:46–48:0 NP's so that these compounds can be blended with straight N-fertilizers to give the farmer a 20:20:0 or similar product. Is this essential?

DSM/Power-Gas NP/ASU Process

Although the NP/ASU process is primarily aimed at the production of high water soluble P_2O_5 NP/NPK fertilizers it is also capable of producing low water soluble P_2O_5 compounds and these will be looked at later in this paper. However it is on the subject of high water solubility that we will dwell at length here.

The process route used can be followed from figure 1 and the chemistry from figure 2. Before elaborating on this it is interesting to compare the basic chemistry of the 'conventional' sulfuric acid based process manufacturing an NP of formulation say 2:1:0, with that corresponding to the NP/ASU process.

Sulfuric acid route

$$(3.5\,CaO).\,P_2O_5 + 3.5H_2SO_4 \xrightarrow{\text{aqua}} 2H_3PO_4 + 3.5CaSO_4.2H_2O\downarrow$$

$$2H_3PO_4 + 2NH_3 \longrightarrow 2NH_4H_2PO_4 \quad \ldots \text{(or to DAP)}$$

$$9HNO_3 + 9NH_3 \longrightarrow 9NH_4NO_3$$

$$(3.5\,CaO)\,.\,P_2O_5 + 3.5H_2SO_4 \longrightarrow 2NH_4H_2PO_4 + 9NH_4NO_3 \quad \ldots\text{Product}$$

$$\text{Overall} + 9HNO_3 + 11NH_3 + 3.5CaSO_4.2H_2O\downarrow \quad \ldots\ldots\ldots\text{Effluent}$$

NP/ASU route

$$(3.5\,CaO)\,.\,P_2O_5 + 7HNO_3 \xrightarrow{\text{aqua}} 3.5Ca\,(NO_3)_2 + 2H_3PO_4$$

$$3.5Ca\,(NO_3)_2 + 3.5\,(NH_4)_2SO_4 \longrightarrow 7NH_4NO_3 + 3.5CaSO_4.2H_2O\downarrow$$

$$3.5CaSO_4.2H_2O + 3.5CO_2 + 7NH_3 \longrightarrow 3.5\,(NH_4)_2SO_4 + 3.5CaCO_3\downarrow$$

$$2H_3PO_4 + 2NH_3 \longrightarrow 2NH_4H_4PO_4 \quad \ldots \text{(or to DAP)}$$

$$2HNO_3 + 2NH_3 \longrightarrow 2NH_4NO_3$$

$$(3.5\,CaO).\,P_2O_5 + 3.5C_2O \xrightarrow{\text{aqua}} 2NH_4H_2PO_4 + 9NH_4NO_3 \quad \ldots\text{Product}$$

$$\text{Overall} + 9NHO_3 + 11\,NH_3 + 3.5CaCO_3\downarrow \quad \ldots\ldots\ldots\text{Effluent}$$

From the overall equations it has been demonstrated that carbonic acid (made from CO_2 which is usually available at no cost from an adjacent ammonia installation) can effectively be substituted for sulfuric acid as an acidulation agent. Sulfuric acid is, therefore, an unnecessary expense. The solid effluents from the two processes are also different. The chalk from the NP/ASU process is more easy to dispose of than gypsum and a saving of about 40% in the effluent tonnages to be handled is achieved.

Referring back to the flowsheet we can see that it consists of two halves. These are the NP production plant and the gypsum conversion plant. Both of these 'halves' are being applied separately, on a commercial scale, in Holland, India, Austria and other countries.

Dutch State Mines, at Geleen, are operating a 550 tons/day nitric-phosphate plant. The ammonium sulfate fed to this plant is an impure by-product of caprolactam manufacture. The process of converting by-product gypsum to am-

Table 2
Fertilizers used in the U.K.

Principal group	Plant food ratios	Main uses
General purpose	1:1:1	Grasslands. Fodder crops. Horticultural crops. Soils of average fertility.
High nitrogen	2:1:1 1½:1:1	Spring cereals. Kale and other leafy crops. Grasslands (intensive).
High phosphate	1:2:1 1:1½:1	Soils that are very deficient in phosphate.
High potash	1:1:2 1:1:1½	Most row crops grown in potassium deficient soils in the drier parts of the United Kingdom. Potatoes. Sugar beet. Many horticultural crops.
High nitrogen	1½:1:2	Root crops grown on well-farmed land. Sugar beet.
High potash	2:1:3 2:1:4	
High phosphate	1:2:2	Peat soils, arable land in wet areas.
High potash	1:2½:2½	Combine drilling with seed of autumn cereals.

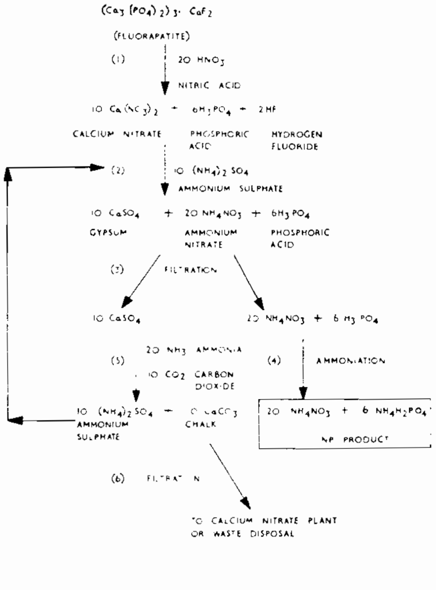

FIG 1 – CHEMISTRY OF THE NP/ASU PROCESS

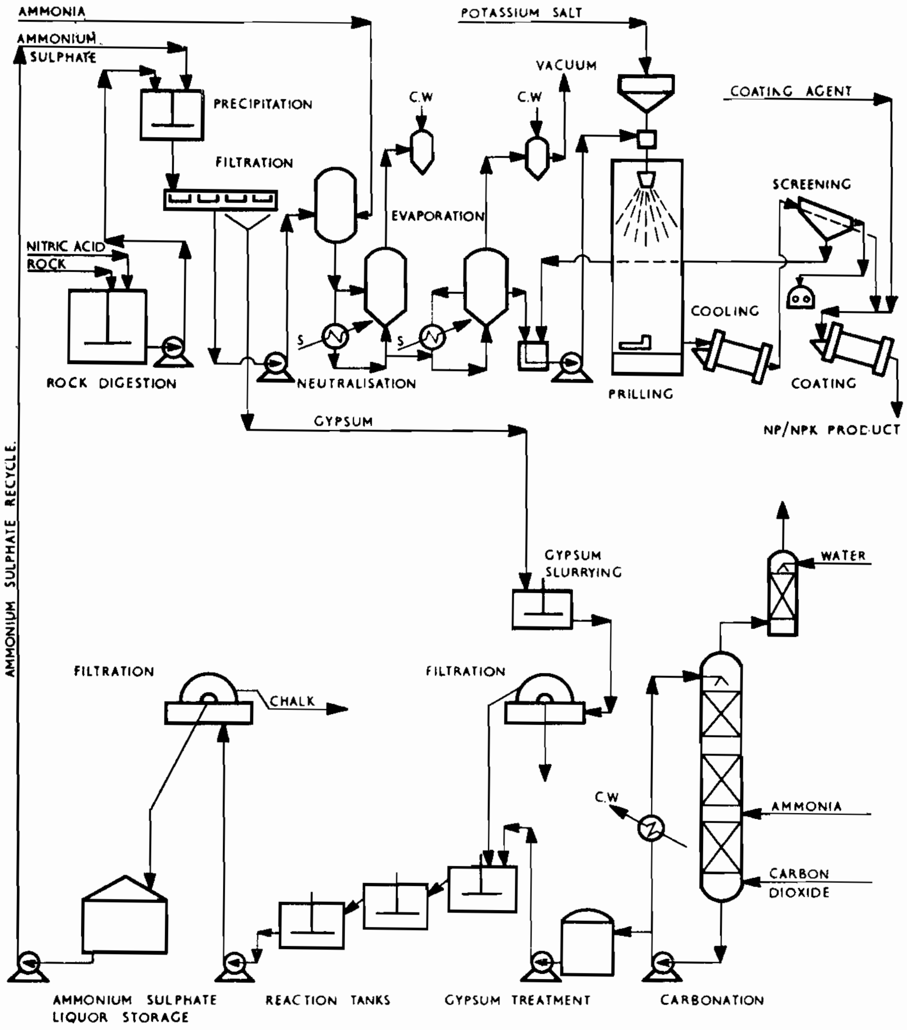

FIG 2 NP/NPK FERTILIZER PRODUCTION BY THE NP/ASU PROCESS

monium sulfate by the Merseberg reaction is being carried out by OSAG and FACT, the latter in a 440 tons/day plant built by Power-Gas. All the steps of the NP/ASU process have, therefore, been operated commercially with the exception of one. This is the addition of the pure ammonium sulfate produced from gypsum, rather than the impure form resulting from caprolactam manufacture, to the double decomposition tanks.

The straight NP/ASU process shown on the flowsheet, and now briefly described, will produce, depending on the phosphate rock impurities (and its CaO/P_2O_5 ratio) 90–95% water soluble P_2O_5 compound fertilizers with an N/P_2O_5 ratio of 1.6 or greater. Many variations are possible to provide an even wider range of products and these will be discussed later.

The process will accept rock particles up to one sixth of an inch enabling a power saving of approximately 25–35 kwh ton P_2O_5 when compared with sulfur based processes.

55–58% w/w nitric acid is reacted with phosphate rock. The reaction is exothermic, the temperature in the acidulation tanks being around 150°F. Anti-foam agents are added.

The reaction between ammonium sulfate and calcium nitrate takes place around 130°F. The gypsum crystals produced are removed on a tilting pan filter.

If a high N/P_2O_5 formulation is required, e.g. 2:1:0, excess nitric acid is used in the acidulation stage and this acid passes through in the filtrate which is essentially composed of phosphoric acid and ammonium nitrate. It is neutralised at nearly atmospheric pressure with ammonia at a pH of 2.5–3:5 under automatic control. During neutralisation the temperature of the solution, or slurry, is at boiling point, i.e. 220–230°F.

The neutralised NP slurry is concentrated to 5% water if it is to be granulated, or to about 1% water if it is to be prilled. Potassium can be introduced in two alternative places, either as potassium sulfate to the acidulation tanks, or as potassium chloride or potassium sulfate to the intermediate slurry going forward to the granulation plant (or to the melt tank located at the top of the prilling tower).

The gypsum filter cake is washed to remove mother liquor, slurried and further washed on a rotary drum vacuum filter. The resulting filter cake (containing around 20% w/w water) is fed to the reaction tanks in the ASU plant. Here reaction with 52–53% w/w ammonium carbonate solution yields ammonium sulfate and chalk. The latter is removed by filtration and, after washing, is suitable for calcium ammonium nitrate manufacture. The 38% w/w ASU filtrate is fed up-stream in the nitricphosphate plant to the double decomposition tanks. It is possible to make directly by this "conventional" NP/ASU process products such as 25:15:0 and 29:9.7:0 containing up to 95% water soluble P_2O_5.

Operating data for high water soluble P_2O_5 and high N/P_2O_5 fertilizers is given in Table 2.

Capital costs and comparative production costs are given in Tables 4 and 5 respectively.

A great number of variations to the process are possible. In order to optimise the process design and plant operation, it is necessary to be aware of both present and future NP/NPK market requirements. The European demand for NP and NPK's is based mainly on NP/P_2O_5 ratios of 1 or more as indicated in the table presented previously.

NPK produced with N/P_2O_5 ratios less than 1.6

The DSM/PGC plant can be very easily modified to produce fertilizers with N/P_2O_5 ratios below 1.6.

The simplest modification would be to add phosphoric acid, MAP etc. to the intermediate NP slurry going forward to ammoniation. For an N/P_2O_5 ratio of 1 this would mean that approximately 58% of the total product P_2O_5 would be derived from nitric acid acidulation. Triple superphosphate with stabilising compounds (urea and ammonium sulfate) could also be employed as a P_2O_5 source.

With this scheme in use the hydrogen ions in phosphoric acid can be made to substitute, to a certain exent, for those of nitric acid. It is preferable to introduce phosphoric acid into the nitric acid acidulation stage, thereby lowering nitric acid usage. Using a 50/50 mixture of Kola/Morocco fluorapatites Dutch State Mines produce a 23:23:0 product with 73% of the product P_2O_5 derived from nitric acid acidulation. The balancing 27% is from phosphoric acid addition. Impurities in the phosphate rock do have a significant effect and Table 2 is based on lower grade Florida rock.

It should not be forgotten that phosphoric acid is a product of the attack of nitric acid on rock. Further possibilities to recycle part of the filtrate from the tilting pan filter to the acidulation tanks. The amount of recycle is limited and the rock impurities again have a significant affect. "Internal recycle" of phosphoric acid would give, in the case of Kola/Morocco

Table 3

High ws P_2O_5 Nitric Phosphates from Standard NP/ASU Process

A) Florida Phosphate Rock		**A**	**B**	**C**
BPL	% w/w	64/66	70/72	74/76
P_2O_5	% w/w	30.27	33.0	34.38
CaO	% w/w	45.30	46.5	49.30
F	% w/w	3.52	3.6	3.77
SiO2	% w/w	10.25	5.3	3.75
CO_2	% w/w	3.85	3.4	3.05
SO_4	% w/w	1.35	0.9	0.90
Fe_2O_3	% w/w	1.15	0.5	1.13
Al_2O_3	% w/w	1.30	1.5	1.15
MgO	% w/w	0.57	0.25	0.42
Na_2O	% w/w	0.57	0.15	0.50
K_2O	% w/w	0.10	0.10	0.10
H_2O	% w/w	1.0	5.1	1.0
Org. & Inerts	% w/w	2.48	0.26	1.5

B) Phosphoric Acid from Rock				
P_2O_5	% w/w	32.654	29.88	32.654
H_3PO_4	% w/w	41.456	38.704	41.456
$McPO_4$	% w/w	3.790	3.538	3.790
$CaSiF_6$	% w/w	2.882	2.691	2.882
H_2SO_4	% w/w	2.775	2.591	2.775
H_2O	% w/w	48.687	52.093	48.687
Inerts	% w/w	0.410	0.383	0.410

C) ASU Liquor Production—Consumption Data Per Ton of 38% Liquor		
By-product gypsum ($100\%\ CaSO_4{\cdot}2H_2O$)	ton	0.551
Ammonia (100%)	ton	0.111
Carbon dioxide (100%)	ton	0.143
Steam (30 psig)	ton	0.019
Process water	US gals	133
Cooling water	US gals	1900
Filtered river water	US gals	68
Power	KWH	12

Notes:

(i) *ASU Solution*

$(NH_4)_2SO_4$	38–40% w/w
H_2O	58–60% w/w
NH_3	0.6–1.0% w/w
CO_2	0.6–1.0% w/w

(ii) Up to 10% NH_3 can be accepted as aqueous 25% NH_3.

(iii) CO_2 of 65% concentration can be accepted by ASU process.

Table 3—continued

D) NP Production—Consumption Data Per Ton of Prilled Fertilizer									
N/P_2O_5 Ratio		1	1.79	2	1	2	1	1.72	2
ws P_2O_5	% w/w	89	89	89	91	92	90	91	91
N	% w/w	22.3	25.4	26.0	22.45	26.4	22.6	25.6	26.4
P_2O_5	% w/w	22.3	14.2	13.0	22.45	13.2	22.6	14.9	13.2
Moisture (max.)	% w/w	0.9	0.9	0.9	1.0	1.0	0.9	0.9	0.9
Phosphate Rock—Florida		A	A	A	B	B	C	C	C
	ton	0.459	0.489	0.448	0.469	0.416	0.424	0.453	0.400
Phosphoric Acid—Florida		A	—	—	B	—	C	—	—
	ton	0.285	Nil	Nil	0.265	Nil	0.274	Nil	Nil
Nitric Acid (55% w/w)	ton	0.742	0.949	0.986	—	—	0.748	0.945	0.996
Nitric Acid (57% w/w)	ton	—	—	—	0.715	0.954	—	—	—
Ammonia (100%)	ton	0.038	0.037	0.051	0.033	0.060	0.039	0.037	0.057
ASU Solution (38% w/w)	ton	1.248	1.343	1.231	1.31	1.18	1.262	1.363	1.204
Coating	ton	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026
Steam (200 psig)	ton	1.84	1.82	1.74	1.60	1.54	1.77	1.83	1.72
Steam (30 psig)	ton	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Cooling water	US gals	18,500	18,500	17,750	16,000	14,500	18,750	18,750	17,750
Power	KWH	23.6	23.6	23.6	22.3	25.4	23.6	23.6	23.6
Overall Efficiency—(C)+(D)									
N	%	97.8	97.7	97.1	97.8	97.8	97.8	97.7	97.5
P_2O_5	%	96.3	95.9	95.8	96.0	96.1	96.1	95.7	95.9

an N/P_2O_5 ratio of 1.35. With Florida rock this ratio would be approximately 1.45. Operating data is given in Table 9.

If external phosphoric acid is to be used it is as well to take it from a point upstream of the phosphoric acid filtration section of a typical wet process phosphoric acid plant. By-passing of the phosphoric acid filter in this way results in:—

a) An acid containing 32% P_2O_5 as opposed to 30% P_2O_5 (since no wash water is added).
b) As a result of (a) above, a lower steam consumption in the concentration section of the NP/ASU plant.
c) An automatic make-up feed of gypsum into the NP/ASU system.
d) Seed crystals for the subsequent double decomposition section. This increases the crystal size and filterability of the nitricphosphate by-product gypsum, and subsequently a reduction in the capital cost of the filter.

A further alternative is to acidulate using a mixture of nitric and sulfuric acid. This is reasonably sensible as phosphoric acid would in any case normally be produced in a standard sulfuric acid acidulation plant. It the rock is first attacked with a deficit of nitric acid "chemical grinding" is achieved and the rock becomes more assailable by subsequent sulfuric acid attack. This reduces costs in the plant concentration section as the effect is of adding P_2O_5 of concentration 60% or higher.

NP/ASU process—low water soluble P_2O_5 content

Considering the basic equations for nitric acid acidulation it can be seen that if calcium nitrate is allowed to proceed to the ammoniation stage then phosphate reversion takes place leading to the formation of water insoluble/citrate soluble dicalcium phosphate. It is even possible to carry this reaction as far as apatite if too much calcium nitrate should slip. This means that a very effective control on NP product water soluble P_2O_5 is the amount of

Table 4
NP/ASU Plant Capital Costs (Turnkey, Battery Limits)

Basis: 65,000 tons/year P_2O_5

Product (prills)	23.8:14.9:0	26.5:10.5:0	26.0:14.1:0	21:11.4:11.4
% ws P_2O_5	60	75	95	95
Output (tons/year)	435,000	620,000	460,000	570,000
US $Millions	4-¼	5	5	5-½

Notes: (1) The capital costs for an NP/ASU nitric phosphate plant are dependent on a number of factors, e.g.
(a) Product formulations and whether these are NPs or NPKs
(b) Product form i.e. granules or prills
(c) Water soluble P_2O_5 content
(d) Raw materials etc.

(2) The following capital costs should be included in the sulphuric acid based routes
(a) Sulphuric acid plant
(b) Phosphate rock grinding equipment
(c) Phosphoric acid plant (with concentration).

(3) When making 1:1:0 NP grades via the NP/ASU process then there will be requirements for sulphuric acid, etc., but these requirements will be ¼–⅓ of those for the conventional sulphuric acid based routes.

(4) The nitric acid requirements of the NP/ASU and conventional processes are virtually identical.

Table 5
Comparative Cost Data

NP/ASU Process Vs. Conventional Sulphur Based Processes

Bases: (1) Phosphate rock (e.g. Tunisian) : 30% P_2O_5 : 49.5% CaO
(2) NPK Product : 21:11.4:11.4 prills 95% ws P_2O_5
(3) Output : 525,000 tons/year NPK fertilizer i.e. 60,000 tons/year P_2O_5

	Nitric Phosphate NP/ASU		Conventional Sulphur Based	
Raw Materials and Intermediates	Tons/Yr	Diff. US $	Tons/Yr	Diff. US $
Phosphate rock @ $17 per ton	208,000	—	213,000	85,000
Potassium chloride	100,000	—	100,000	—
Sulphur @ $40 per ton	—	—	58,000	2,320,000
Sulphuric acid	—	—	174,000	—
Phosphoric acid (100% P_2O_5)	—	—	61,000	—
Ammonia @ $35 per ton	142,500	3,500	142,400	—
Nitric Acid	224,100	—	223,800	—
ASU Liquor	234,000	—	—	—
CO_2 (no cost if from adjacent ammonia plant)	79,000	—	—	—
Gypsum make-up @ $7.50 per ton	20,000	150,000	—	—
Steam @ $1 per ton	819,000	686,500	132,500	—
Cooling water @ 3¢ per 1000 US gals	18×10^9 gals	90,000	15×10^9 gals	—
Power @ 0.5¢ per KWH	25.5×10^6 KWH	—	36.5×10^6 KWH	55,000
Minimum Annual Cost Saving			US $	1,540,000
Minimum Cost Saving Per Ton P_2O_5			US $	25.66

Table 5—continued

Further Savings	**US $ Saving Per Ton P_2O_5**
(i) If ASU washing of the nitric phosphate by-product gypsum is employed, approx. 20% of steam requirements of NP/ASU plant may be saved, i.e.	2.75
(ii) If gypsum make-up is from an adjacent phos. acid unit then gypsum is at no cost and the ASU plant acts as an effluent disposal unit.	2.50
(iii) The capital cost of the NP/ASU factory complex is approx. US $1½ million cheaper than the conventional sulphur based process and this on a 10-year write-off is equivalent to	2.50
(iv) Power figures do not include for rock grinding requirements of the conventional route which, at 30 KWH/ton P_2O_5 represents a further saving in favor of the NP/ASU process.	0.15
(v) Labor, maintenance etc. are less for the NP/ASU route.	+ ?
(vi) The on-stream time of the NP/ASU plant is in excess of 333 days/year and allows for maximum integration with adjacent ammonia and nitric acid facilities.	+ ?
Possible Annual Cost Saving	US $ 2,004,000
Possible Cost Saving Per Ton P_2O_5	US $ 33.40

Note: Under U.K. conditions it has been independently[17] estimated that with sulphur costing £20 per long ton, the NP/ASU process will produce water-soluble P_2O_5 at approx. £10/ton cheaper than an existing conventional sulphur based plant. For a 20:10:10 NPK fertilizer, this means approx. 4% reduction in price to the farmer. For a 23:23:0 NP fertilizer (made via NP/ASU with phos. acid addition), the corresponding reduction is about 5½%.

ammonium sulfate solution sent to the double decomposition section of the plant. This of course, determines the amount of calcium precipitated as gypsum. The balancing calcium ions, therefore, go forward as calcium nitrate to the ammoniation stage.

If it is decided at the outset to limit the water soluble P_2O_5 to say 70%, then a by-pass from the acidulation section to the NP intermediate storage tank can be installed. This allows reduction in the capital cost of the double decomposition and filtration sections.

A further alternative is to allow excess nitric acid to pass through the double decomposition and filtration stages. This excess acid can then be mopped up in a second reaction stage into which the balance of the phosphate rock is fed. The products, including calcium nitrate, pass via intermediate storage to the ammoniation section.

Operating data for low water soluble P_2O_5 nitricphosphates is given in Table 7.

Calcium nitrate removal—
combination of freeze-out and ASU

Part freeze-out can have decided advantage in adding greater flexibility to the NP/ASU process. This is especially so where large scale operations are envisaged for the simultaneous production of 1:1:X and 1.5 —3:1:Y NP/NPK products. While it is not for us to go into the pro and con of freeze-out versus ammonium sulfate recycle the main arguments against freeze-out are the high power requirements arising from the refrigeration load involved, and also the need to process by-product calcium nitrate.

Comparative data is given in Table 8. In the context of a large fertilizer complex the freeze-out process, when making 75-80% water soluble P_2O_5, leaves an N/P_2O_5 ratio of 2.0-2.2:1. In the case of the NP/ASU process making 95% water soluble P_2O_5, this ratio is 1.35-1.45. Both processes of course, are totally independent of sulfur or sulfur products or in fact make-up supplies of phosphoric acid.

TABLE 6 - Typical NP Compound Fertilizer

Product			Analysis	% w/w
N/P_2O_5 ratio		1.67	NH_4NO_3	62.7
N	% w/w	25.3	$NH_4H_2PO_4$	20.6
P_2O_5	% w/w	15.2	$Ca(H_2PO_4)_2$	1.6
ws P_2O_5	% w/w	92	$MePO_4$	2.3
			$(NH_4)_2SO_4$	4.0
Prill Size:			$(NH_4)_2SiF_6$	1.1
95% between Tyler 6-14			CaF_2	1.6
Mean diameter, Tyler 8-9			$CaSO_4$	1.4
Crushing Strength:			SiO_2	0.8
Greater than 500 psi			Inerts	0.4
			Coating	2.5
			H_2O	1.0

Table 7 - Low WS P_2O_5 Nitric Phosphates from Standard NP/ASU Process

NP Products - Consumption Data Per Ton Prilled Fertilizer

N/P_2O_5 Ratio	% w/w	1	1	1.69	1.71	2	2	1	1	1.6	1.62	2	2
ws P_2O_5	% w/w	70	80	70	75	70	75	70	80	70	79	70	78
N	% w/w	20.8	21.3	24.4	24.7	25.5	25.7	21.1	21.6	24.4	24.8	25.8	26.1
P_2O_5	% w/w	20.8	21.3	14.4	14.5	12.7	12.8	21.1	21.6	15.2	15.3	12.9	13.0
Moisture (max)	% w/w	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Phosphate Rock - Florida		A	A	A	A	A	A	C	C	C	C	C	C
(Table 2a)	ton	0.464	0.469	0.496	0.499	0.439	0.442	0.431	0.434	0.459	0.462	0.391	0.396
Phosphoric Acid		A	A	-	-	-	-	C	C	-	-	-	-
(Table 2b)	ton	0.231	0.246	Nil	Nil	Nil	Nil	0.219	0.232	Nil	Nil	Nil	Nil
Nitric Acid(55%w/w)	ton	0.780	0.752	0.963	0.968	1.018	1.021	0.791	0.790	0.958	0.964	1.029	1.031
Ammonia (100%)	ton	0.056	0.049	0.049	0.047	0.068	0.065	0.058	0.051	0.052	0.047	0.075	0.071
ASU Solution(38%w/w)	ton	0.854	[illegible]	1.088	1.142	0.962	1.012	0.854	0.879	1.074	1.158	0.915	0.992
Coating	ton	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026	0.026
Steam (200 psig)	ton	1.46	1.58	1.61	1.66	1.53	1.61	1.45	1.56	1.60	1.67	1.50	1.56
Steam (30 psig)	ton	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Cooling water	US gals	14,750	[illegible]	16,250	17,000	15,500	16,000	14,500	15,750	16,250	17,000	15,250	16,250
Power	KWH	20.9	22.8	23.6	23.6	23.6	23.6	20.9	23.6	22.7	23.6	22.7	23.6
Overall Efficiency													
N	%	97.2	97.3	97.3	97.3	97.4	97.2	97.3	97.5	97.3	97.3	96.9	97.2
P_2O_5	%	96.3	95.6	95.9	96.0	95.5	[illegible]	96.0	96.0	96.3	96.3	96.0	95.5

Table 8
Calcium Nitrate—Freeze-Out Vs. ASU

Consumptions—Per Ton NP

		Conventional "Odda"		**Basic NP/ASU**
N/P_2O_5 ratio	% w/w	1.36*		1.69
ws P_2O_5	% w/w	51.8	—	70
N	% w/w	17.2	15.0	24.4
P_2O_5	% w/w	24.2	—	14.4
Moisture (max)	% w/w	0.9	13.6	0.9
Phosphate Rock—Florida (Table 2)		A	—	A
	ton	0.829	Nil	0.496
Nitric Acid (57% w/w HNO_3)	ton	0.874	0.057	0.929
Ammonia (100%)	ton	0.122	0.016	0.049
ASU Solution (38%) w/w	ton	Nil	Nil	1.088
Coating	ton	0.025	0.010	0.026
Steam (200 psig)	ton	0.45	0.363	1.61
Steam (30 psig)	ton	0.02	—	0.025
Cooling water	US gals	7,200	4,000	16,250
Power	KWH	68.2	37.8	23.6
By-product (as calcium nitrate end product)	ton	1,038	—	Nil
Ammonia (cooling agent)	ton	0.30	—	Nil

**Note*: If ammonium nitrate by-product, instead of calcium nitrate is made, then N/P_2O_5 ratio is approx. 2.

Surplus nitrogen from a freeze-out operation is available as calcium nitrate, calcium ammonium nitrate, or ammonium nitrate. It should be noted that these straight N-fertilizers are unacceptable in some markets for a variety of reasons.

Whether or not some or all of the ammonium nitrate is to be fed back into the freeze-out process in order to obtain the required product N/P_2O_5 ratios, it is always necessary to push the freeze-out system to its design limits if maximum water soluble P_2O_5 is needed. Variations in rock feed can prove critical.

A nitricphosphate factory complex producing 100,000 tons per year P_2O_5 and including a 1,000 tons per day ammonia plant, could include a freeze-out process which would leave about 100,000-125,000 tons per year of ammonia available for, say, urea manufacture. The corresponding NP/ASU process leaves 180,000-185,000 tons per year ammonia available for urea. This is an important consideration. Not only is urea becoming more 'fashionable" but its analysis of 46.5:0:0 can be a decided advantage in terms of bagging, handling, and freight over its "competitors" such as CAN, calcium nitrate and ammonium nitrate.

Blending back of urea into NPK products from the nitric-phosphate process leads to higher analysis products. Up to 15% of the total N in the nitricphosphate NPK can be as urea without entering areas of thermal instability.

Multi-stream operations—
freeze-out plus ASU

A simple variation of the NP/ASU process, in terms of large scale multiple stream operations, where two or more NP/NPK's are to be simultaneously produced is illustrated in figure 3.

If one stream is to produce, say, a 23:23:30 grade and another is to produce high N/P_2O_5 ratio material, e.g. 27.4:13.7:0, then it is possible to consider freezing out calcium nitrate from the lower N/P_2O_5 stream and transferring this to the stream making high N/P_2O_5 products. The calcium nitrate so removed and transferred need not be washed with nitric acid and this is a distinct advantage over a straight freeze-out process. Here, freeze-out is being employed only as a control over N/P_2O_5 ratio. Water soluble P_2O_5 content is under the independent control of ammonium sulfate addition.

The ratio of high and low N/P_2O_5 fertilizers from streams 1 and 2 (etc.) can be modified by incorporating other schemes such as internal phosphoric acid recycle.

Again the overall N/P_2O_5 ratio of a factory complex based on NP/ASU will be lower than the corresponding freeze-out type complex. This leaves a greater ammonia surplus for urea production and gives greater flexibility of operation and storage in the straight N-fertilizers sections of the overall complex.

Phosphate recycle

The basic reactions given for nitric acid acidulation and subsequent ammoniation indicate that the question of water-soluble P_2O_5 in the final NPK fertilizer is bound up with the removal of calcium nitrate formed in the acidulation

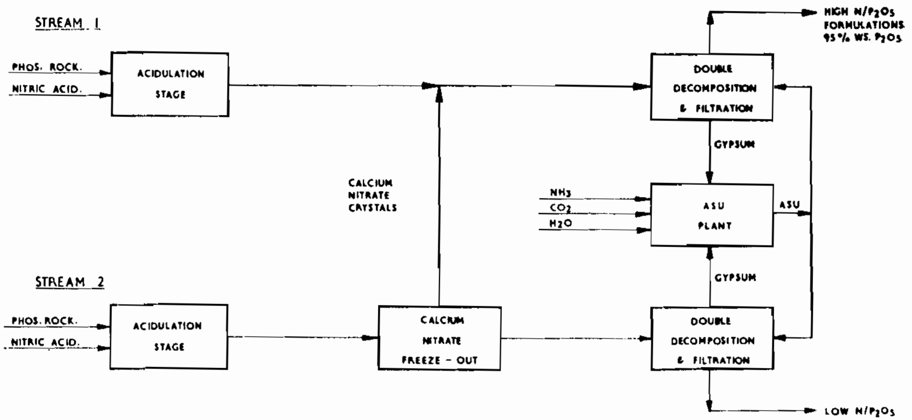

FIG. 3

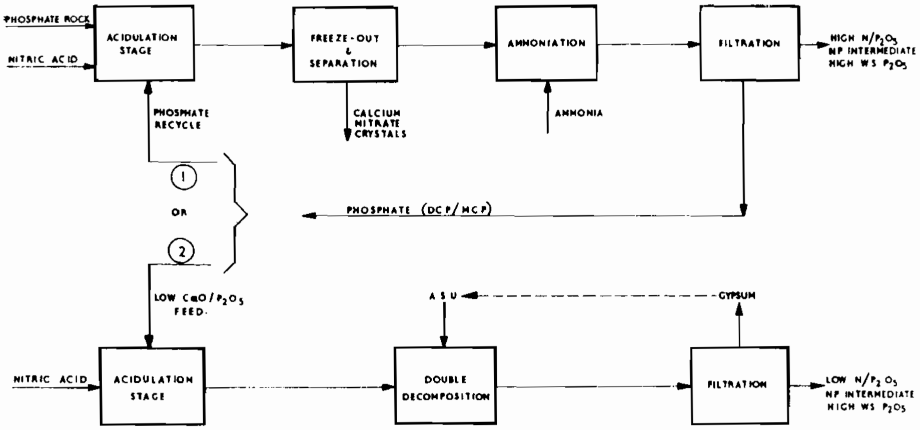

FIG. 4

stage. The amount of calcium nitrate so formed is governed by the CaO/P_2O_5 ratio of the rock feed. If there is a reduction in the latter ratio this will lead to a reduction in the N/P_2O_5 ratio of the final product.

Two possible process operations (see Figure 4) have been followed up on bench scale by Power-Gas and appear to be very promising. The basis is:—

a) Nitric acid attack on phosphate rock.
b) Calcium nitrate freeze-out and removal.
c) Ammoniation of the intermediate NP. Residual calcium nitrate is reacted with phosphoric acid to produce calcium phosphates (dicalcium phosphate and monocalcium phosphate).
d) Filtration of the dicalcium phosphate / monocalcium phosphate precipitates. The precipitates can be recycled or fed to a second stream making low N/P_2O_5 products. All the NPK's from these two alternative operations can be high water soluble P_2O_5 products.

Reducing the CaO/P_2O_5 ratio of the feed to the process

One way of reducing the CaO/P_2O_5 of the "rock" feed has been dealt with. Another possibility is to start from monocalcium phosphate.

The basic reactions using monocalcium phosphate[18] feed are:

$$\begin{aligned} Ca(H_2PO_4)_2 + 2HNO_3 &\longrightarrow Ca(NO_3)_2 + 2H_3PO_4 \\ Ca(NO_3)_2 + (NH_4)_2SO_4 &\longrightarrow CaSO_4 \downarrow + 2NH_4NO_3 \end{aligned}$$

Ammoniation can now yield $2NH_4H_2PO_4 + 2NH_4NO_3$. The N/P_2O_5 ratio is now about 0.6 at 100% water soluble P_2O_5.

The reaction between reagent grade monocalcium phosphate and ASU solution with the direct production of MAP has proved possible in the laboratory.

$$Ca(H_2PO_4)_2 + (NH_4)_2SO_4 \xrightarrow{\text{aqua}} CaSO_4 \cdot 2H_2O + 2NH_4H_2PO_4$$

The use of commercial grade TSP has been found unsatisfactory because the gypsum formed is difficult to separate by filtration.

Gypsum washing with ammonium sulphate

There is no novelty[13] in the suggestion that ammonium sulfate solution be used to wash the gypsum formed in the NP/ASU plant. Since the need to use wash water on the tilting fan filter can be done away with by using ASU washing, there is a reduction in the steam requirements of the NP evaporation/concentration section.

All the sulfate solution fed to the double composition section of the plant can, if desired, be used for gypsum washing and thus the present need (cf wet phosphoric acid manufacture) to find a compromise between wash water requirements, P_2O_5 efficiency, and steam consumption is avoided.

The ASU solution adhering to the gypsum crystals may be regarded as an inert in the Merseberg reaction since it is precisely this solution which is being made in the OSAG/FACT plant. Thus, in effect, the by-product gypsum is "dry". The strength of the sulfate solution from the existing plant is 38–41% w/w. Its strength is governed by the 20–25% water in the gypsum filter cake. If "dry" gypsum is used, then 44–45% w/w ASU solution can be made with the limit being set by ammonium sulfate solubility in water and the risks arising from crystal deposition in the plant. The need to make 52–54% weight ammonium carbonate solution in the OSAG/FACT plant is also removed and leads to the adoption of a cheaper carbonation system. Obviously the steam savings arising from this system are dependent on the product formulation but they can be about 20%.

Prilling or granulation of the NP/NPK products?

At the production rate of about 1,000 tons per day of NP or NPK, the capital cost of a prilling plant is approximately 20% cheaper than a corresponding granulation plant. It also offers lower power consumption and greater heat efficiency in product drying, therefore reducing operating costs.

Another major advantage of the prilling plant is its simplicity of operation, combined with minimum dust production, and the use of very low recycle rates (about 0.05:1 as opposed to 3:1 for a conventional granulation plant).

The prilling process does suffer from limitations arising from N/P_2O_5, N/K_2O, P_2O_5/K_2O and water soluble P_2O_5/citrate soluble P_2O_5 ratios. This is because of the high viscosities which can be encountered.

For an NP product the lower limit for N/P_2O_5 ratio is about 0.6.

Co-production of straight N-fertilizers

If an NP/ASU plant is to be installed, depending upon the availability of ammonia and carbon dioxide, it is possible to consider using natural gypsum or by-product gypsum to make ammonium sulfate (21:0:0) a saleable straight N-fertilizer.

The cost of increasing the size

of the ammonium sulfate recycle plant to produce, say, an extra 500 tons per day of saleable ammonium sulfate would only be around US $1 million turnkey-battery limits. Of course, the additional capacity would be "free" from labor costs. In the context of a complex one could almost regard an ASU plant as an effluent treatment unit as it converts by-product gypsum into the more easily disposable chalk effluent. This results in a 40% tonnage handling saving.

Should ammonium sulfate be of too low analysis then ammonium nitrate can be added to produce ammonium sulfate nitrate (26:0:0). Considerable tonnages of ammonium sulfate nitrate are currently being produced in Europe.

One interesting possibility for the disposal of by-product chalk is its conversion into foam concrete.[16] A large size trial plant for the production of foam concrete has been in operation for some time at Koennern K.G. of Bernburg in E. Germany. Foam concrete is a very light building material and is a good thermal insulator. The concrete is based on quartz and chalk (from sodium carbonate manufacture) and cement with gasifying additives. The material is claimed to have high resistance to compression and to be easily drilled, nailed or sawn. Building panels measuring 20′ x 5′ are being produced.

The use of ammonium sulfate in conventional phosphoric acid plants

In Europe, up to 15% of the sulfate ions of sulfuric acid have been replaced by using ASU liquor in wet phosphoric acid plants where the P_2O_5 production is immediately to be converted to NP/NPK, MAP or DAP.

"Conventional"

$$(3.5\ CaO) \cdot P_2O_5 + 3.5H_2SO4. \\ \text{aqua} \downarrow \\ 3.5\ CaSO_4 \cdot 2H_2O + 2H_3PO_4.$$

"Ammonium sulfate addition"

$$(3.5\ CaO) \cdot P_2O_5 + 2.975\ H_2SO_4 + 0.525\ (NH_4)_2SO_4 \\ \downarrow \text{aqua} \\ 3.5\ CaSO_4 \cdot 2H_2O + 1.05\ NH_4H_2PO_4 + 0.95\ H_3PO_4$$

In a 1,000 TPY P_2O_5 wet phosphoric acid plant, the use of ammonium sulfate can save approximately 14,000 tons of sulfur, or over $0.5 million per year. That is $5/ton of P_2O_5. The corresponding ammonium sulfate capacity to be installed would be around 180–190 tons/day.

Centrifuges versus filters

As stated previously, the NP/ASU process has not been put into commercial operation as a single entity, although both halves of the overall process have been in full scale operation for some time now.

Integration of the two halves does raise afresh the question of centrifuges versus filters. While it seems probable that the first plants will be based on gypsum removal by tilting pan filters, one can anticipate a case being made in favor of centrifuges on the grounds of lower costs, both capital-and operational-wise.

Centrifuges could be incorporated as illustrated in Fig. 5.

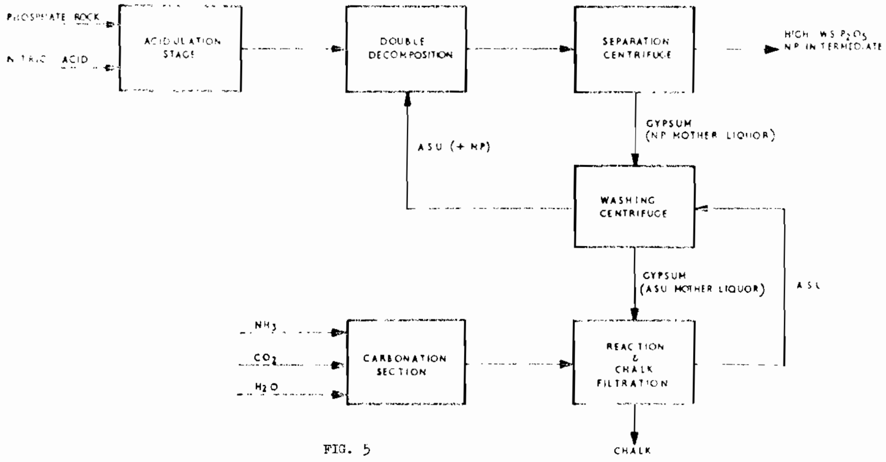

FIG. 5

Conclusions

Excluding the common ammonia and nitric acid facilities an NP/ASU plant will cost 15–20% less on a turn-key, battery limits basis than a sulfur based conventional plant.

With sulfur costing US $40 per ton, a 60,000 tons/year, 90–95% water soluble P_2O_5 factory, saves over US $2 million per year in terms of sulfur alone. P_2O_5 can be produced at least $25–30 per ton cheaper than in a sulfuric acid base conventional plant at this sulfur cost.

The product NP/NPK fertilizers readily substitute for a great many present day products, with regard to high analysis and high water soluble P_2O_5 content. Both high and low water-soluble P_2O_5 NP/NPK compound fertilizers can be produced, the water solubility being under simple control. Without the use of sulfur, sulfuric acid or phosphoric acid (and without the co-production of unwanted straight N-fertilizers) N / P_2O_5 ratios 1.35 can be achieved. Again with no separate straight N-fertilizer production N/P_2O_5 ratios of 1.0 are possible, consuming only a quarter or one third of the sulfur required by a conventional plant. In a two-train plant, NP/NPK products with N/P_2O_5 ratios of 1 and say 2, can be produced without the co-production of an N-fertilizer and without directly using sulfur or sulfur derivatives.

This type of plant is also able to process low grade phosphate rocks, e.g. 25% P_2O_5 with high CaO (P_2O_5).

The NP/ASU plant will operate continuously for over 335 days per year. This allows close integration with the ammonia and nitric acid facilities while at the same time minimising intermediate storage requirements. It will also utilize a substantial amount of already installed equipment in a conventional sulfuric acid based factory complex, i.e. plant conversion to NP/ASU may be possible depending on individual circumstances. Where wet phosphoric acid plant is installed the ASU plant will, of course, provide a disposal unit for noxious by-product gypsum effluent.

If the ammonium sulfate sec-

Table 9
Phos. Acid Recycle

NP Production—Consumption Data Per Ton of 95% Solution		
N/P_2O_5 Ratio		1.48
ws P_2O_5	% w/w	92
N	% w/w	24.2
P_2O_5	% w/w	16.4
Moisture	% w/w	5.0
Phosphate Rock—	Florida	B (see Table 2)
	Ton	0.510
Nitric Acid (57% w/w)	Ton	0.825
Ammonia (100%)	Ton	0.021
ASU Solution (38% w/w)	Ton	1.446
Steam (200 psig)	Ton	1.780
Steam (30 psig)	Ton	0.026
Power	KWH	30

tion is enlarged it will provide a relatively cheap gypsum to ammonium sulfate facility to make straight N-fertilizers such as 21:0:0 or 26:0:0. A small increase in the capacity of the ammonium sulfate section can enable up to 15% of the sulfuric acid requirement of an adjacent wet phosphoric acid plant to be saved, the saving being effected by substitution of ammonium sulfate.

There have been criticisms of the NP/ASU process such as high capital cost but it is hoped that the table of capital costs included in this paper negates this. It is hoped this paper shows a way round the problem of high N/P_2O_5 ratio without at the same time inundating the market with straight N-fertilizers.

The problem of high steam consumption cannot be avoided even with ammonium sulfate washing.

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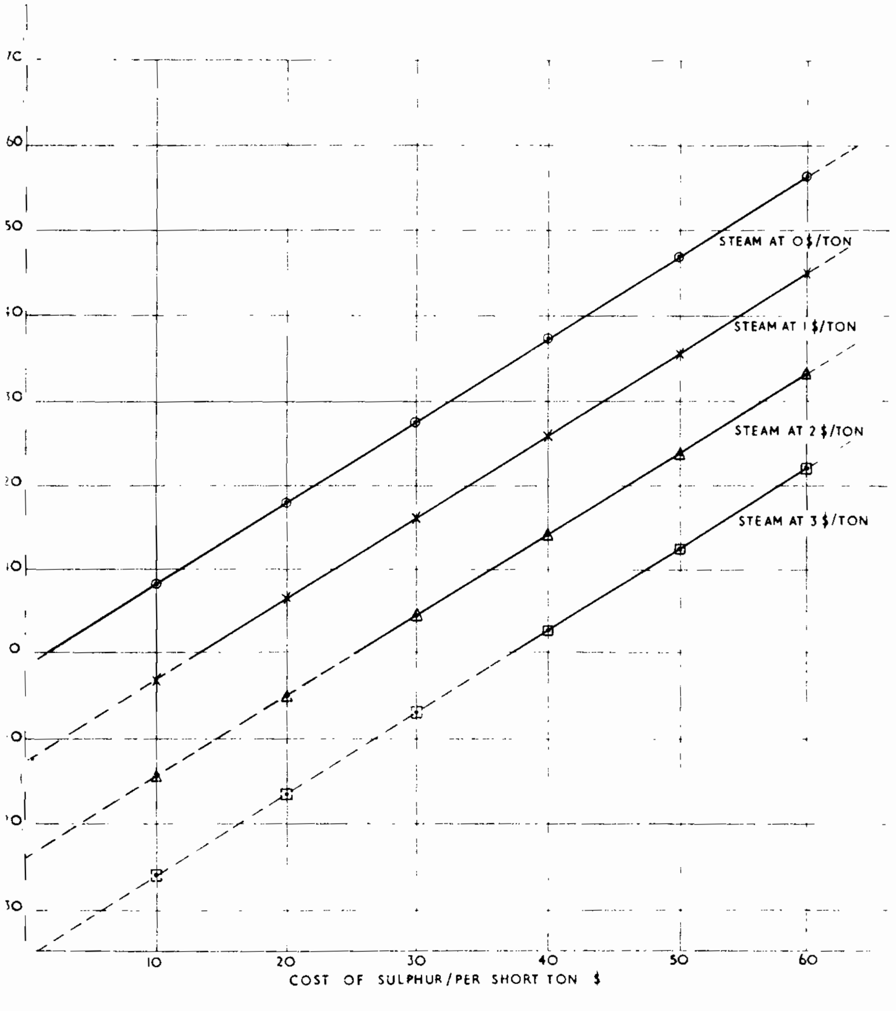

FIG 6 PRODUCTION COST SAVINGS – NP/ASU PROCESS

MODERATOR HECK: Thank you Mr. Dumain. I shall now turn the meeting back to Chairman SAUCHELLI.

CHAIRMAN SAUCHELLI: Thank you Bob. Our next paper, a continuation of the general discussion on nitrophosphates, will be discussed by Samuel Strelzoff, Senior Vice President and George Dell, Senior Process Engineer, Chemical Construction Co. At last year's meeting Mr. Strelzoff extolled the advantages of nitric acid for making phosphate fertilizers and predicted that it would become a very challenging competitor of sulphuric acid for this purpose.

At the July meeting of the American Institute of Chemical Engineers he presented a detailed evaluation of the various processes for making nitrophosphates. It was an excellent study.

He has had more than 42 years of experience in chemical engineering, process plant research, design, construction and operation. Before joining Chemco he held an executive position with Defense Industries, Limited of Quebec, Canada, and Societe Belge de l'Azote, Liege, Belgium.

Sam is a loyal booster of the Round Table and earnestly cooperative in making our annual meetings a success. He and George Dell will discuss the economics of nitrophosphate fertilizer materials.

Chemico Nitrophosphate Process

Samuel Strelzoff and George Dell

Mr. Chairman and Gentlemen;

The idea of using nitric acid instead of sulfuric acid for the digestion of natural phosphates is more than 100 years old. In 1868 Eben N. Horsford of Cambridge, Massachusetts obtained Letter Patent No. 75,271 dated March 10, 1868 which covered a process for treating rock phosphate with nitric acid. Moreover he proposed using sulfuric acid to remove the major part of the calcium as gypsum.

The commercialization of this idea had to wait for the creation of economical processes for the production of nitric acid: first by oxidation of atmospheric nitrogen in an electric arc furnace, begun in 1903 by E. Birkenland and S. Eyde in Norway, and then the Ostwald process of ammonia oxidation. The latter process was first used in a 3 T/D unit built near Bochum, Germany, in 1908. The Haber Bosch ammonia synthesis process which was put into operation at BASF's Oppau plant in Germany in 1913, yielded inexpensive ammonia and led to a dramatic expansion in the use of the Ostwald process. By the end of the first World War, large production facilities, using the ammonia oxidation process, were erected at Muscle Shoals, Alabama. These were designed and built during the war by Chemical Construction Corporation.

The radical reduction in the production cost of nitric acid produced by the ammonia oxidation process, as compared with the older process for the decomposition of Chilean saltpeter by sulfuric acid, became a strong stimulant for the idea of using nitric acid for the digestion of rock phosphate. However, as long as elemental sulfur was relatively low priced and available in sufficient amounts, the phosphate fertilizer industry utilized sulfuric acid for digestion of rock phosphate. This process, being relatively simpler than other technological processes involved, remained more economical.

The recently experienced sulfur shortage and its increased price, coinciding with the radical reduction of ammonia and nitric acid costs, have led to a revival of interest in the processes for the manufacture of nitrophosphates based on the use of nitric acid alone for the digestion of rock phosphate. Many papers have been presented at various scientific meetings in the U.S.A. and abroad, pointing out the economic advantages of these processes as compared with those based on the use of sulfuric acid.

Before describing, in some detail, Chemico's Nitrophosphate process and its economics, a brief historical development appears in order. A long list of patents have been issued in the U.S.A. as well as in Europe covering nitrophosphate production processes.

Without any claim of having established a complete list of these patents, it is interesting to note, as mentioned above, that a patent was issued in the U.S.A. to Eben N. Horsford of Cambridge, Massachusetts covering the digestion of rock phosphate in nitric acid. The amount of nitric acid proposed is sufficient to convert the calcium phosphate into calcium nitrate and monocalcium phosphate. Sulfuric acid is then added to precipitate calcium sulphate, leaving in solution monocalcium phosphate and an excess of nitric acid. The nitric acid is evaporated by heat. The monocalcium phosphate contains a small amount of sulfuric acid which is neutralized by lime, yielding a dry finished product.

U.S. Patent 872,757 filed January 3, 1906 by Johannes Schlutius, Karow, Germany describes a process for the digestion of rock phosphate in nitric acid solution expressed by the following equation:

$$Ca_3P_2O_8 + 4\ HNO_3 = CaH_4P_2O_8 + Ca\,(NO_3)_2$$

U.S. Patent 936,317 dated October 12, 1909 (appl. April 25, 1908) to B. F. Halvorsen of Norsk Hydro, Norway also describes a process for the digestion of rock phosphate in nitric acid expressed by the equation given in 1906 by Schlutius. Hot calcined calcium nitrate is added to the dissolved phosphate to ultimately form, after evaporation, a product containing 15% P_2O_5 and 11% N_2.

A number of other U.S. patents are listed in Appendix I.

BASF described the process for precipitation of calcium in the form of gypsum in its German patent application on December 16, 1926 (U.S. Patent 1,788,828, dated January 13, 1931). The process consists of the digestion of rock phosphate by a mixture of nitric acid with sulfuric acid or sulphates of ammonia and potassium. The precipitated gypsum is separated by filtration. The remaining solution is neutralized with ammonia and concentrated by evaporation. For a rock phosphate containing 30% P_2O_5, the final product components would be in a ratio of $1.0N:1.2P_2O_5:1.2K_2O$.

Very likely, the first commercial plant using only nitric acid for the digestion of rock phosphate was erected in Norway by the process patented by Erling B. Johnson of Odda Smelterverk, A. S. in Norway (Patent application in Norway dated October 27, 1928 and U. S. Patent 1,816,285 dated July 21, 1931). In this process, the calcium nitrate produced by the digestion of rock phosphate in the solution of nitric acid, as per the following general equation: $CaF_2 \cdot 3Ca_3(PO_4)_2 + 20HNO_3 = 10Ca(NO_3)_2 + 6H_3PO_4 + 2HF$, is crystallized out, in the presence of excess nitric acid by refrigeration of the acid solution. A long list of similar, processes for the digestion of rock phosphate in nitric acid has been described in patents and published literature. They all indicate that although the digestion of rock phosphate in nitric acid solution does not present any special problems, the separation of insoluble residual materials and the products are not easy operations. Nevertheless, plants using those processes have been operated in Norway, Germany, Netherlands, France, Finland, Sweden, the U.S.S.R. and others.

It can be pointed out that the users of the Odda process, in which a large part of calcium is separated in the form of calcium nitrate crystals, still face this serious problem of separation of residuals. At the ISMA (International Superphosphate Manufacturers Association) conference held in September 1968 in Brussels, papers were presented by Norsk-Hydro and Hoechst Uhde. Both described their versions of the Odda process. Both use some kind of settling device to separate the residuals from the digested solution. Norsk Hydro uses sand traps, a rather cumbersome piece of equipment requiring a great deal of labor. In addition, both processes indicate problems in proper control of crystallization of calcium nitrate. As a matter of fact, Norsk Hydro still uses batch type crystallizers followed by a vacuum filter.

Chemico's experience in the nitrophosphate field dates back 40 years, when a plant was put into operation in Belgium to manufacture dicalcium phosphate from rock phosphate and nitric acid. Various kinds of equipment for the separation of insoluble materials were tried, including filter presses, vacuum filters and centrifuges. None of this equipment could be adopted as a final solution to the problem. The addition of various standard flocculants also proved unsuccessful in removing the residuals. Finally, the problem was resolved by adding a small amount of sulfuric acid (about 10% of the total acid requirement) to the nitric acid digestion operation. The precipitated gypsum would form a filter cake retaining the residuals. This prevented the clogging of the filter cloth and, therefore, allowed the separation of the clear solution at a constant and acceptable rate.

The use of sulfate recycle technology eliminates the need for the separation of residuals. These materials are retained by gypsum and later on by calcium carbonate cake. The crystallization of gypsum does not require any artificial refrigeration as is the case for the Odda process. Besides Chemico's own demonstration, first made about 15 years ago in its pilot plant, TVA is now carrying out an extensive program with the identical process at a pilot plant handling about 500 pounds of rock phosphate per hour. At a demonstration visit in October 1968, about 500 visitors from the U.S.A. and foreign countries (more than 100 foreign visitors) were given the opportunity to witness the pilot plant operation. Excellent results were shown for the separation of gypsum, as well as for calcium carbonate cake produced by the reconversion of gypsum into ammonium sulfate solution.

In regard to the reconversion of the gypsum, it should be noted that millions of tons of ammonium sulfate were (and still are) produced by I.C.I. in England; ANIC in Italy (1500 MT/D plant designed and built by Chemico), the Sindri plant in India (1200 MT/D plant designed by Chemico); and the Gujarat plant in India (450 MT/D plant designed by Chemico), which operates on by-product gypsum from a phosphoric acid plant. For these plants Chemico uses the I.C.I. process with improvements initiated by its engineering staff.

In summation, it can be concluded that all the steps of Chemico's nitrophosphate process are now well established, providing a sound basis for the design of large industrial production units.

The Chemico process, using a much simpler technology, has bypassed operating problems indicated for the Odda process.

The Chemico process has a maximum flexibility in producing a great variety of formulations, all containing nearly 100% water soluble P_2O_5.

We shall now review in more detail the specific steps of several variants of the Chemico nitrophosphate process.

We find the name of the game we play to produce available and water soluble P_2O_5 in fertilizers really should be called "catch the calcium ion". Due to the physical chemistry of the calcium sulfate system, and the availability and inexpensiveness of sulfur in the past, sulfuric acid has served admirably to "catch" the calcium so it could be removed from the system.

Recently however, the creation of more economical processes for the manufacture of large amounts of ammonia and nitric acid, has resulted in the decreased cost of nitric acid — making it a strong competitor for sulfuric acid in the manufacture of fertilizers. The nitrogen of the nitric acid provides a potential source of plant food; and when potassium is added, nitric acid treatment of phosphate rock offers a source of compound nitrogen - phosphorus - potassium (N-P-K) fertilizers without any loss of nitrogen value.

The digestion of rock phosphate by nitric acid is idealized according to the following equation:

$$(1.)\quad CaF_2\ (Ca_3(PO_4)_2)_3 + 20\ HNO_3 = 10\ Ca(NO_3)_2 + 6\ H_3PO_4 + 2\ HF$$

Large amounts of calcium nitrate, produced by this reaction have been removed in crystal form by the Odda process and sold as such. The crystallization of calcium nitrate however, unlike gypsum, is not an easy process; and when separated, it is hygroscopic and hard to handle. In addition, its low nitrogen content (15.5–16% N_2) limits its ability to compete with ammonium nitrate and urea which have a much higher nitrogen content. Some of the present users of the Odda process are investigating various methods of disposing of calcium-nitrate since marketing it as a fertilizer has become very difficult in the international markets.

As mentioned previously, the resulting NP or NPK products from this Odda process have a relatively limited ratio of water soluble P_2O_5. This is the second reason why such nitrophosphate processes have not achieved widespread acceptance in the United States; the first, of course, being that sulfur prices have been relatively low. The European agricultural market, contrary to the practice in the United States, is not adverse to the use of phosphate fertilizers in which only half or less of P_2O_5 is water soluble.

In order to produce marketable fertilizers, the acidic solution resulting from dissolving the phosphate ore must be neutralized. This is done with ammonia, according to the idealized reactions:

(2.) $H_3PO_4 + NH_3 = NH_4\ H_2\ PO_4$

(3.) $H_3PO_4 + 2NH_3 = (NH_4)_2\ H\ PO_4$

(4.) $HNO_3 + NH_3 = NH_4\ NO_3$.

During such ammoniation, however, any calcium nitrate present causes secondary reactions, depending on the degree of ammoniation:

(5.) $H_3PO_4 + Ca\,(NO_3)_2 + 2NH_3 = 2NH_4NO_3 + CaHPO_4$

(6.) $2CaHPO_4 + Ca\,(NO_3)_2 + 2NH_3 = 2NH_4NO_3 + Ca_3\,(PO_4)_2$

(7.) $2HF + Ca\,(NO_3)_2 + 2NH_3 = 2NH_4NO_3 + CaF_2$

(8.) $3Ca_3\,(PO_4)_2 + CaF_2 = 3\,(Ca_3\,(PO_4)_2) \cdot CaF_2$

These four secondary reactions, known as reversion reactions occur in proportion to the amount of calcium nitrate and fluoride ion present in the reaction liquor. The danger of reversion is greatest when ammoniation is permitted to go beyond the requirements for the formation of dicalcium phosphate. Additional ammoniation will produce apatite, a chemically similar composition to the one in the natural phosphate.

Among the products of the neutralization reactions, monoammonium and diammonium phosphate are water-soluble; dicalcium phosphate is water-insoluble but citrate-soluble; tricalcium phosphate is water-insoluble and sparingly citrate-soluble; while apatite is insoluble both in water and neutral citrate solution. The amount of each product present determines the quality of the fertilizer. Water-soluble monocalcium phosphate may also be present in the reaction mixture during acidulation. However, it is usually converted to the water-insoluble dicalcium phosphate during ammoniation.

If the calcium could be totally removed from the digestion liquor, neutralization with ammonia would produce ammonium nitrate, monoammonium phosphate and diammonium phosphate. Of the last two, monoammonium phosphate is preferred, since it can be readily separated from the ammonium nitrate by crystallization in the Chemico process. For example: When a solution containing 55% ammonium nitrate and 21% monoammonium phosphate is cooled to 30°C., monoammonium phosphate will be crystallized in a relatively pure form, leaving only about 2% in the mother liquor. On the other hand, if a solution containing diammonium phosphate is cooled, the separation is not as sharp. Figure 1 is a block flow diagram of the complete Chemico sulfate recycle process.

The Chemico process starts with the digestion of phosphate rock with sufficient nitric acid to convert all the rock phosphate into phosphoric acid. Fifty to sixty percent nitric acid is used to control the water content of the slurry, which is then mixed with a (38-

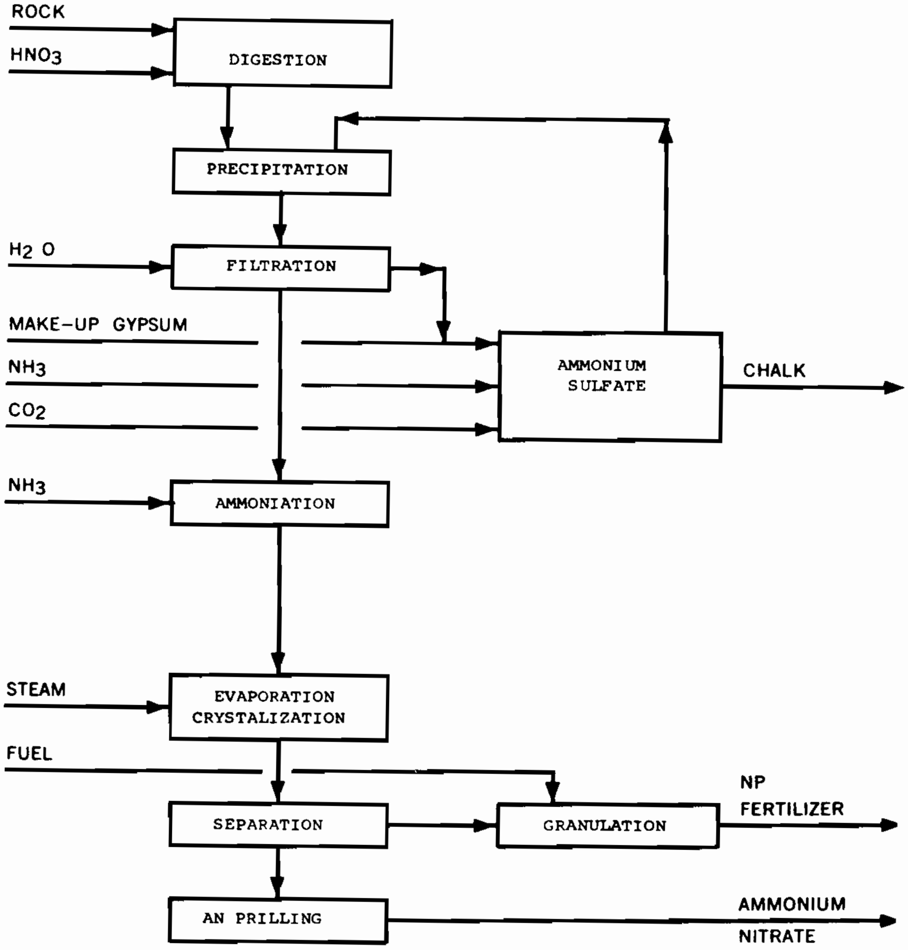

Figure 1
Chemico Sulfate Recycle Process

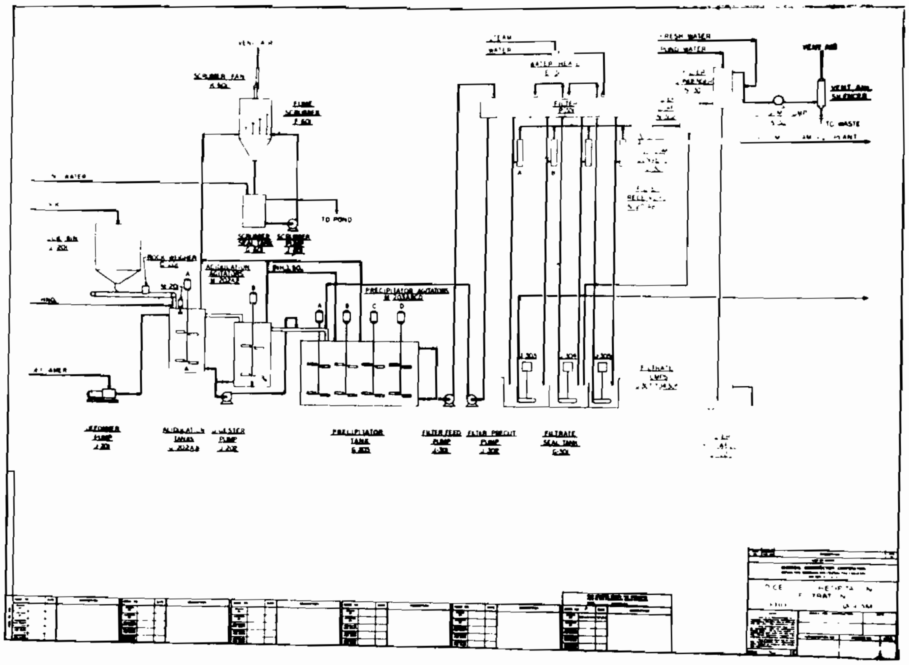

Figure 2
Digestion Precipitation Filtration Process Flow Diagram

40%) ammonium sulfate solution. The latter reacts with the calcium nitrate to produce calcium sulfate dihydrate (gypsum). The gypsum is separated from the mother liquor, which is principally phosphoric acid and ammonium nitrate with small amounts of iron, aluminum, magnesium, calcium, flourine as well as vanadium and rare-earth metals present in the phosphate ore. Figure 2 provides a more detailed process flow diagram for this part of the process.

The gypsum is washed free of phosphate and is sent to the ammonium sulfate plant where it is treated with ammonia and carbon dioxide; the gypsum is converted to ammonium sulfate and a calcium carbonate precipitate. When filtered from the liquor, the calcium carbonate can be dried and used as agricultural lime or mixed with ammonium nitrate to make nitro-chalk (ammonium nitrate-lime stone fertilizer having a 20 to 26-0-0 grade). Nitro-chalk fertilizers are extensively used in the European countries to increase the yield of forage crops on grazing land, but they have been of relatively little interest in this country. The purpose of limiting the nitrogen content to 20 to 26% as compared to pure ammonium nitrate with 34.5% nitrogen is to reduce the hygroscopic capacity and minimize the fire hazard of the product.

The ammonium sulfate liquor, having 38 to 40% concentration, is recycled to the precipitator where calcium, solubilized by the reaction of nitric acid with the phosphate rock, is removed. Since 95 to 98% of the gypsum is converted to ammonium sulfate and a small excess of ammonium sulfate is required for complete precipitation of the calcium, a cheap source of make up gypsum or ammonium sulfate is required.

Figure 3 is a process flow diagram of the concentration crystallization step. Here the mother liquor product of the gypsum separation is ammoniated to a pH of about 3.5 for the conversion of the phosphoric acid to monoammonium phosphate.

The solution which now contains about 58% water must first be concentrated to 20% water and fed to a vacuum crystallizer. With proper design, the monoammonium phosphate is produced as crystals that are easily separated from the ammonium nitrate, as shown in Figure 4.

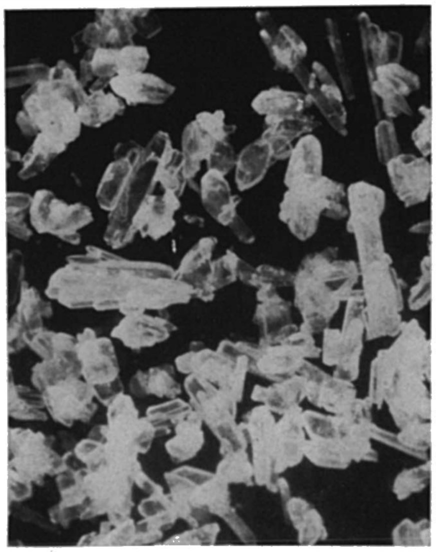

Figure 4
Monoammonium Phosphate crystallized from Ammonium Nitrate Solution. Magnification 70X.

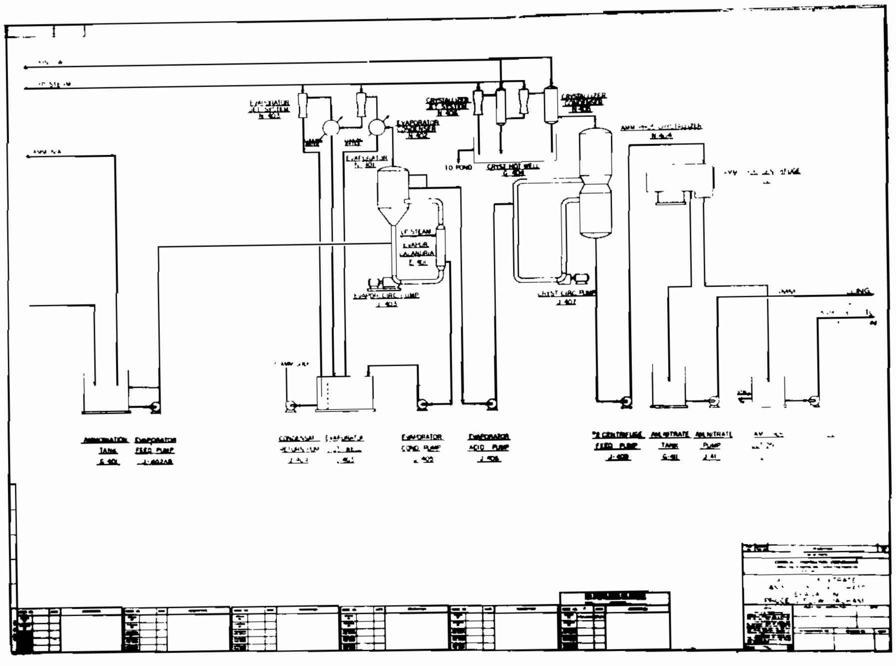

Figure 3
Ammonium Nitrate Ammonium Phosphate Separation Process Flow Diagram

Table 1
System $NH_4H_2PO_4$—NH_4NO_3—H_2O

Liquid Phase, Weight %			
$NH_4H_2PO_4$	NH_4NO_3	H_2O	Solid Phase
		Isotherm 70°C	
51,0	0	49,0	$NH_4H_2PO_4$
15,2	30,4	54,5	
12,5	37,5	50,5	
2,89	68,0	29,1	
1,6	82	16,4	$NH_4H_2PO_4 + NH_4NO_3$
0	83,3	16,3	NH_4NO_3
		Isotherm 80°C	
54,8	0	45,2	$NH_4H_2PO_4$
16,7	33	50,0	
13,6	41,9	45,5	
3,8	67,3	28,9	
2,0	84,2	13,8	$NH_4H_2PO_4 + NH_4NO_3$
0	86,2	13,8	NH_4NO_3
		Isotherm 90°C	
59,6	0	40,4	$NH_4H_2PO_4$
25,7	25,8	48,5	
18,1	37,4	45,5	
14,5	43,5	42,0	
5,0	66,5	28,5	
2,5	87,0	10,5	$NH_4H_2PO_4 + NH_4NO_3$
0	88,9	11,1	NH_4NO_3
		Isotherm 95°C	
61,6	0	38,4	$NH_4H_2PO_4$
27,0	87,1	10,2	$NH_4H_2PO_4 + NH_4NO_3$
0	89,8	10,2	NH_4NO_3
		Isotherm 100°C	
63,5	0	36,5	$NH_4H_2PO_4$
28,5	28,5	43,0	
19,8	39,7	40,5	
15,7	47,1	37,2	
6,5	66,2	27,3	
3,3	88,5	8,2	$NH_4H_2PO_4 + NH_4NO_3$
0	91,0	9,0	NH_4NO_3
		Isotherm 110°C	
68,3	0	31,7	$NH_4H_2PO_4$
31,2	31,3	37,5	
21,3	42,7	36,0	
16,9	50,6	32,5	
8,9	63,8	27,3	
3,98	89,82	6,2	$NH_4H_2PO_4 + NH_4NO_3$
0	93,0	7,0	NH_4NO_3
		Isotherm 130°C	
80,0	0	20,0	$NH_4H_2PO_4$
6,05	90,41	3,54	$NH_4H_2PO_4 + NH_4NO_3$
0	98,5	1,5	NH_4NO_3

The sharpness of the separation is indicated by data published in the U.S.S.R.* An essential part of which is reproduced here in Table 1 and Table 2. An overall phase diagram for the system is shown in Figure 5.

The MAP crystals are readily redissolved and fed to a standard TVA drum granulator or a blunger. To produce about a 14-42-0 fertilizer with over 90% of the P_2O_5 water soluble and essentially 100% citrate soluble. The ammonium nitrate solution is concentrated and prilled for use as fertilizer.

The granular fertilizer produced if ammonium nitrate is not separated would be about 28-14-0 varying somewhat with the phosphate rock used as raw material.

Using Florida float concentrate phosphate rock with 33.6% P_2O_5 and 48% CaO we would obtain 1.8 to 2 tons of ammonium nitrate per ton of 14-42-0 fertilizer.

By blending all or part of the ammonium nitrate into a granulator solids stream we have a flexibility to make for example a 1-3-0, 1-1-0, or 2-1-0 NPK fertilizer according to the agronomic requirements of our customers.

Figure 6 is an Economic Production Analysis that compares the cost of producing one ton of P_2O_5 and 1.73 tons of nitrogen as fertilizer by three routes.

The Chemico Process, DAP plus ammonium nitrate and phosphonitric mixed acid plus ammonium nitrate were the routes selected for this comparison.

Sulfur cost was varied from $30 to $55 per long ton and ammonia from $20 to $35 per short ton while the rock phosphate cost was held constant for this study.

Utilities, operating labor, maintenance, depreciation of capital invested, taxes, and insurance were included for each of the plants involved for the three routes. You will note that the cost of producing equal amounts of plant nutrient by the Chemico process and the DAP plus ammonium nitrate routes are the same when sulfur price is $32 per long ton or more. For the mixed acid phosphonitric route, the break even point is considerably high. Also you will note that variations in ammonia cost only reflect changes in total product cost, while variations of sulfur cost reflect increased advantage for the Chemico process.

Besides the sulfate recycle system which we have just described, Chemico has developed and laboratory tested a number of processes based on partial neutralization of the liquor produced by reacting phosphate rock with nitric acid and ammonia to precipitate a calcium phosphate. Figure 7 shows the basic process as a block flow diagram. By making a separation of the partially neutralized solu-

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* F. G. Margolis and T. V. Glasova. Published on behalf of Academy of Sciences USSR Publications, Moscow 1966 by "Science"—Moscow.

Table 2
System NH_4NO_3—$NH_4H_2PO_4$—H_2O

Liquid Phase						
Weight %			Moles/100 Moles			
NH_4NO_3	$NH_4H_2PO_4$	H_2O	NH_4NO_3	$NH_4H_2PO_4$	H_2O	Solid Phase
			Isotherm —10°C			
27,2	0,0	72,8	100	0,0	1188,5	Ice
22,0	5,5	72,5	85,1	14,9	1245,8	Ice + $NH_4H_2PO_4$
28,8	3,8	67,4	91,6	8,4	951,9	
38,9	2,4	58,7	95,9	4,1	642,6	$NH_4H_2PO_4$
45,0	2,0	53,0	97,1	2,9	507,2	
45,6	1,8	52,6	97,3	2,7	498,3	NH_4NO_3 + $NH_4H_2PO_4$
47,0	0,0	53,0	100,0	0,0	501,2	NH_4NO_3
			Isotherm 0°C			
0,0	18,4	81,6	0,0	100,0	2830,6	$NH_4H_2PO_4$
8,8	12,4	78,8	50,5	49,5	1986,4	
18,3	8,2	73,5	76,3	23,9	1360,0	
28,6	4,8	66,6	89,5	10,5	926,6	
38,7	3,1	58,2	94,7	5,3	633,6	
44,9	2,4	52,7	96,4	3,6	502,6	
49,0	1,9	49,1	97,5	2,5	433,9	
51,2	1,5	47,3	98,0	2,0	402,0	NH_4NO_3 + $NH_4H_2PO_4$
53,6	0,0	46,4	100,0	0,0	384,5	NH_4NO_3
			Isotherm 10°C			
0,0	21,4	78,6	0,0	100,0	2345,7	$NH_4H_2PO_4$
8,4	15,5	76,1	43,75	56,25	1760,0	
18,4	10,0	72,0	72,1	27,9	1280,8	
23,5	7,7	68,8	81,4	18,6	1057,9	
28,1	6,2	65,7	86,7	13,3	890,9	
38,2	4,1	57,7	93,0	7,0	624,4	
44,6	3,0	52,4	95,5	4,5	498,8	
48,8	2,2	49,0	97,0	3,0	432,4	
54,1	1,6	44,3	98,0	2,0	356,4	
58,0	1,2	40,8	98,6	1,4	308,2	NH_4NO_3 + $NH_4H_2PO_4$
59,6	0,0	40,4	100,0	0,0	301,6	NH_4NO_3
			Isotherm 20°C			
0,0	25,5	74,5	0,0	100,0	1862,7	$NH_4H_2PO_4$
8,1	18,8	73,1	38,3	61,7	1536,7	
17,5	12,2	70,3	67,4	32,6	1200,6	
27,6	8,1	64,3	83,4	16,9	860,0	
30,5	7,0	62,5	86,2	13,8	783,1	
37,9	5,1	57,0	91,5	8,5	612,0	
44,3	3,7	52,0	94,5	5,5	493,3	
48,6	2,8	48,6	96,2	3,8	427,6	
53,8	2,2	44,0	97,2	2,8	353,4	
59,0	1,6	39,4	98,1	1,9	291,2	
64,0	1,2	34,8	98,8	1,2	238,8	NH_4NO_3 + $NH_4H_2PO_4$
65,1	0,0	34,9	100,0	0,0	238,3	NH_4NO_3
			Isotherm 30°C			
0,0	30,2	69,8	0,0	100,0	1478,6	$NH_4H_2PO_4$
7,8	22,7	69,5	33,0	67,0	1312,2	
16,9	15,1	68,0	61,7	38,3	1103,5	
26,9	10,3	62,8	79,1	20,9	820,2	
37,5	6,2	56,3	89,7	10,3	598,7	
43,9	4,5	51,6	93,4	6,6	487,9	
48,2	3,5	48,3	95,2	4,8	424,2	
53,5	2,7	43,8	96,7	3,3	351,8	
58,8	2,0	39,2	97,7	2,3	289,7	
68,7	1,2	30,1	98,8	1,2	192,5	NH_4NO_3 + $NH_4H_2PO_4$
69,7	0,0	30,3	100,0	0,0	193,1	NH_4NO_3

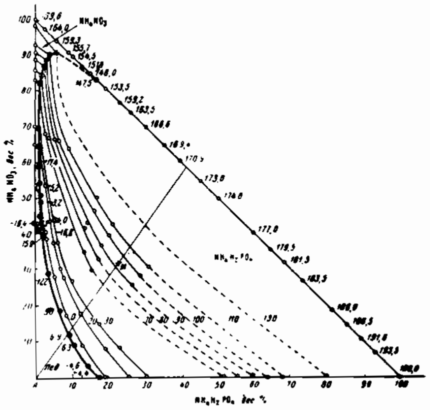


Figure 5

Politherma of the system.
$NH_4H_2PO_4$—NH_4—NH_4NO_3—H_2O
The figures indicated on curves and points.
Temperature in °C.

tion, an appreciable amount of the calcium is removed as calcium nitrate with very little P_2O_5 remaining in the filtrate. The cake is redissolved with nitric acid and the remaining calcium removed as gypsum by adding ammonium sulfate. This reduces the amount of ammonium sulfate required and thus the amount of gypsum to be converted. The second filtrate can then be ammoniated and granulated to yield a 23-23-0 fertilizer. However, since ammoniation will be to a pH of about 4, the impurities including iron, aluminum etc., will precipitate reducing the precipitation rate of the dicalcium phosphate.

To overcome this problem, Figure 8 shows a dual precipitation arrangement of the basic process. You will note, though, the introduction of additional neutralization and filtration steps increases capital investment and operating requirements.

There are numerous other variations of this basic principle that we have investigated. Figure 9 shows one in which the iron and aluminum are removed before the dicalcium phosphate is precipitated. The iron, aluminum and other impurities are treated separately before being recombined with the main phosphate stream. Under certain circumstances this variation of the basic process could have definite advantages and be economically attractive.

We have noticed that according to the recent inquiries we have received, there is a definite trend by fertilizer manufacturers abroad

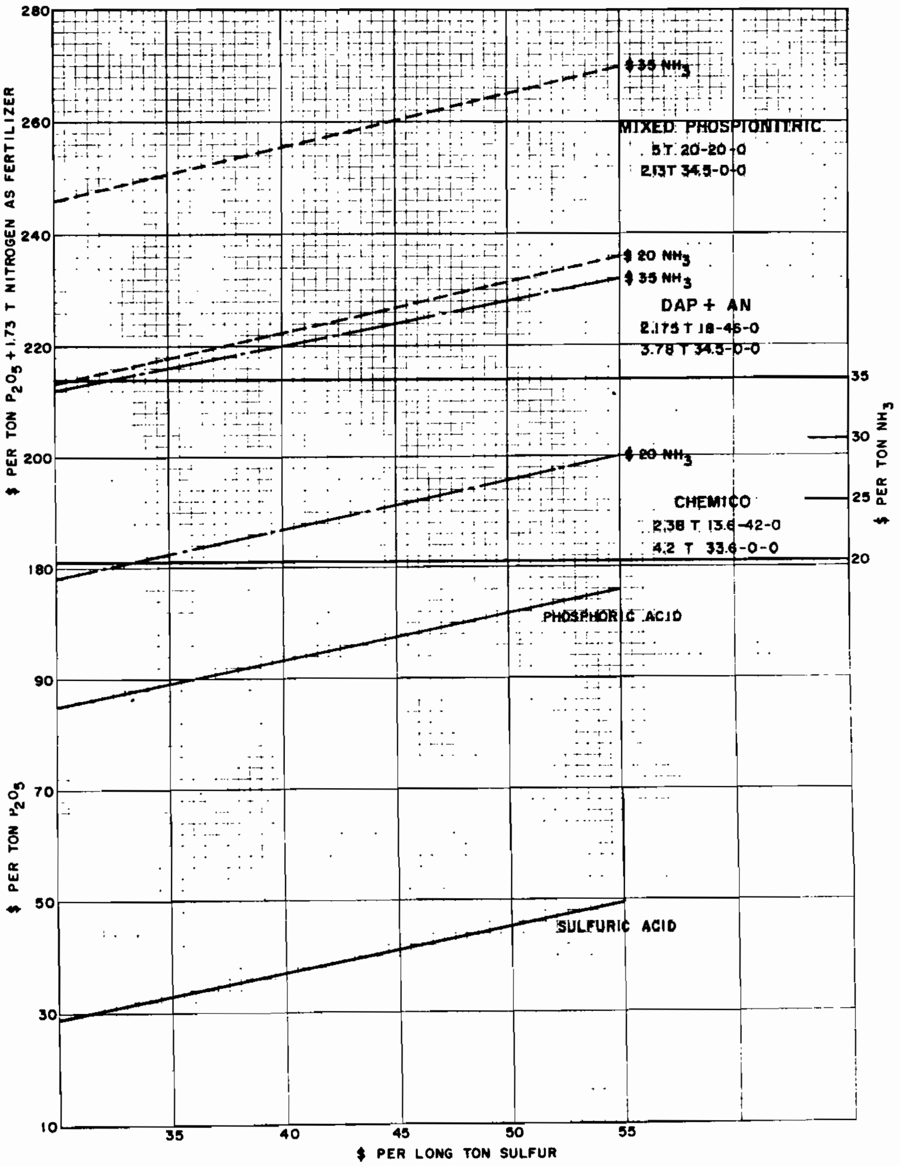


Figure 6
Economic Production Analysis

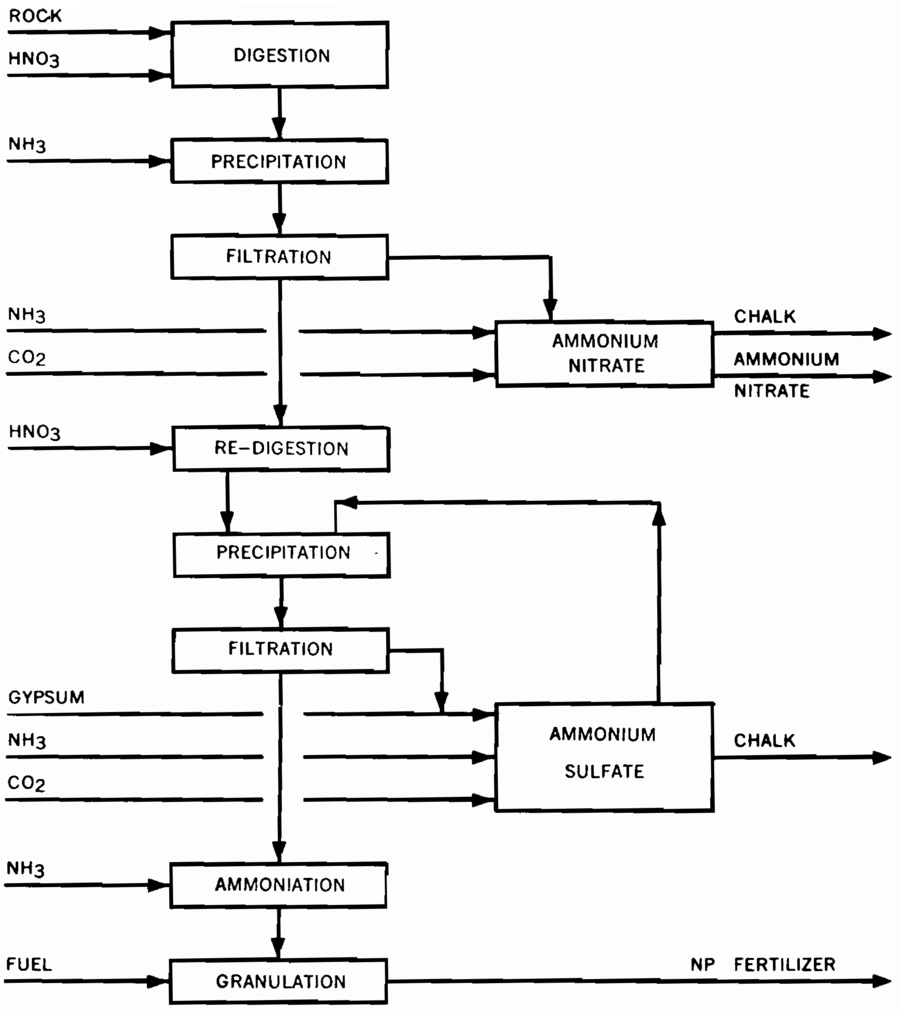


Figure 7
Chemico Dicalcium Phosphate Precipitation Process No. 1

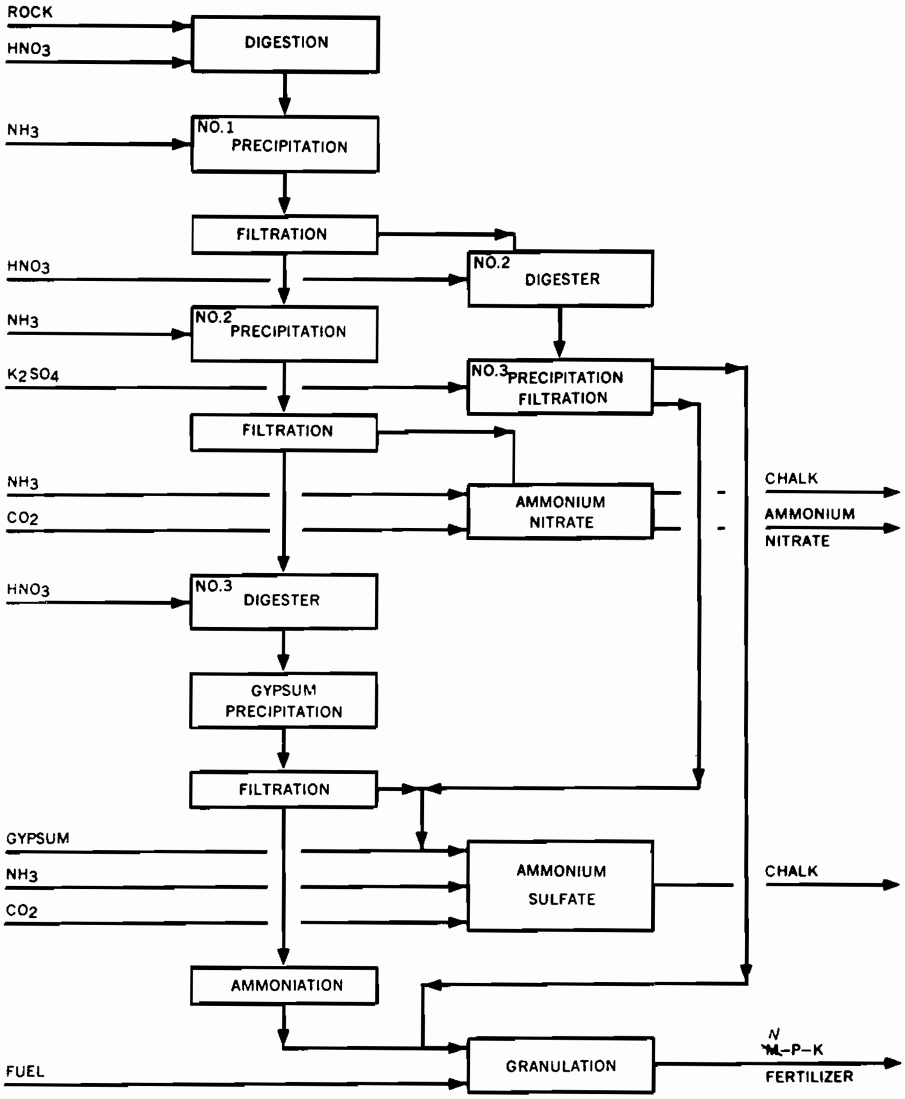


Figure 8
Chemico Dicalcum Phosphate Precipitation Process No. 2

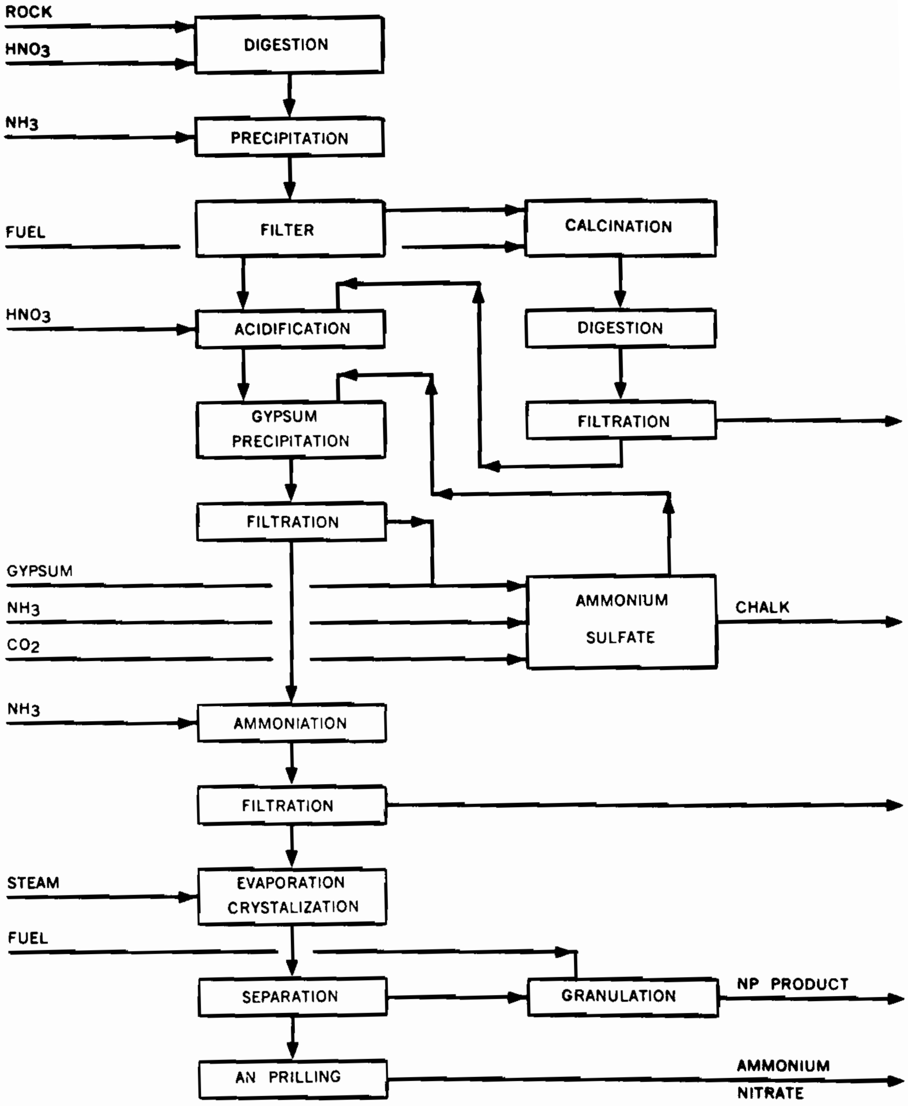


Figure 9
Chemico Dicalcium Phosphate Precipitation Process No. 3

to produce higher and higher water soluble products. It is our feeling that this trend will continue to the point where high water soluble P_2O_5 in the fertilizer will be required by farmers on a worldwide basis not just the United States and Great Britain.

We fully believe that our processes have been sufficiently demonstrated technically and provide a positive technique of catching the calcium ion so that high water soluble phosphate fertilizers will be available to meet the requirements of agriculture.

As a result of the work done by TVA and ourselves, we are satisfied that we have proven the Chemico process to be an economically and technically sound route for making high water soluble P_2O_5 ratio within wide limits. We are now in a position to design and build such plants and guarantee their performance.

As we have had the good fortune of being able to work very closely with Mr. Hignett, Mr. Meline and many others at TVA on many of our studies, we would like to express our sincere thanks to them for sharing their experience with us.

Appendix I.

United States Patents

75,271	Horsford	March 10, 1868
872,757	Schlutius	January 3, 1906
436,317	Halvorsen (Norsk Hydro)	October 12, 1909
982,466	Blackmore	January 24, 1911
1,011,909	Bretteville	December 19, 1911
1,023,133	De Jahn	April 16, 1912
1,057,876	Samuel Peacock	April 1, 1913
1,058,145	Braun	April 8, 1913
1,292,293	Toss	January 21, 1919
1,788,828	BASF	January 13, 1931
1,816,285	Odda	July 21, 1931
2,013,970	Moore	Sept. 10, 1935
2,312,047	Ogburn	Feb. 23, 1943
2,683,075	Caldevele	July 6, 1954
2,689,175	Strelzoff	Sept. 14, 1954
2,728,635	Miller	Dec. 27, 1955
2,753,252	Barnes	July 3, 1956
2,757,072	Kapp et al	July 31, 1956
2,759,795	Archer	August 21, 1956
2,767,045	McCullough	Oct. 16, 1956
2,857,245	Fallin	Oct. 21, 1958
3,049,416	Brown	August 14, 1962

This list cannot necessarily be considered as a complete record of all U.S.A. patents covering processes for the treatment of rock phosphate by nitric acid. We have not tried to assemble lists of patents issued in other countries.

CHAIRMAN SAUCHELLI: Thank you, Dr. Strelzoff and George Dell.

With your indulgence, we have one more paper by William A. Lutz. He promised that it wouldn't take more than 10 or 15 minutes.

He is President of the Weston Process Design. He was too late for getting on the printed program. Mr. Lutz is an experienced chemical engineer. He also co-authored a chapter in my Monograph. He has given his talk the provocative title, Nitric Phosphates—Fact, Fiction and Philosophy. Mr. Lutz please.

Nitric Phosphates Fact, Fiction and Philosophy

W. A. Lutz

Summary

It must be concluded that the historic objections to nitric phosphate fertilizers would be difficult to defend in light of recent practice and experience. Complex fertilizers being produced by this route in Europe are superior to the majority of equivalent compounds made in the United States with respect to total grade and water solubility. It is also highly probable that they are superior in some of the less tangible areas such as product quality, storage and handling characteristics. The opportunities for cost reduction appear to be excellent but detailed cost comparisons are necessary to firmly establish overall differences. A large potential market does exist for fertilizers which can be made using this type of process.

The selection of processes to be used in a new or modernized installation is a difficult and complex problem. Nitric phosphate processes do merit full consideration, along with other technical developments, in this progressive and expanding industry. As with most other developments, they do not represent a universal solution to all the problems in the industry. There does appear to be a place for them.

Nitric Phosphates

In the past few years increasing attention has been focused upon the nitric phosphate routes for making fertilizers. One of the major reasons has been a shortage of sulfur[1] and corresponding increases in sulfur prices, which must lead to consideration of processes using little or no sulfur, either directly or indirectly. Another factor is the advent of large ammonia plants which have resulted in price reductions on nitrogen, as well as policy modification in marketing and distribution.

Nitric phosphate plants have been in operation in Europe for over thirty years and an extensive experience background on these plants and their products is available. On the basis of this experience, the first American plant, which uses no sulfur either directly or indirectly, is now under construction for the Farmers Chemical Association at Tunis, North Carolina. The plant is being built under license by Norsk Hydro and is being constructed by Wellman-Lord, Incorporated. This plant will use a version of the

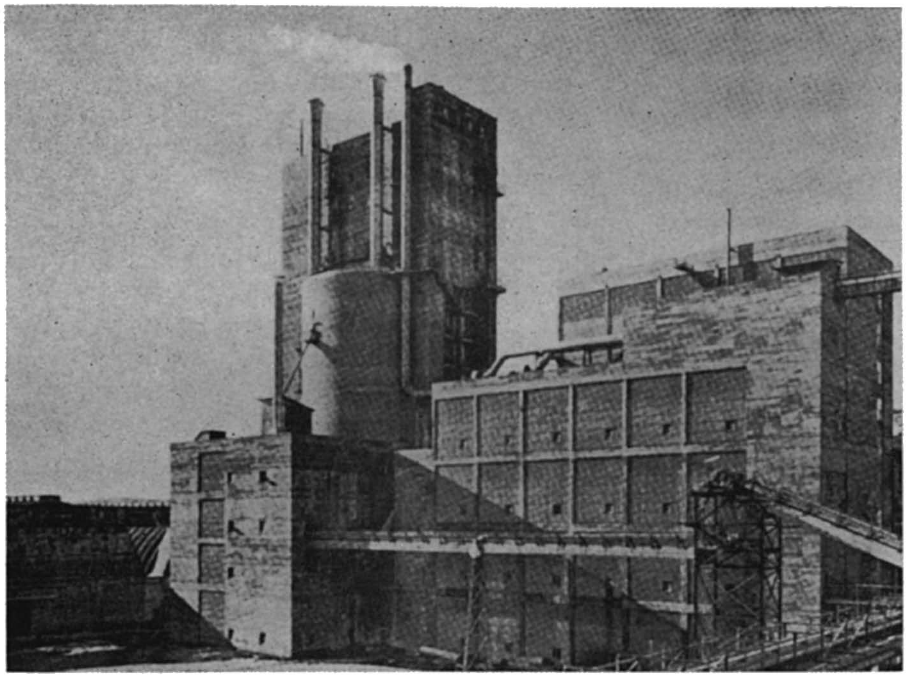


Figure I
Photograph of A Norsk Hydro Plant for Prilled NPK Fertilizers

Odda Process and will include two relatively recent improvements[2]:

1. Deep cooling which will permit product water solubility of approximately 85% without the use of sulfate additions, and
2. The use of prilling rather than granulation to produce fertilizers of superior physical characteristics.

Both of these improvements have been fully demonstrated in commercial operations in Norway. Figure I is a photograph of this installation.

In past years a number of objections have been voiced concerning nitric phosphates, either formally or informally. Among those most frequently heard are:

1. Low water solubility of P_2O_5 content.
2. Inflexible grade limitations and N/P_2O_5 ratios in products.
3. Poor physical and storage characteristics.
4. High product cost ultimately applied to fields.

The question then arises as to whether these processes fit into existing practice in the United States and in other parts of the world. Are these objections really firmly based in light of present experience? Do these processes require modification to make them acceptable? In what way do products from nitric phosphate processes differ from those being manufactured by existing processes and supplied to existing markets?

It is obvious that there are no all-inclusive answers to such questions. However, a brief look at existing practice can provide partial answers and perhaps provide some basis for a realistic, non-emotional appraisal.

Water Solubility

The original Odda Process patents described the means of attaining 90% water solubility. The plants that have been built utilizing calcium nitrate crystallization have generally been operated at a level of around 50% water solubility because this was considered to be satisfactory for Northern Europe. It is perhaps for this reason that the impression has arisen that Odda Process units cannot produce over 50% water solubility.

In most European countries 50% water solubility is considered to be acceptable, while Norway and Sweden require only 30%. It is of some interest to note that in England, where water solubility has been stressed more than in other countries, approximately 27% of the P_2O_5 consumed in 1965-66 was in water insoluble form.

Recent large scale commercial operations have demonstrated that processes of this type are capable of producing fertilizers wherein the water solubility is about 85%. Process modifications involving the use of sulfates[3] for calcium removal have been described by which water solubility can be increased to 90-95% and certain crystallization techniques[4] have been described by which essentially 100% water soluble can be produced. Increasing water solubility will inevitably carry with it some degree of increasing processing costs which can be determined only by detailed analyses of the particular process involved.

The required level of water solubility is a highly controversial subject[5] and there are no real standards established for the United States. Areas in the far west are requesting 90% while 40% has been suggested as a minimum for the Southeastern states. The general lack of standards and apparent lack of real interest by users for the whole subject can be inferred from the results of surveys which show the water solubility on a large number of samples of materials commercially marketed. This data is shown on Figure II.[10,11,12]

The most recent curve, which also shows the highest water solubility, shows that 53% of the samples were below 60% water solubility, while approximately 90% of the samples were below the level of 85% water solubility which can be obtained by deep freeze processing without the use of a supplementary step for calcium removal. Even 36% of the superphosphates which are con-

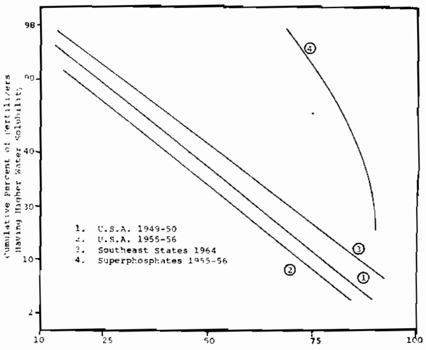


Figure II
Water Solubility of Mixed Fertilizers United States

sidered as highly water soluble are below this level.

Versions of the Odda Process, therefore, appear to be entirely capable of meeting the requirements for the majority of mixed fertilizers marketed in the United States. The level of water solubility in these products will approach those of DAP which will be, normally, in the range of 85-95%. Fertilizers made by processes involving ammoniation of superphosphates will normally be lower in water solubility than those attainable by the nitric phosphate route.

If it becomes the objective of the industry as a whole to upgrade the level of water solubility in fertilizers marketed in America, then it would seem logical to direct such effort toward those materials now on the low end of the scale. Some effort applied to eliminating those below 50% water solubility, which is considered by many authorities to be a reasonable minimum, could be more rewarding overall, than similar effort to produce minor improvements at the high end of the scale.

Product Grade

Nitric phosphate fertilizers are definitely not inherently low grade. Fertilizers of 1:1:1 ratio from this source would normally assay in the range of 15-15-15 to 17-17-17, depending on the product water solubility and the character of the phosphate rock used for their manufacture.

In the case of the 1:1:1 grades reported to have been sold in quantities in excess of 10,000 tons, the distribution by grade is approximately as follows:

Table I
Distribution of Fertilizers Consumed by Grade

Grade of Fertilizer	Cumulative Percent Having Indicated or Lower Grade
8-8-8	12.9
10-10-10	47.0
12-12-12	78.5
14-14-14	87.8
15-15-15	95.0
16-16-16	98.0

The average grade of all fertilizers reported is approximately 11.3-11.3-11.3.

The product grade of nitric phosphates is related to the water solubility. For most high grade rocks, the following relationship would be typical:

Table II
Grade of Nitric Phosphate Fertilizers

Percent Water Solubility	Grade of 1:1:0 Nitric Phosphate
30	20-20-0
50	21-21-0
70	22-22-0
85	23-23-0

The production of highly water soluble fertilizers will entail some increase in production costs resulting from a nominal increase in capital cost and an increase in utility requirements because of heavier refrigeration loads. On the other hand, some credit against the higher production costs is obtained in the form of reduced storage, bagging, shipping and distribution costs. In many cases the credit thus obtained may be greater than the increase in production costs.

The attainable fertilizer grades are thus competitive with those attainable by other routes and are certainly well above the average of those now commonly used in the United States.

Nitrogen to Phosphate Ratio

Nitric phosphate plants now commercially using the Odda Process can produce a minimum $N:P_2O_5$ ratio in the phosphatic fertilizer of about 0.7. Since most countries tend to use ratios that can be expressed in small, whole numbers, this means that for practical purposes the minimum ratio suitable for direct marketing is essentially 1.0.

Although no commercial operations are known, workable processes are known for the production of lower $N:P_2O_5$ ratios. One of these involves a relatively minor variation of the Odda Process wherein additional phosphate rock is added following the calcium nitrate removal step. This rock will react with the remaining free acid in the slurry to ultimately reduce the $N:P_2O_5$ ratio sufficiently to allow the production of 1:2 ratio. Product water solubility would be reduced to about 70% by the addition of the secondary rock.

Variations of the nitric phosphate processes using the sulfate recycle system have been proposed whereby it is possible to crystallize substantially pure monoammonium phosphate[6] which would presumably yield a product having an $N:P_2O_5$ ratio of 1:5.

In 1966-67 there were approximately 3900 grades of fertilizer consumed in the United States[7] but only 189 of these grades were produced in quantities in excess of 10,000 tons. Among these 189 grades representing about 85% of total sales, the distribution as a function of $N:P_2O_5$ ratio is reported as follows:

Table III
Distribution of Fertilizers Consumed by $N:P_2O_5$ Ratio

$N:P_2O_5$ Ratio	Tons Actual	Tons Cumulative	Percent of Total Cum.
2:1 and Higher	645,351	645,351	3.0
>1:1 –<2:1	454,926	1,100,217	5.2
1:1	2,989,006	4,089,283	19.2
1:2	4,489,073	8,578,356	40.3
<1:2	6,433,746	15,012,102	70.5
All Others	6,311,815	21,323,917	100.0

On the basis of $N:P_2O_5$ ratio only, the existing Odda Process can theoretically meet requirements for approximately 20% of the fertilizers consumed in the United States, and with some modifications, could be extended to cover requirements for approximately 40%. The use of nitric phosphate fertilizers as a base for bulk blending might further extend the market potential.

On the other hand, the proposed sulfate recycle processes, which do not involve separation of nitrogen from the phosphate component, can yield a minimum $N:P_2O_5$ ratio of about 1.7 unless supplemental P_2O_5 is supplied from other sources. The direct market for such compounds is presently comparatively limited and accordingly, would be considered to constitute a serious commercial limitation on such processes.

The approximate total P_2O_5 utilization in mixed fertilizers within the $N:P_2O_5$ ratio limits for Odda type processes is shown on Table IV.

Table IV
Utilization of P_2O_5 in Mixed Fertilizers

N/P_2O_5 Ratio	Tons P_2O_5	Cumulative Tons P_2O_5
1:1 and Higher	430,000	430,000
1:2–1:1	640,000	1,070,000
Total All Mixtures	—	3,460,000

It is, of course, quite obvious that only a fraction of this market potential could be attained in the immediate future. One of the apparent problems is the fact that nitric phosphate grades, as normally produced, will be much higher than those commonly used and will, therefore, require either heavy dilution or, alternately, considerable revision in consumer practice.

It would appear, however, that sufficient sales potential does exist to justify the construction of a fair number of Odda Process type plants within the next decade.

The production of nitric phosphate fertilizers will yield a co-product amounting to something of the order of 5.5 tons of ammonium nitrate per ton of P_2O_5 produced. Production of fertilizer grade ammonium nitrate in the United States is given in the following Table V.

Table V
Production of Fertilizer Grade Ammonium Nitrate in United States
(Thousands of Tons)

Year	Solid	Liquid	Total
1960	1,572	1,253	2,825
1962	1,668	1,378	3,046
1966	2,414	2,119	4,533
1969 P	2,896	2,746	5,642
P = Projected			

Table VI
Characteristics of Nitric Phosphate Fertilizers

	Prilled	Granulated
Bulk Density—Packed lbs/ft^3	76.5	70.5
Bulk Density—Loose lbs/ft^3	71.8	65.6
Angle of Repose—Degrees	25	30
Percent Moisture—Approx.	0.5	0.5
	Percent Cumulative Plus	
Size Analysis—Typical		
+ 3mm (7 mesh approx.)	Trace	Trace
+ 1.5 mm (10 mesh approx.)	98	—
+ 1.0 mm (16 mesh approx.)	98	—

The existing market for ammonium nitrate appears to be generally sufficient to absorb all the co-product ammonium nitrate that would be produced as a result of the production of nitric phosphates. The fundamental change involved is only the routing of nitric acid to the nitric phosphate plant where it is converted to ammonium nitrate instead of sending it directly to neutralization and ammonium nitrate production.

Calcium Nitrate Utilization

In North America calcium nitrate is not expected to be widely used. It is now generally visualized that this material will be reacted with ammonia and carbon dioxide to make ammonium nitrate for marketing, either in solid form or as solution fertilizers and calcium carbonate as a waste product.

Other potential uses for calcium nitrate would be its inclusion in liquid fertilizers, since substantial percentages of nitrogen from this source can be included without appreciable reduction of total nitrogen content of the solution. It is unlikely that calcium nitrate would be acceptable in ammoniating solutions for fertilizer granulation, since the presence of calcium would adversely affect the chemistry of the granulation step.

Ammonium nitrate limestone can be manufactured using calcium nitrate as a base. It has also been suggested that the calcium nitrate be thermally decomposed to yield lime, and regenerate nitric acid for reuse in the acidulation step.

Except under unusual circumstances, thermal decomposition of the calcium nitrate does not appear to be economically justifiable.

Prill or Granulate

The prilled product would be considered to be greatly superior to that produced by more or less conventional granulating techniques. The prilling operation has been in operation for three years at Norsk Hydro and must be considered to be completely commercially demonstrated.

Material having an analysis of 16-16-16 would have the typical characteristics shown in Table VI.

With granulation, size range will normally be greater and flexibility in control of size range is improved.

Fig. III is a photograph comparing the two types of product.

The amount of KCl that normally can be incorporated in prilled mixtures as a function of $N:P_2O_5$ ratio is shown on Table VII.

In circumstances where it is proposed to manufacture grades containing very high percentages of potash or substantial amounts of filler or other compounds, it may

Table VII
Ratio Limitations for Prilled Fertilizers

N/P_2O_5	Maximum K_2O/P_2O_5
0.7	1.7
1.0	2.3
1.5	3.3
2.0	4.4

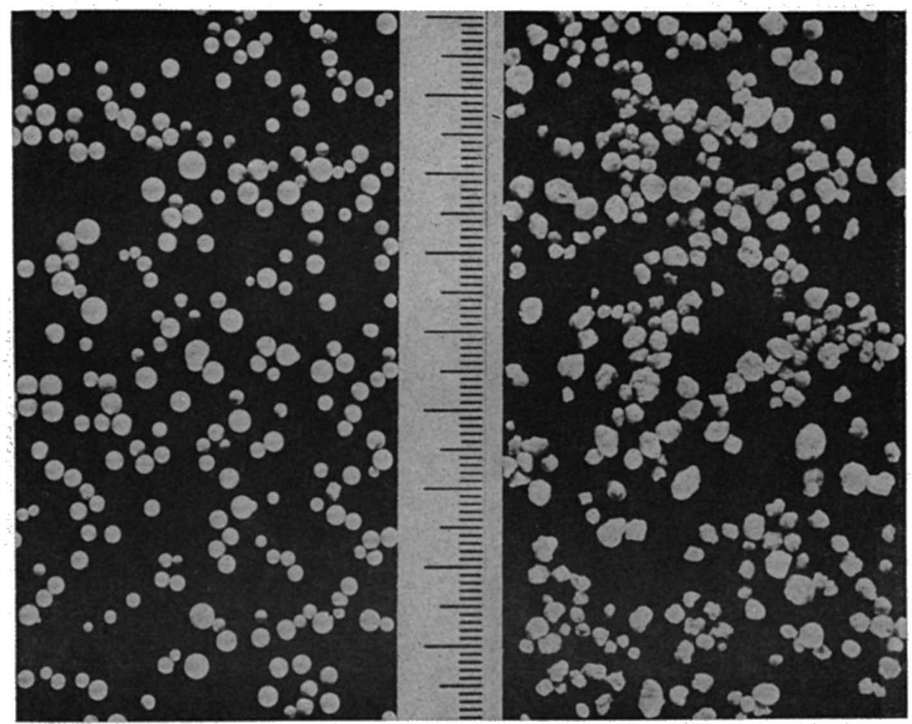


Figure III
Comparison of Granular and Prilled Nitric Phosphate Fertilizers

be necessary to consider granulation as an alternate to prilling.

Although the exact break-even point is a matter of local consideration, it is believed that prilling would be less expensive than granulation for plants having a capacity in excess of about 500 tons per day of fertilizer.

Storage and Handling

The statement that nitric phosphate fertilizers are difficult to store and handle is often heard. This statement is quite true and can be applied equally well to almost any commercial chemical fertilizer produced today. The wealth of published patents, data and test work relating to caking, demonstrate that storage problems are not unique to any particular processing route.

Fertilizers containing ammonium nitrate in conjunction with other soluble salts will pick up moisture from the air if the relative humidity exceeds about 55%. Nitric phosphates, if protected from moisture pick up, have generally been found to remain free flowing for long periods. No degradation or breakage of granules or prills has been observed to result from temperature cycling across the transition temperature of 32.1°C.

Many years of experience are available on the behavior of these materials. In Norway, bulk storage buildings holding up to 25,000 tons in a single pile having a center depth of 30–35 feet, are used. These buildings are not air conditioned, but are kept closed insofar as practicable to avoid excessive intake of moist air. Conveyors are enclosed to avoid moisture pick up from precipitation as the material moves from one area to another.

During long storage there is some tendency to form a light crust on the surface of the pile where it is exposed to air. Subsequent handling with payloader is carried out with no undue difficulties. Figure IV is a photograph of the interior of a Norsk Hydro storage building for N.P.K.

In test programs, nitric phosphates have been stored in silos lined with plastic sheeting for periods up to nine months. The fertilizer has always remained free flowing and could be recovered from the silo with no difficulty. Such a silo with the reclaim and spreading, is shown in Figures V, VI, and VII.

Samples of the prilled material have been sent to the United States for tests in North Carolina and Georgia where conditions are somewhat more rigorous than in Norway. While tests are still in progress, examination after approximately six months has provided considerable information as to its behavior.

Bulk storage piles which had been covered with polyethylene sheeting were found to be in excellent condition. As far as could be determined, the material was

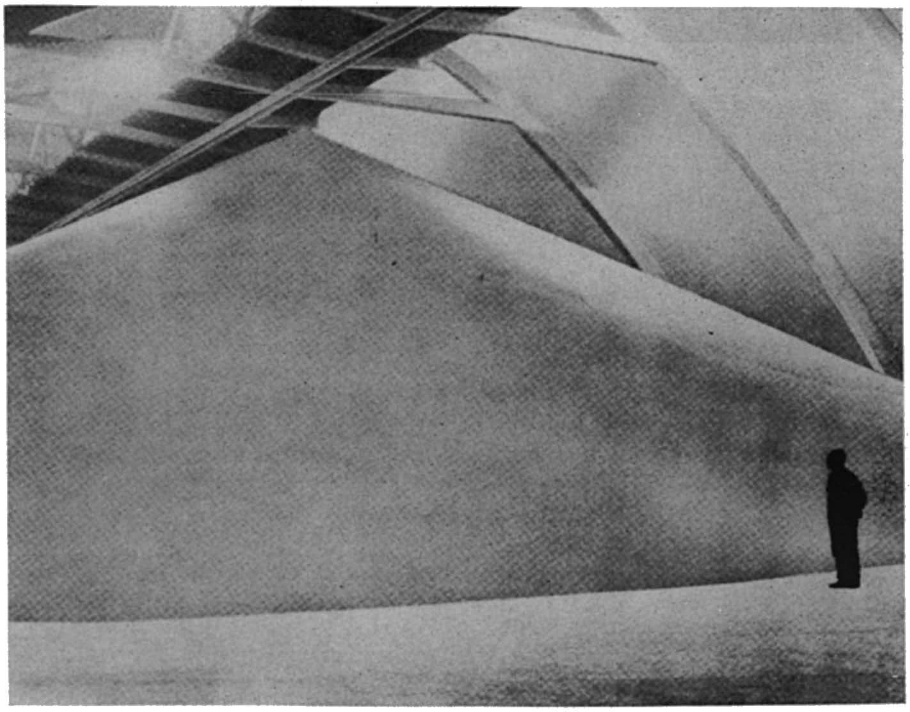


Figure IV
Bulk Storage Building in Norway

Figure V
Silo Used for Storage Tests

Figure VII
Spreading of Nitric Phosphates

just as good as the day it was received. The prills were completely free flowing and had still retained their original hardness. No lumps were found when the pile was probed to floor level, or walls, where some tendency toward caking would be expected.

In an adjacent pile, not covered, the top of the pile was crusted and lumps were found along the wall and down into the pile. Prills at the floor line were wet and mushy. The comparison illustrated very clearly the necessity of preventing fertilizers of this type from contacting humid air from which it could absorb moisture.

Small amounts of fertilizer were exposed to simulate spillage. The prills picked up so much moisture that they lost their identity, leaving a soupy mess.

Any conclusions regarding fertilizer storage characteristics must be based on a detailed consideration of the related circumstances and conditions which might affect the behavior. Information available to date would seem to indicate that if nitric phosphates are reasonably protected from moisture pickup, their behavior in storage will probably be better than most of the competitive grades presently available in America.

Figure VI
Reclaiming from Silo

Chemical and Agronomic Considerations

The chemical composition of nitric fertilizers is presumably not appreciably different from those manufactured by ammoniation of superphosphates with added ammonium nitrate, although the percentages of the various chemical phases may differ substantially. Among the major compounds that would be present in the final N-P product would be found:

Monoammonium Phosphate
Diammonium Phosphate
Calcium Phosphates
Ammonium Nitrate
Calcium Fluoride
Iron Phosphate
Aluminum Phosphate
Plus other impurities.

Only traces of sulfur would normally be present. Sulfur could be included, if required, by several known means. One way that this can be done is to use potassium sulfate instead of potassium chloride in the N.P.K. grades, or smaller amounts of $MgSO_4$ when Mg is desirable. Potassium sulfate may replace potassium chloride when a chloride free fertilizer is required, such as for tobacco culture.

Trace elements can be added as required ahead of prilling and granulation.

Safety Aspects

It is well known that fertilizers (not only nitric phosphates) containing certain proportions of nitrate and potassium chloride are capable of maintaining self sustaining decomposition, sometimes called "cigar burning". Temperatures in the range of 300–450°F are required to initiate the reaction. This phenomenon has been extensively investigated[8, 9] and it is now possible to formulate stable compositions.

While some precautions must be taken in storing and handling of N-P-K fertilizers, they do not limit availability and use of these materials. Additional costs resulting therefrom, will in most cases, be negligible.

Quality

As produced in a nitric phosphate process, every granule of fertilizer contains very nearly the same ratio of nutrients. Segregation or separation during storage, transportation and application will not affect the uniformity of distribution of nutrients on the field. The use of bulk blended fertilizers does create a possibility of such uneven distribution.

Even distribution of nutrients becomes increasingly important as the quantity of fertilizer per unit area is increased. This factor appears to have been stressed more heavily in European countries than in the United States.

Phosphate Solubility

It is beyond the scope of this discussion to go into the agronomic aspects regarding water solubility of the phosphates. In view of the wide acceptance of what might be termed low water soluble phosphates, there appears to be no real issue regarding nitric phosphates. It must be concluded that they are broadly acceptable in this respect.

Ratio of Ammonia and Nitrate Nitrogen

Nitrophosphates manufactured by existing developed processes contain both ammonia and nitrate nitrogen, normally in a ratio of about 55% ammonia nitrogen and 45% nitrate nitrogen. The nitrogen content is fundamentally derived from a mixture of ammonium phosphates and ammonium nitrate. The nitrate content is easily available for rapid response, while the ammonia content represents a longer lasting component.

Nitric phosphates would not generally be considered to be advantageous for use on rice paddies. For such usage fertilizers containing only ammonia nitrogen are preferred.

Production Costs

In a free society a fertilizer operation must be profitable if it is to survive. By the time the fertilizer has been applied to the fields, it has moved through a long and complex chain beginning with phosphate rock, potash and sulfur at their respective mines, plus gas in wells, which ultimately produces the nitrogen content.

An almost infinite variety of combinations with respect to raw materials, processing conditions and transportation of intermediate or final products exist within this chain. Consequently, it is impossible to draw any broad and sweeping conclusions regarding final costs unless the entire system is examined in detail.

Some of the major factors which influence costs are illustrated in the comparison of three routes for making a 1:1:1 fertilizer. These processes are:

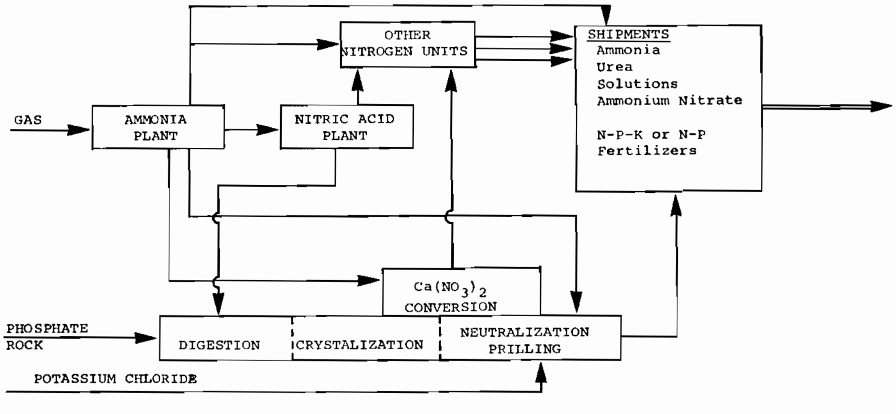
1. Nitric phosphates by the Odda Process.
2. Diammonium phosphate by conventional routes followed by bulk blending with solid ammonium nitrate and potash to yield a final high grade N-P-K compound.
3. Production of superphosphates, both normal and triple, by conventional paths, followed by granulation in a TVA type granulation plant. This diagram and raw material estimates have been somewhat simplified insofar as the granulation operation is concerned.

The approximate raw material requirements are assumed to be anhydrous ammonia, elemental sulfur, North Carolina phosphate rock and postassium chloride. Material requirements are expressed as tons raw material per ton APA produced and include reasonable allowance for losses during processing.

Figure VIII shows the essential process steps and raw material requirements for a nitric phosphate operation. The entire operation would probably be a single integrated unit operating under a single management. Raw materials are natural gas, phosphate rock and potassium chloride.

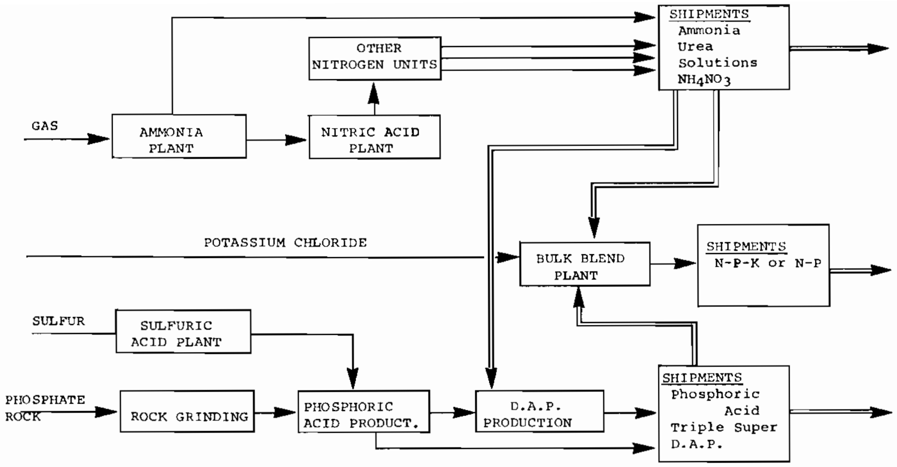
The primary product from the N-P-K plant would be a 1:1:1 compound assaying between 15-15-15 and 17-17-17, depending on water solubility. Other products originating from the same complex might well include ammonium nitrate, urea, anhydrous ammonia and solutions. Other N-P or N-P-K solid fertilizers can also be made. The CO_2 needed for conversion of the calcium nitrate to ammonium nitrate is obtained from the ammonia plant.

A capacity of 100-200 tons per day P_2O_5 would be considered a



RAW MATERIALS Tons/Ton P_2O_5	
Phosphate Rock	3.16
Total Ammonia	2.73
Carbon Dioxide	0.93
Potassium Chloride	1.68
By-Product NH_4NO_3	3.32

FIGURE VIII
NITRIC PHOSPHATE FERTILIZERS



RAW MATERIALS Tons/Ton P_2O_5	
Phosphate Rock	3.35
Sulfur	1.01
Total NH_3	1.42
Potassium Chloride	1.68

FIGURE IX
GRANULAR FERTILIZERS USING D.A.P. FOR BULK BLENDING

realistic and economical size for the nitric phosphate unit, although this would have to be established in accordance with the market potential for the various plant products in the marketing area.

Figure IX indicates raw material requirements and movement of semi-finished materials in cases where the final product is to be produced by bulk blending. In many cases the three unit operations; phosphate production, nitrogen production, and bulk blending, may be remotely located and under different ownership. Insofar as raw materials are concerned, sulfur is now necessary in addition to those used in the nitric phosphate operation.

The size of the phosphate operation will typically be in the range of 500–1000 tons P_2O_5 per day, while bulk blending would be carried out in a number of quite small plants. As compared to the nitric phosphate operation, there has been an increase in flexibility with respect to ability to produce small tonnages of unusual grades. But nitric phosphates can also be used as a base for bulk blending. Additional intermediate products such as phosphoric acid and other phosphatic compounds also become available for direct application or further processing, which also contribute to added flexibility.

Figure X indicates raw material requirements when superphosphates are used as a base for the production of granulated fertilizers. Theoretically, a 30% saving in sulfur is obtained in this manner. Basically, the advantages and disadvantages of this procedure are similar to those for the bulk blend route.

In comparing the different processes, the major advantage of the nitric phosphates is the saving in sulfur. Based on $40.00 per ton sulfur delivered plantsite, the savings are of the order of $28.00–$40.00 per ton P_2O_5 produced. Beyond this, comparative costs are difficult to define, but a number of studies do indicate that net overall savings will be of similar magnitude.

In considering a nitric phosphate operation, this must be looked upon as a supplement to a nitrogen producing facility. Nitric acid on its way to being converted to ammonium nitrate can be utilized to make APA from phosphate rock in passing. In any operation where the production of ammonium nitrate is scheduled, there would appear to be an excellent opportunity to make phosphatic fertilizers at low cost by the nitric phosphate route. Such possibilities are well worth investigation.

The total costs of transportation, handling, and distribution are indeterminate. Materials basically originate at the phosphate mines, the ammonia plants, the sulfur mines and the potash mines, and move through their respective production chains to the fields. It does seem quite possible that any differences in this respect could, theoretically, favor nitric phosphates on the average, when compared to today's practice. The product grades attainable certainly average higher than those for corresponding ratios commonly used today. The assignment of charges for movement of the excess ammonium nitrate is perhaps more one of accounting procedures than anything else. Large tonnages of ammonium nitrate are going to move from manufacturing plants to fields, regardless of the exact procedure used in its manufacture.

Acknowledgment

The writer wishes to express his appreciation to members of the staff of Norsk Hydro-Elektrisk Kvoelstofaktieselskab, Oslo, Norway, who have supplied certain information not previously published regarding the operation of the Norsk Hydro Plant in Norway.

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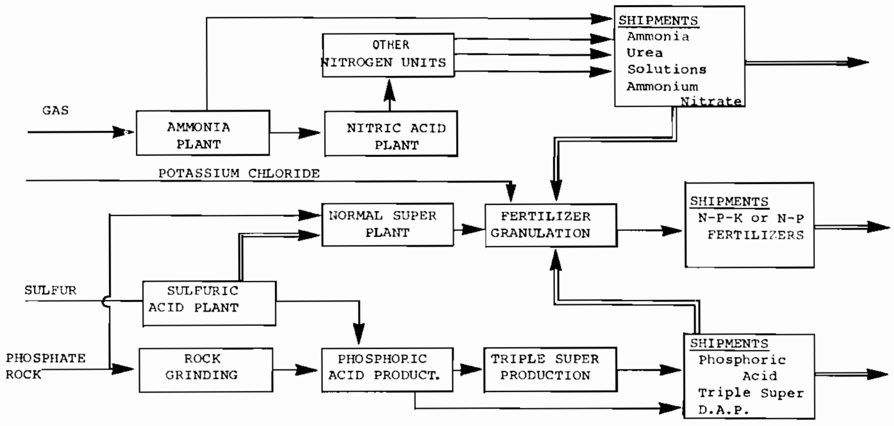

RAW MATERIALS Tons/Ton P_2O_5	
Phosphate Rock	3.36
Sulfur	0.73
Total Ammonia	1.30
Potassium Chloride	1.68

FIGURE X
GRANULAR FERTILIZERS USING TRIPLE SUPER BASE

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12. Ensminger, Commercial Fertilizer and Plant Food Industry, Oct. 1966.

CHAIRMAN SAUCHELLI: I am sure Mr. Lutz will be around for those who have questions so you can check with him. Thank you Mr. Lutz.

CHAIRMAN SAUCHELLI: We have a treat here that Dr. Strelzoff has provided which is going to take only about 12 minutes. It is a motion picture that was a feature at the last TVA demonstration. I think it has to do with the ammonium sulfate recycle process. So those who would like to stay to see it, the picture is now going on.

(The Meeting adjourned at five-forty-five o'clock p.m.).

Friday Morning Session, Nov. 15, 1968

The Round Table Reconvened at 9:45 o'clock A.M.
Vincent Sauchelli and Billy E. Adams, Moderators

MODERATOR SAUCHELLI: Our first paper this morning has to do with nitrophosphates. It seems to me that the Round Table has been a forum for nitrophosphate for three sessions now and I believe that our proceedings will constitute a good volume on all phases of the nitrate phosphate question. I think people will regard it as a valuable asset because of that.

The paper titled "USS Agricultural Chemicals Nitric Acid Digestion Nitrophosphate Process" is co-authored by Richard F. McFarlin, Vice President, Commercial Development USS Ag. Chem. and Donald E. Brown, Manager Fertilizer Plant Sales, Foster Wheeler Corporation. Mr. Brown will discuss the paper.

USS Agricultural Chemical Nitric Acid Digestion "Nitrophosphates" Process

R. F. McFarlin[*] and W. E. Brown[**]

The Role of Nitrophosphates in Agriculture

During the past several years few people involved in the fertilizer industry have been unaware of the profusion of articles and technology in the subject area, "Nitrophosphates". Equally few people have understood the potentials and limitations of this technology—such as the U. S. Market.

Let's define "nitrophosphate processes" first, to insure that we have a common understanding of the term. We will use the term "nitrophosphate process" to describe the acidulation of phosphate rock with nitric acid followed by the substantially complete separation of CaO and P_2O_5 components. The related processes that immobilize the calcium as an insoluble compound—still in the presence of the phosphate—are thus eliminated by this definition. Process variations differ primarily in method and degree to which the calcium is separated from the phosphate. One may categorize "nitrophosphate" processes as follows:

A. Those in which part of the calcium is removed, while the remainder is rendered water insoluble *in situ*. These are:
   Odda, Norsk-Hydro, Kampka-Nitro, S.B.A.

B. Those which remove the calcium completely from the presence of the phosphate, normally as gypsum:
   DSM sulfate recycle, TVA, Liljenroth, St. Paul Ammonia, Chemico and the subject USSAC NAD

There remains some hazard in classifying the various processes under the above headings, because each process has broadened its options to gain product flexibility. More about this later.

Is the Nitrophosphate Process competitive with DAP?

Inevitably, people rush to compare a nitrophosphate process with the conventional sulfur-based process for di-ammonium phosphate.

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[*] USS Agri-Chemicals, Inc.
[**] Foster Wheeler Corporation.

This is simply not valid. The DAP plant is a P_2O_5 process which necessarily produces some nitrogen; the nitrophosphate process is primarily a nitrogen process which produces some P_2O_5. The basic or primary phosphate producer will have little interest in a nitrophosphate process unless he has a defined market for nitrogen products.

What, then, is the role of nitrophosphate technology?

Having ruled out the producer, who wants P_2O_5 only, the answer to this question is obvious. The ideal customer is a nitrogen producer who has an existing market for nitrogen materials and wants relatively small tonnages of P_2O_5. He is motivated by the prospect of getting double duty from his nitric acid. He can solubilize some phosphate before converting the nitrate ion into a solid carrier of ammonia. It is apparent that the nitrophosphate process is ideally suited to co-produce ammonium nitrate and ammonium phosphate.

In our analyses we find that if the following conditions are met, the economics overwhelmingly favor a nitrophosphate plant:

A. The producer has an ammonia plant and consequently a source of free carbon dioxide, and

B. The producer has a market for products such as 28-14-0, 23-23-0, 20-30-0 and ammonium nitrate.

How does one select the most appropriate Nitrophosphate Process?

The producer must select the most economical variation consistent with the demands of his market place: These considerations are,

A. The degree and importance of water-soluble P_2O_5:

Even though U. S. agronomists assure us that 50-60% water-soluble P_2O_5 content is adequate for most applications, the commodity P_2O_5 products, DAP and TSP, have an 85-90% water-soluble content. Less than 85% could put the producer at a disadvantage in some competitive areas, particularly those areas with a limited growing season or short-term truck crops.

In the first mentioned nitrophosphate category, the calcium is ultimately removed as $CaCO_3$ thereby producing ammonium nitrate and an X-X-O product. The Odda, or modified Odda process can remove sufficient Ca to produce up to 85% P_2O_5 water solubility, although 60% may be a more practical target. The ammonium sulfate recycle processes can produce P_2O_5 water solubility as high as 90-95%. Virtually all the calcium is removed, so the P_2O_5 in the final product exists as mono- or di-ammonium phosphate —exactly as in the conventional sulfur-based route.

B. Grade flexibility and total nutrient content:

The nitrophosphate product should be competitive in total plant food content. Those nitrophosphate variations which leave calcium in the phosphate product necessarily produce a lower analysis product than the NAD process.

C. The desired nitrogen to phosphate ratio:

Because of the stoichiometry of the common rock digestion step, nitrophosphate processes suitable for most markets produce about two tons of nitrogen/ton P_2O_5. Thus, the producer must be certain that he can market, in some acceptable product mix, the total quantity of nitrogen involved. The nitrophosphate process should provide maximum separation of the ammonium nitrate/ammonium phosphate constituents—so the producer can offer a wide range of NP products.

Foster Wheeler has made a thorough review of the nitrophosphate technology available today and has concluded that the USS Agri-Chemicals NAD Process offers the maximum advantages in terms of low N/P ratio grades, minimal capital investment and high P_2O_5 water-soluble products.

Technical Description — USSAC NAD Process

The NAD Process is classified basically as a sulfate recycle process with additional steps to separate ammonium nitrate and thus provide N/P ratio flexibility. An N/P_2O_5 ratio as low as 0.67/1 is possible in the phosphate product. Lower ratios such as 0.5/1 or 0.25/1 require very little supplemental P_2O_5 from an outside source.

Chemistry and Basic Process

The chemistry and overall flow scheme of the process are presented in Figure 1. Phosphate rock is digested with a mixture of nitric acid and ammonium sulfate. The resulting slurry contains gypsum and a solution of ammonium nitrate and phosphoric acid. The gypsum is filtered and the solution is further treated accordingly to

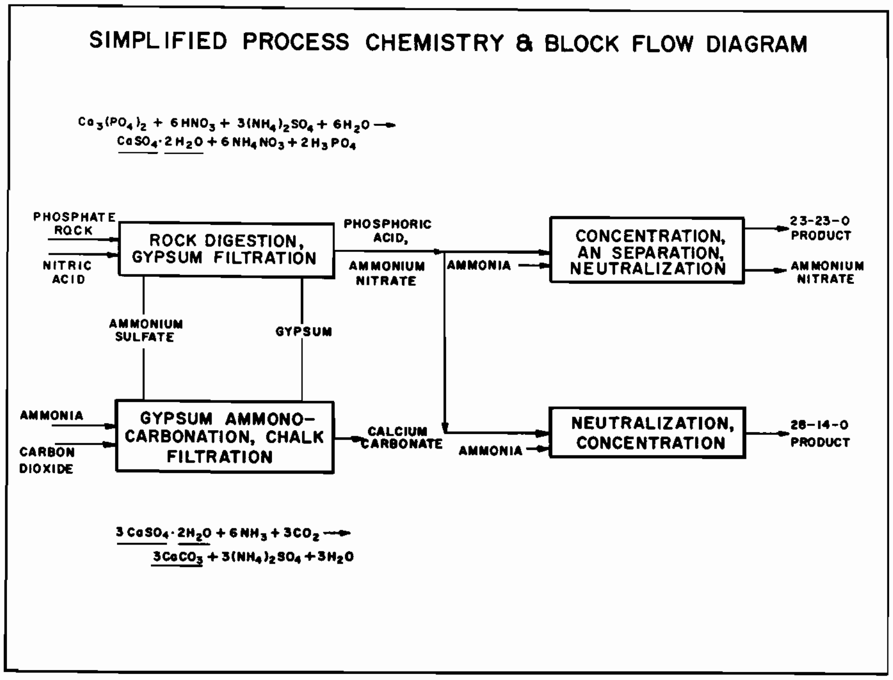

Figure 1

the desired final product as shown on the right hand side of the chart. A product having an N/P_2O_5 ratio of about 2 is made by simultaneously ammoniating and concentrating the filtrate and granulating the resultant slurry. Low N/P_2O_5 ratios are manufactured by separating part of the ammonium nitrate before neutralization. These low N/P_2O_5 ratio products yield ammonium nitrate as a co-product.

The gypsum is reacted with ammonia and CO_2 to form calcium carbonate and ammonium sulfate solution. The solution is filtered from the chalk solids and recycled to the rock digestion system.

Rock Digestion

The attack system contains an attack solution mixing tank, a rock feed system, and a multicompartment digesting vessel. Recycled ammonium sulfate solution and nitric acid are mixed and cooled in an agitated tank prior to entering the first digester. Phosphate rock is wet with recycled digestion slurry in a small premixer before entering the first digester. High-speed turbine impellers agitate the rock and slurry in the premixer. Slower axial-flow impellers provide gradually decreasing degrees of mixing as the slurry proceeds from the first to the third digester. A flash cooler removes the exothermic heat of reaction between apatite and the attack solution and the off-gases are scrubbed with water.

The nitric acid used for attacking the rock is equivalent to the calcium, iron, and aluminum in the rock. Although the principal reaction is with the calcium; iron and aluminum also consume nitric acid to form iron and aluminum nitrates. The amount of ammonium sulfate used is about 98% of the stoichiometric equivalent of the calcium in the rock. Although a small amount of defoamer is necessary when starting up an attack system, no additional control of foaming is required after operating for about 3 hours.

The digestion slurries gradually become less viscous as the slurry proceeds from the premixer to the third digester. The slurry exiting the third reactor has a specific gravity of about 1.5 and a pH of about 0.5 or lower. P_2O_5 recovery is comparable to the conventional wet process acid route.

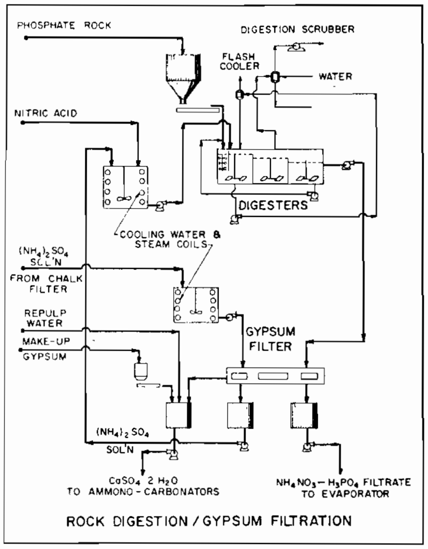

Figure 2

Gypsum Filtration

The digestion slurry is fed to a tilting pan filter for separating the gypsum from the ammonium nitrate—phosphoric acid solution. Recycle ammonium sulfate solution is heated and used for washing the gypsum cake. The gypsum is repulped with water and pumped to the sulfate recycle unit where a gravimetric feeder adds a small amount of make-up gypsum to the repulp tank.

Digestion slurry at 170°F. filters at 700 gal./hr.-ft.^{2} with 20 in. Hg vacuum for a 1-in. cake. Comparable wash rates are obtained when the wash solution is 200°F. Using the entire ammonium sulfate recycle stream for washing the gypsum corresponds to a wash ratio of about 1.8 lb. solution/lb. dry cake. A single, once-through wash reduces phosphoric acid losses in the gypsum cake to about 0.5% of the total P_2O_5 fed to the system. The gypsum cake, containing about 70% solids, is repulped to 50% solids before additional processing.

Digestion Filtrate Evaporation

The mother liquor from the gypsum filter is concentrated in a forced-circulation vacuum evaporator. The ammonium nitrate-phosphoric acid solution, containing small amounts of impurities, is concentrated to reduce the water content from about 50 to 12%. Monitoring the evaporator effluent density provides control. The solution boils at about 165°F. when under 25 in. Hg vacuum. The concentrated solution has a specific gravity of about 1.6.

Nitrogen losses are very low and the evaporator can be equipped for ammonia injection and used as a neutralizer when making high N/P_2O_5 ratio products. The pH of the solution is approximately 0-0.5. The low pH is essential to achieve a good AN separation.

Ammonium Nitrate Crystallization

The concentrated solution is cooled by heat exchange with water in a classifying-type crystallizer. The supersaturated solution is contacted with a circulating bed of crystals and saturated liquor. A crystallizer operating temperature of 92°F., and feed solution containing about 12% water, allows removal of about 60% of the total ammonium nitrate from the solution. These conditions are sufficient to yield the 1-1-0 ratio product after ammoniatization of the centrifugate. By adjusting the crystallizer operating conditions additional AN can be removed to yield a 1:1.5:0 product after final processing.

Cooling water at 80-90°F., circulating concurrently with the slurry, removes the sensible heat and latent heat of crystallization. The feed solution salts out at about 150°F. and contains 40-50% suspended solids when cooled to 92%F. A circulating velocity of 1-2 ft./sec. through the cooler prevents scaling on the heat transfer surfaces.

Ammonium Nitrate Centrifugation

Ammonium nitrate crystals are grown in size to 50-100 mesh before centrifuging. The crystals are rice shaped and contain less than 2% adhering mother liquor. The viscosities of the centrifuge feed and centrifugate liquor at 92°F. are about 750 and 15 cp., respectively. The centrifugate cake weighs about 55 lb./ft.^{3}. The ammonium nitrate cake is suitable for melting and prilling, for granulating, or for use in solutions.

Neutralization-Concentration

The ammonium nitrate-phosphoric acid solution is first used to scrub the unreacted ammonia

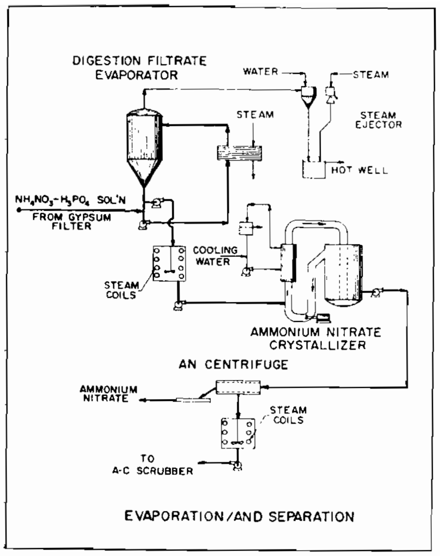

Figure 3

and carbon dioxide off-gases from the ammono-carbonators. The ammonia neutralizes part of the phosphoric acid, and the carbon dioxide passes through the scrubber to the atmosphere. The liquid portion of the scrubber effluent is then routed back to the product neutralizer.

The solution is concentrated from 20 to 10% H_2O in the neutralizer-concentrator. Ammonia is injected directly into the circulating leg of this unit. The total amount of water removed in this unit is about one-tenth of the water removed in the previous evaporator. The neutralizer is operated at a pH of about 5.3 to allow formulation of the 1-1-0 ratio product and provide optimum conditions for neutralization and concentration. Between 5.0 and 5.5 pH, the solubility of ammonium phosphates is at a maximum. Neutralization of the phosphoric acid generates about four times as much heat as that required to concentrate the solution. The excess heat is removed either by cooling water or direct addition of water that is flashed off as steam.

After concentration, the product solution is pumped to a surge tank which serves as a granulator feed vessel.

The neutralization and concentration can be conducted under atmospheric pressure without increasing ammonia losses appreciably. This type of design might be favoured for large commercial units. In this case, the heat absorbed by the cooling water could be used to preheat the feed to the first stage of the digestion filtrate evaporator, also operating under atmospheric pressure.

Granulation

The granulation system is a typical TVA-type unit, operating at a recycle ratio of about 4:1.

Gypsum Ammono-Carbonation

The repulped cake from the gypsum filter, which contains calcium sulfate dihydrate with small amounts of P_2O_5 and ammonium sulfate is routed through a feed tank to a four-compartment sulfate synthesis vessel. The gypsum slurry cascades through three reactors where direct injection of anhydrous ammonia and CO_2 converts the gypsum to a slurry containing calcium carbonate solids in a solution of ammonium sulfate and ammonium carbonate. Part of the slurry from the third reactor is recycled to the first to control foaming and aid calcium carbonate crystal growth. The slurry overflowing the third reactor is heated to vaporize excess ammonium carbonate and decrease the slurry viscosity before filtration. The ammonia and CO_2 off-gases are scrubbed as previously described.

The gypsum feed slurry contains only that amount of water which is necessary to prevent crystallization of ammonium sulfate in the chalk filter feed slurry. This amounts to 50-55% solids in the gypsum feed. The total ammonia and CO_2 fed to the three reactors is about 1.1-1.2 times the stoichiometric amount needed for converting all the gypsum to ammonium sulfate.

The slurry pH in the reactors is controlled at 8.5-9.0. Recycling slurry from the third to the first reactor at about twice the gypsum feed rate eliminates reactor foaming and improves filtration rates. The third reactor slurry effluent contains about 27% suspended solids and has a specific gravity of 1.45.

The conversion of gypsum to ammonium sulfate is controlled by the agitation supplied in the three reactors. The degree of conversion increases as additional power is consumed by the reaction slurries. However, calcium carbonate filtration rates are inversely related to conversions. About 91% conversion of gypsum to ammonium sulfate represents the best compromise between choosing either a high filtration rate or high sulfate recovery for design.

The fourth compartment in the reaction vessel is a steam-heated hold tank. The slurry is heated to about 200°F. before being fed to the chalk filter.

Chalk Filtration

The slurry from the ammono-carbonation hold tank is filtered under vacuum on a rotary drum filter to remove the precipitated carbonate and other solids. The filter cake is then washed countercurrently with water to recover the ammonium sulfate adhering to the chalk solids. The chalk cake is repulped with water and discarded.

The ammonium-sulfate-chalk slurry filters at a rate of about 40 gal./hr.-ft.^{2} for a 0.5-in. cake thickness and 20 in Hg vacuum. The filter cake contains about 70% solids and consists of spherical calcite particles about 10-15 microns in diameter. The ammonium sulfate solution is recycled to the rock digestion unit via the gypsum filter.

A wash ratio of about 0.5 lb. H_2O/lb. dry cake leaves a chalk cake containing about 1% ammonium sulfate. This corresponds to about 1% of the total input sulfur lost because of incomplete washing.

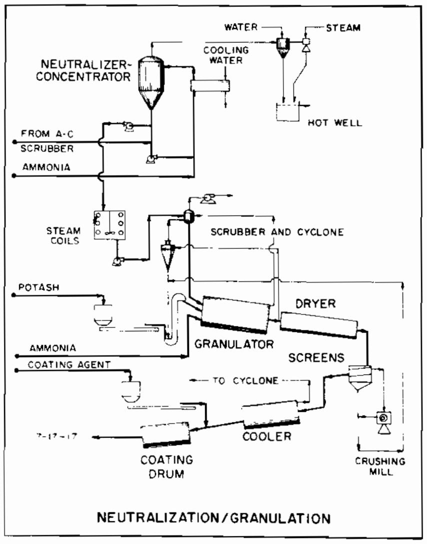

Figure 4

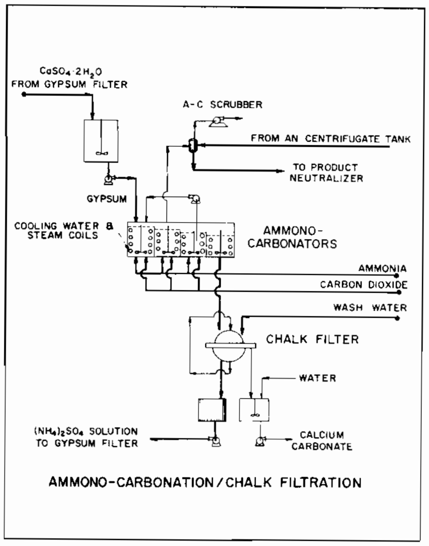

Figure 5

Raw Materials, Products, and Utilities

The raw materials, products, and utility requirements for a 17-17-17 design are estimated in Figure 6. The make-up gypsum can be imported from a wet-process phosphoric acid plant. This type of gypsum can be processed under the same conditions as gypsum made in an NAD unit. Alternatively, a small amount of sulfuric acid or ammonium sulfate can be used to provide the makeup sulfate.

Potassium Sulfate Modification

One modification of the NAD process involves substitution of potassium sulfate for all or part of the ammonium sulfate in the attack solution. This replaces ammonium ion in the final product with potassium and results in lower N/P_2O_5 ratios without separation of ammonium nitrate from the digestion liquor. These N-P-K grades contain potassium nitrate rather than the conventional potassium chloride.

The lowest N/P_2O_5 ratio product which can be obtained by crystallizing potassium nitrate at ambient temperatures analyzes about 17-34-17. In this modification the total amount of nitrogen in the combined products is about equal to the total P_2O_5.

Economic Evaluation

To put this process technology in perspective let's look at the economics.

There is once again no truly equitable basis for comparing the cost of producing P_2O_5 by the NAD route and a conventional sulfur-based phosphoric acid plant. If we attempt to compare the two on the same P_2O_5 tonnage level, we must either consider an unrealistically small wet-process phosphoric acid plant or a nitrogen plant that would produce an unrealistically large tonnage of nitrogen products.

There are three basic situations which favour nitrophosphate technology:

A. Sulfur—cost, supply, balance of payment factors.

B. A market which demands high N/P_2O_5 ratios, or

C. A basic nitrogen producer who wants to co-produce a relatively small quantity of P_2O_5: i.e. 200 TPD or less.

We chose situation C. as the basis for presenting the economics of the NAD process. Typical production rates are given in the next slide.

	Production, Short Tons		
Grade	Annual	As P_2O_5	AN Co-product
28-14-0	157,000	22,000	—
23-23-0	96,000	22,000	63,000
20-30-0	73,000	22,000	85,000
	326,000	66,000	148,000

To simplify the presentation, the production costs are based on 23-23-0 only. However, this same plant can produce any of the above ratios (with potash added as required) at no increased capital cost.

Additional case conditions are as follows:

1) Nitrogen works include the following existing plants: ammonia, ammonium nitrate, nitric acid and NPK granulation with potash handling facilities.

2) The plant currently operates with purchased phosphoric acid and markets the previously listed grades, so that the only change proposed is that the P_2O_5 come from the NAD process.

3) Addiional capital investment will include the following:

	$
a) phosphate rock handling facilities	500,000
b) NAD wet section	5,500,000
c) Chalk disposal pond	500,000
	6,500,000

4) The NAD P_2O_5—ammonium nitrate slurry to the existing granulation plant will be delivered with the same water content and chemical composition as the present H_3PO_4 process.

5) Any ammonium nitrate by-product from the NAD PROCESS is returned to existing A/N facilities as a clean melt of 83% concentration.

6) Prices assumed for raw materials are as follows:

Figure 6
Raw Materials, Products, and Utilities Estimated Requirements
Basis: 1 ton 17-17-17

Feed Materials	Net Ton	Products	Net Ton	Utilities	
Phosphate Rock (68 BPL)	0.61	N-P-K 17-17-17	1.00	Steam, ton	0.85
Nitric Acid (100%)	0.73	Ammonium Nitrate (100%)	0.50	Elec. kwh	48
Ammonia (anhydrous)	0.25				
Carbon Dioxide	0.28	Calcium Carbonate (dry)	0.71	Natural Gas (Dryer) MCF	0.7
Make-Up Gypsum	0.11			Process Make-up Water, M gal.	0.34
Potash (62.5% K_2O)	0.27				
Coating Agent	0.02				

	$/Ton
68 BPL Rock, delivered	14.00
Cost of make-up ammonia	30.00
Cost of make-up nitric acid	15.00
Cost of make-up gypsum	4.00

The cost includes only those items associated with producing the P_2O_5 solution which serves as feed to a granulation plant. Therefore, this value should be directly comparable to P_2O_5 purchased as phosphoric acid.

We were unfortunately unable to obtain approval for public release of detailed economic data. However, based on our computations with the most realistic information available, we calculated a P_2O_5 value of $83.50/ton P_2O_5, which includes all cost factors except return on investment. This value compared with $120-125/ton market price of P_2O_5 delivered to this same upper Midwest area would give somewhere between 35-40% pretax ROI.

The principal advantage of the USS Agri-Chemical NAD process is that by extracting the ammonium nitrate from the basic nitrophosphate mix, practical ratios can be made and the economics therefore, have real significance. It still has some of the nitro-phosphate limitations, but we feel that many possibilities have been opened up by this improvement and that the fertilizer industry should evaluate this opportunity to modernize its nitrogen and P_2O_5 manufacture.

MODERATOR SAUCHELLI: Thank you Don. That was a very comprehensive paper. I am sure there are going to be some questions.

Comments on Nitrophosphate Discussions

Samuel Strelzoff, Donald E. Brown, Ray Ewell,
William F. Sheldrick and Gero F. Lüth

STRELZOFF: Yesterday we had a rather short time to present certain papers which were not given a chance to be commented on.

First of all, I would like to congratulate our speaker, Mr. Brown, for a very clear and clean cut presentation of his paper which confirms, in many respects, statements made by us many, many years ago, that ammonium sulfate recycle process is a process that I think resolves a great deal of problems for the production of nitrophosphate. As a matter of fact, Chemical Construction have had the patent granted way back in 1952.

So far as potassium sulfate, as a route, it was already offered in 1927 by Mr. Tossell, whom I mentioned yesterday. There is nothing new so far as the sulfate recycle features of the process presented to us.

What I would like to suggest to Dr. Sauchelli, since we have here mostly presented papers by the people who are promoting various variations of processes, trying, of course, to use this platform for commercial purposes, wouldn't it be desirable to have some kind of an unprejudiced person, I think Dr. Ewell tried to do it, however, possibly, he has not yet completed his work to present a comparison of all of the nitrophosphate processes without, let us say, any special slant toward the commercial end of it. We did try to do that in St. Louis by presenting all of the processes that were available at that time but, of course, I am prejudiced too. Really, I do not want to prod my own views on nitrophosphate which I was already trying to sell for 43 years.

I wanted to say yesterday, and I had no chance to, however, Mr. Brown did very well say that 60 percent water soluble is just as good as 95 percent water soluble. We have here in this country very large production facilities for water soluble phosphate fertilizers like diammonium phosphate and tiple-superphosphate. Freeport Sulphur and Texas Gulf Sulphur have a big advantage to be able to control their own sulphur price.

So regardless of whatever we will say, engineers or chemists, that 60 percent or 50 percent is good in the United States, we will have to produce nitrophosphate, which will match for water solubility, diammonium and triple-superphosphate.

I will comment on this particular presentation. I would say that for some reason or other it had increased the complexity of the process by adding various steps that I do not think were absolutely necessary. Is it really necessary to crystallize out ammonium nitrate from the solution which can be separated much more simply later on directly by the process that we indicated when ammonium nitrate really pushes monoammonium phosphate out and gives us a much higher nitrophosphate product and much more flexibility. I don't know what this paper has told us more than we knew before except that it seems to me we now have quite a race between engineering companies. Really what we need, Dr. Sauchelli, is somebody that will have nothing to do with the sales of any processes, some one who can say to us "All right, we have compared all of these processes and here are their economics, and let the industry decide which one is most attractive to them."

MR. BROWN: I would answer that comment by saying I do think the chemical system is more sophisticated but it is not as simple as the process described. How simple can you get besides crystallizing out ammonium nitrate? It comes out with very little P_2O_5. You make a clean cut separation and you produce a low N to P_2O_5 ratio. How much simpler would you want it than this?

MR. STRELZOFF: It looks very simple to design ammonium nitrate crystallizers but you try to operate them.

MR. BROWN: This process has been patented and we think it is a unique application of ammonium nitrate crystallization from a P_2O_5 nitrogen mixture. We have found from our literature survey, which was fairly extensive, a good basis for the patent.

RAY EWELL: I do want to congratulate Mr. Brown on a very clear, well presented paper. In fact, I have just selected him as one of the commentators on the report I am writing for the United

Nations. I will solicit and seek your comments.

I might say first that it seems to me this mass multiplicity of relatively small changes in process is going to serve to confuse an awful lot of people. It is going to take a tremendous effort on somebody's part to really establish the relative economics of these seven or eight different variants of the nitrophosphate process and one of the biggest unknowns in all of this is what the capital costs are going to be and the capital costs loom very large in the ultimate comparative economics.

My experience in getting estimates of capital costs on chemical plants is that you never know till you get the bid in from the bidding contractors, it's an unknown quantity till you get the bids in. Again, I congratulate you, Mr. Brown.

Mr. Sheldrick: I have been provoked to say a few words in defense of the phosphoric acid route this morning. I have heard Mr. Strelzoff say that he has had 40 years trying to sell nitrophosphates and I have heard him on many occasions, usually from the floor, say there is nothing new in nitrophosphate processes. I also have been very closely associated with nitrophosphates, both in development work and on economic assessments, over the last 14 years and I think it's fair to say that everything I have heard within that time has been a variation on the same theme of elementary chemistry with very little new thinking.

What we find in all these assessments is that the nitrophosphate route shows some economics in materials. These papers are usually presented by engineering companies or academics, who don't have to operate fertilizer plants, and they usually finish up by saying there is some lack of flexibility. What they don't tell us is what this is worth in economic terms.

Now, my company, "Fisons", is probably about the best example you could find of a company that theoretically should be making nitrophosphates. We produce about half a million tons a year of high nitrogen compounds of two-to-one ratio, or even above. We also have waste ammonium sulfate solution from a caprolactam plant. Also, in the U.K. sulfur costs between $45 and $50 per ton.

Now, this appears to be an ideal setup for nitrophosphates. But when we go into the costs and we try to estimate what this lack of flexibility would mean to an operating company which has to cater for two peak seasonal demands with very largely differing nutrient requirements, we find that this lack of flexibility in economic terms far outweighs the savings in materials that we get from the nitrophosphates.

I think it's a very significant fact that in Europe, which is traditionally the home of nitrophosphate processes, there are more people who are changing from nitrophosphate processes to the phosphoric acid route than there are people who are building new nitrophosphate plants.

Mr. Brown: Let me comment on Bill Sheldrick's statement first. This is difficult to do since we represent Fisons and we are going to see them Monday morning. I can't get him too mad at me.

I think he's right in many respects. I think we pointed out in the paper and we tried to do this as clearly as possible, there is no direct comparison between a sulfur route and a nitric acid route. They are different processes. They produce different products.

If you want phosphoric acid, you forget nitrophosphate. If you want ammonium nitrate-ammonium phosphate, you consider nitrophosphates. If this is your product, the economics we have, as I said, showed about 40 per cent return on investment and we find nothing wrong with these numbers. These are not hairbrained numbers. These are based on our own estimates and we see nothing wrong with them and, if there is something wrong with them, we wish someone would point it out to us because we're spending a lot of money, as other contractors are, in developing and pushing these processes.

Back to Mr. Ewell's comment in talking about the 7 or 8 variants, I'm not so sure this is correct. We could go back to the campaign and quote from George Wallace and say there's not a dime's worth of difference between them, in the first half of the processes; that is, the attack and filtration portions.

As Mr. Ewell's paper pointed out, they all produce essentially the same products, from the same raw materials. It is only when you get into the separation step where there is any significant variation at all.

The Norsk-Hydro process essentially produces a one-to-one ratio product with extra ammonium nitrate. The process we are talking about, can go as low as a 0.7 ratio with ammonium nitrate by products.

Chemico's process does the same thing with a little bit different twist. It is only when you get to the back half of the process that you have these essentially three variations. As far as I am concerned, these are the only three variations which you should be considering.

Mr. Strelzoff: They talk about Europe and about nitrates. What about economics where no sulphur and study of agronomy exists, where they have separate positions to take in regard to the process of fertilizers? They cannot afford to take sulphur, even today, at $60.00 per ton. They have to make something out of phosphorus and they use nitrophosphorus. This is logical for them.

There are gentlemen here who can tell you that their companies are now producing about one million tons of nitrophosphate per year. I can mention to you one project behind the Iron Curtain where they produce 1000 tons of ammonia per day all converted to nitrophosphates without any sulphuric acid being involved. This means one and a half million tons of nitrophosphate per year.

I have no doubt that the sulfuric acid route is good for those who have sulfur and that the nitric acid route is good for those who cannot afford to buy sulfur. We in Chemico, as I said last year, don't take any position one way or another as to the sulfuric acid route or the nitric acid route.

Mr. Brown: One comment I forgot on Mr. Sheldrick's comment. If you use our definition, which pretty much coincides with Dr. Ewell's definition, not many of the European plants are nitrophosphate operations because we are using 75-85% water soluble P_2O_5, and most European plants produce about 40% water soluble P_2O_5. There are very few nitrophosphate plants existing in the world today by this definition. In fact, there is the Norsk-Hydro Plant, the plant in North Carolina, which is not on steam yet, and perhaps one plant in Czechoslovakia. All of the rest do not fit this stringent definition. These are in the 40 to 60 percent solubility range which I feel are simply just not part of the economic situation, particularly in the States or England. Where P_2O_5 is sold competitively 80-90% P_2O_5 water solubility is almost essential.

The nitrophosphate technology has improved in the last three or four years because it is only in this period that high water-soluble P_2O_5 has been offered commercially, and without water soluble P_2O_5 the processes in my opinion are worthless.

DR. LÜTH, BASF. AG., West Germany: I wish to comment on the last paper about nitrophosphate. As I told you last year we already produce nearly a million tons of nitrophosphates. We decided to leave this process when we started up a very big plant in Antwerp, our second big fertilizer plant in Europe. In this plant we decided to use the mixed acid process and to use phosphoric acid. We found our costs were so high that we had to consider that we made a mistake.

Our accounting people told us that if we had decided on an Odda process, and pumped the calcium nitrate to the ocean, it would be cheaper to produce our fertilizers than along the mixed acid process. This reasoning was due to the high sulphur prices, or increased sulphur prices in the three years from the decision to start up of the Antwerp plant.

I think the main reason why the Fison's people have another thinking about this is that in England the water soluble P_2O_5 is subsidized by the government and another thing is, which would probably be of interest to you, prices for fertilizer in England increased 5% the last time and on the continent of Europe prices decreased 5%. On the continent of Europe we use the Odda or similar processes. I think this is also an interesting view and I say this to make a complete picture about these things.

MODERATOR SAUCHELLI: That was Dr. Lüth of Badische Anilin and Soda Fabrik of West Germany. We are glad to have you here.

MR. HEMSLEY: I am a phosphoric acid man, so I am going to leave it at that.

MODERATOR SAUCHELLI: The next speaker is well known to us. He was on our program two years ago, Mr. J. D. C. Hemsley of Fisons Limited. Fisons is one of the very progressive companies of Europe. It is a privilege to have representatives from Fisons on our program.

Mr. Hemsley is going to discuss The New Fisons Process For Powder Monoammonium Phosphate. When he was here last time, he told us something about the process in the pilot plant stage. Now he is going to continue the discussion. Mr. Hemsley.

The New Fisons Process for Powder Mono-Ammonium Phosphate

J. D. C. Hemsley*

Summary

Fisons Limited new process for the manufacture of a monoammonium phosphate fertilizer intermediate known as MINIFOS is described. The process has two basic steps. The first involves the pressure ammoniation of wet process phosphoric acid and formation of a highly concentrated yet fluid ammonium phosphate solution. The second step is the flash drying of the solution to a powder material suitable for use as phosphate donor in conventional granulation plants. The manufacturing process is simple, cheap and efficient, whilst the product is compatible with all other fertilizer raw materials, including urea. MINIFOS is a high analysis material containing sixty units or more of plant food nutrient which can be easily transported in bulk. The process should be of especial interest to the phosphate rock producer as a cheaper and simpler way of transporting P_2O_5 than either phosphate rock or concentrated phosphoric acid.

Introduction

The paper presented to the 16th Annual Meeting of the Fertilizer Industry Round Table[1] described the development of a novel, cheap and efficient process for the manufacture of powder monoammonium phosphate intermediate. At that time only pilot plant work at production rates in the range 1.1-1.7 tons per hour had been attained, whilst use of the product had been limited to laboratory experimental work. Nevertheless sufficient confidence was established in both process and product to justify the construction and commercial operation of an eight tons per hour unit at Fisons Avonmouth Factory. This plant was successfully commissioned in August, 1967 and the product used to replace granular MAP hitherto employed in the manufacture of high analysis granular NPK fertilizers. During January, 1968 a second plant of sixteen tons per hour was brought on stream at Immingham, Fisons largest factory, so that a considerable proportion of Fisons ammonium phosphate requirement for the granulation of NPK fertilizers is now provided by these new facilities.

The purpose of this paper is to discuss the process as it stands at the present time with particular reference to the ways in which Fisons believes this process can be exploited for the advantage of both process operator and the product consumer.

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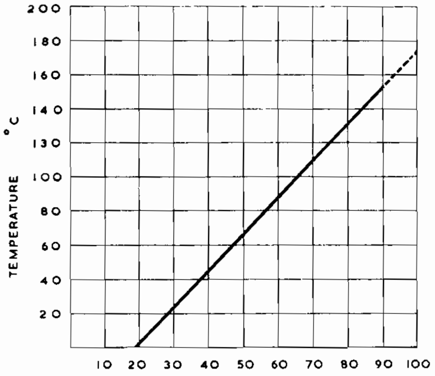

FIGURE I

SOLUBILITY OF MONO - AMMONIUM PHOSPHATE IN WATER

Process Philosophy

There are two main steps in the new process. The first step is the reaction between concentrated wet process phosphoric acid and anhydrous ammonia under conditions which allow of the formation of an exceptionally concentrated yet fluid mono-ammonium phosphate solution. The second step is concerned with the flash drying and cooling of the concentrated MAP solution to a powder or micro-prill.

Examination of the solubility data[2] (Figure I) shows that concentrated solutions containing less than ten per cent water can exist at solution temperatures above 155°C. In conventional ammonium phosphate reaction systems the operating temperature is typically 110-115°C. and, at a mole ratio NH_3:H_3PO_4 of around 1:1, the minimum water content that can be tolerated without serious problems in slurry handling is 25-30 per cent. The reaction system developed by Fisons however is designed to take advantage of the considerable boiling point elevation occasioned by operation at moderate pressure. In practice these operating conditions are 2.1 kg/cm.,^{2} gauge (45 psia), 170°C., and 9-10 per cent water content (Figure IA). The ammonium phosphate solution produced in this pressure reaction system is completely fluid, and it can thus be handled safely in pipework and simple flow systems without fear of blockage or build-up.

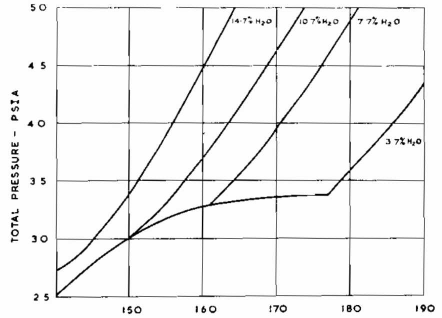

FIGURE IA

VAPOUR PRESSURE OF MAP - H_2O SYSTEM

The required phosphoric acid concentration to attain such concentrated MAP solutions is dependent on a number of factors, but chiefly, the acid temperature and whether it is "black" or clarified acid, and the physical state of the anhydrous ammonia feed. For example, gaseous ammonia with "black" phosphoric acid at ambient temperature would necessitate a concentration of around 49 per cent P_2O_5. Phosphoric acid at 90°C would need a concentration of around 45 per cent P_2O_5 under similar conditions. On the other hand the use of liquid ammonia would require a feed phosphoric acid concentration of 52 per cent.

In practice, it is usual to employ a slightly stronger phosphoric acid than the minimum in order to allow for the normally expected variations in concentration, temperature and solids content. A small quantity of water is thus added to the reactor to allow for these variations and thus maintain the reactor operating temperature constant. It has been found that the operating temperature has an important relationship with the water content of the reactor solution and the final product. A change of 2°C. affects the product water content by about one unit of per cent (Figure II).

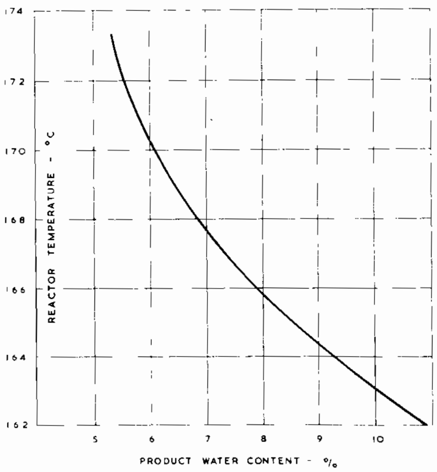

FIGURE II

EFFECT OF REACTOR TEMPERATURE ON PRODUCT WATER CONTENT

The considerable heat of reaction between phosphoric acid and ammonia is sufficient to drive off a large quantity of water as superheated steam. At an NH_3:H_3PO_4 mole ratio of 1:1, approximately 1.4 lbs of water are removed per lb of ammonia feed in the reaction step. Since the vaporization of one lb of ammonia requires little more than 0.6 lb of steam, there is more than sufficient waste steam available for this purpose and a notable steam economy in the preceding phosphoric acid concentration stage is entirely viable.

The partial vapour pressure of ammonia above concentrated ammonium phosphate solutions where the mole ratio NH_3:H_3PO_4 does not exceed 1:1 is negligible, even at temperatures of 170°C. Since the reaction system is always operated at a pH of 3.5-4.0, the process can operate with a high nitrogen efficiency without the need for a scrubbing system, provided that sufficient mixing is designed into the reactor. The pilot plant data showed that a nitrogen efficiency well in excess of 99.5 per cent could be returned. This experience has been adequately confirmed on the full-scale plants now in operation.

In the second step, the concentrated MAP solution is ejected from a nozzle into an environment at ambient pressure. Under these conditions, further water is flashed off and in doing so the MAP solution is rapidly cooled and solidifies into small particles. The product becomes further cooled by the natural draught air stream as it falls down the tower and it is recovered as a powdery material containing approximately six per cent water.

The overall quantity of water driven off in the process is slightly in excess of 1.7 lbs per lb of ammonia feed. The water lost in the flash drying step represents therefore some 20 per cent of the total. Since however this amount of water is not sufficient to saturate the air-flow through the tower, no

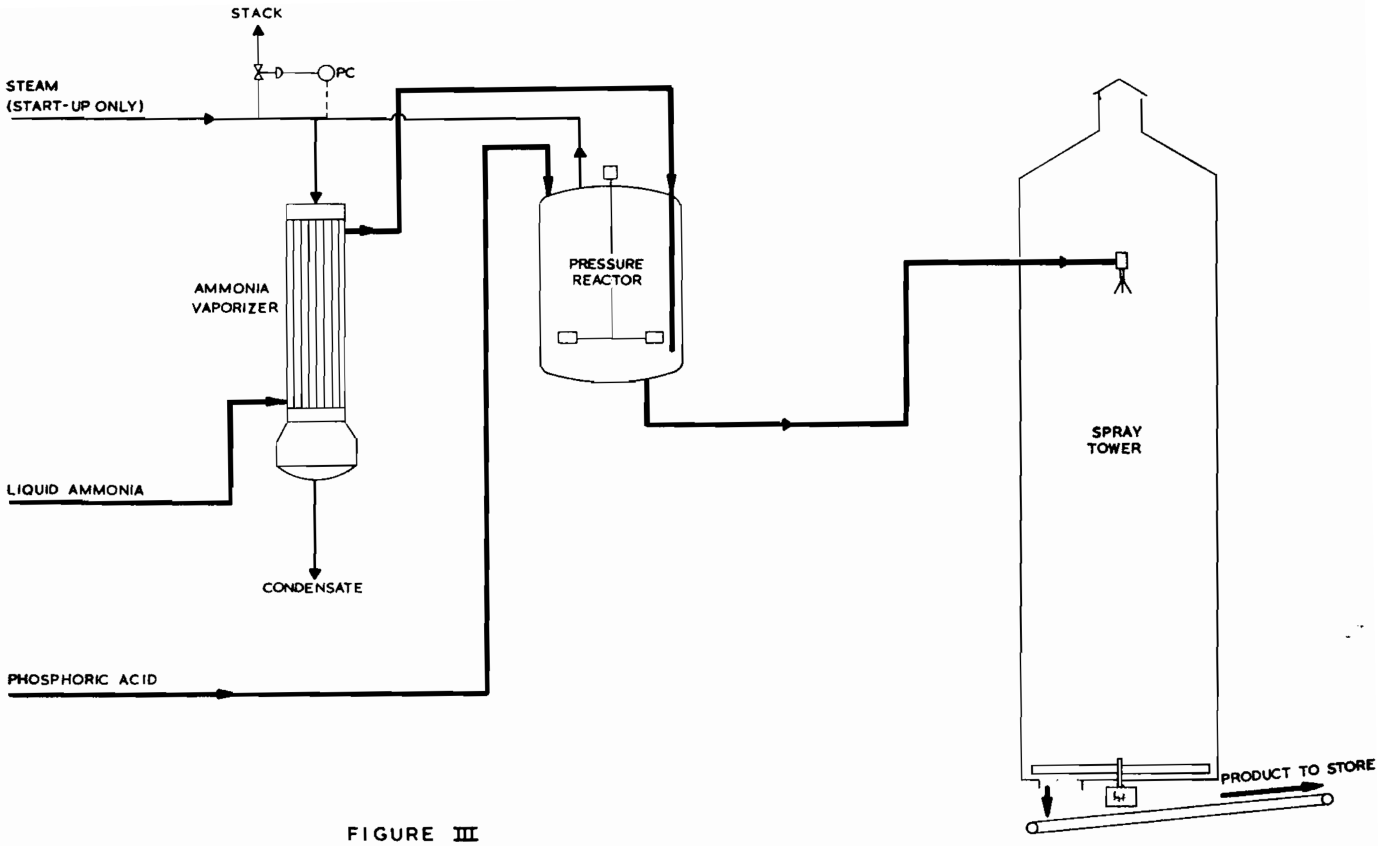

FIGURE III

'MINIFOS' PROCESS

plume is visible from the exhaust stack.

Process Description

A simplified flowsheet is shown in Figure III. Wet process phosphoric acid is pumped to a stirred tank reactor capable of operating at up to 3 kg/cm.,[2] gauge. The reactor is fitted with a turbine impeller and wall baffles to promote a high degree of agitation. The material of construction is generally 316 ELC or its equivalent unless a significant chloride content is present. In this case the material may be of the type typified by Incaloy 825.

Ammonia gas from a vertical shell and tube vaporizer is piped to the base of the reactor where it is injected into the eye of the reactor impeller. The vaporizer is supplied with waste superheated steam from the reactor except at start-up when boiler steam is required for a few minutes. Surplus steam from the reactor is let down through a back-pressure control valve and it is then vented to atmosphere, condensed, or passed to another process unit. Part of the vaporizer condensate is returned by means of a pump to the reactor, the flow being regulated to maintain the reactor temperature, and thus the product water content, constant at the desired level.

Where stronger acid of around 52 per cent P_2O_5 is available, there is no need to vaporize the liquid ammonia and this represents a relatively considerable saving in equipment and instrumentation. As with gaseous ammonia, the liquid is injected into the eye of the impeller. Water for reaction temperature control has to be supplied in this case from outside the plant battery limit.

The pilot plant data have shown that very high steam release rates from the reactor could be achieved without entrainment. The highest rate noted was 235 lbs/hour.ft.[2] Full scale plants have been operated at steam release rates of 160 lbs/hour.ft.[2] without entrainment and there is evidence to suggest that higher loadings can be expected in the future. There seems little doubt that pressure ammoniation does enable the use of smaller cross-sectional area reactors for MAP production than is possible with atmospheric ammoniation.

The concentrated MAP solution flows from the bottom of the reactor and through steam jacketed pipework to a special nozzle at the top of a short natural draught tower. This nozzle combines the duty of flow control and spray formation. The nozzle has a pneumatically actuated valve plug which is positioned by automatic control to maintain the solution in the reactor at a constant and optimum level. The level control primary element used for this purpose is of the type based on the buoyancy of a submerged float. Considerable changes which can occur in the density of the reactor contents due to changes in the operating conditions affect the output from this type of level element, and a supplementary device based on electrical conductivity is employed to determine the absolute level so that the main control system can be reset as necessary.

The tower itself is a very simple structure which can often be installed within an existing process unit building. The tower walls

Table I
Comparative Data

	Fisons Powder Map Process	Conventional Granular Map Process
Material properties		
Water Content	5-7%	0.5%
Size Range	0.1-1.5 mm	1-3 mm
pH	3.5-4.0	4.0-4.5
Utility Requirements		
Steam	200 lbs per hour	100 lbs per hour
Water	Nil	10 imp. gallons /ton
Power	2 kwh/ton	24 kwh/ton
Fuel	Nil	2.5 imp. gallons/ton
Labour Requirements	0.5 men per shift	4 men per shift
Capital Requirements	£60,000	£400,00
Maintenance	5% per annum	7½% per annum

are fabricated from plastic covered canvas or similar material tied back to a supporting structure. The top of the tower is vented to atmosphere through a stack or louvres. The bottom of the tower is fitted with air entry louvres and a simple rotary scraper for product recovery.

The process is adequately instrumented to ensure push button starting and stopping, whilst the process conditions are fully automated to ensure stable operation with the minimum of attention. Phosphoric acid is metered by means of an electro-magnetic flowmeter; ammonia by orifice plate. The make-up flow is automatically regulated to maintain the reactor temperature constant, and the vapour space pressure is also maintained constant by automatic means. A simple pH determination by means of test papers is the only local analytical control required.

Utility and Capital Requirements

Hitherto the most important source of MAP for use by Fisons as an intermediate in the manufacture of high analysis NPK granular fertilizers has been pin-head granular material manufactured itself on a granulation plant. In its use, the material has necessitated crushing treatment to reduce the larger granular material and to prepare it for subsequent granulation with ammonium nitrate solution, potash, superphosphates, and ammonium sulphate as required by the particular grade formulation.

The new process represents an important technological and economic step forward in the manufacture of MAP intermediate. The comparative data presented in Table I serve to indicate the most important advantages and differences, and are based on a process unit capacity of 30 long tons per hour.

Properties and Use of Minifos

Following the successful commissioning of the two Fisons units at Immingham and Avonmouth, and the establishment of the product as an important fertilizer intermediate, the Board of Fisons Limited approved the name MINIFOS for the new material. This name is now formally registered with the Board of Trade.

Many thousands of tons of MINIFOS have now been manufactured by the two units operating within the Fisons organization. A third unit has recently been successfully commissioned for a company in the Netherlands. At the present time, four other plants are under construction in Spain, Australia and South Africa.

MINIFOS is stored in bulk and can be handled by all the conventional mobile and fixed handling equipment used in the fertilizer industry. Immediately after manufacture the material takes on a slight initial "heat-set" but there is no difficulty in recovery from bulk store and its storage properties can be generally regarded as equivalent to cured superphosphates and other fertilizer raw materials. The absence of fine dust during handling operations is particularly noteworthy. The product is non-hygroscopic, and under normal storage conditions will tend to lose moisture.

The most important properties of MINIFOS are listed below:

Analysis 12-56-0 (dry basis, settled Morocco acid)
P_2O_5 Water Solubility : 96 per cent
Water Content 6 per cent
Size Range : Substantially in the range 0.1-1.5 mm.
Bulk Density : 53 lbs per cubic ft — loose
59 lbs per cubic ft — tamped
Angle of Repose : 38 degrees
pH Number : 3.5-4.0 (10 per cent solution)

Apart from the advantages of extremely low capital investment for the process plant, and the minimal operating costs, there are other important economic and process reasons why considerable benefit can be derived from the use of this material.

Firstly, MINIFOS can be used to augment or replace completely the traditional superphosphates to satisfy the increasing demand for more concentrated fertilizers. In this respect its physical form is eminently suitable for use as an intermediate since it requires no more treatment than that accorded to the superphosphates and other solid fertilizer raw materials at the intake of the consumer granulation plant. As a solid material it embodies all the advantages of a P_2O_5 carrier such as single or triple superphosphate, in that it can be economically manufactured at a larger central site and distributed cheaply by bulk carrier to satellite granulation plants, but with the added advantage that it carries at least sixty units of plant food per ton.

Fisons has incorporated this material into a very wide range of fertilizers and it has been found to

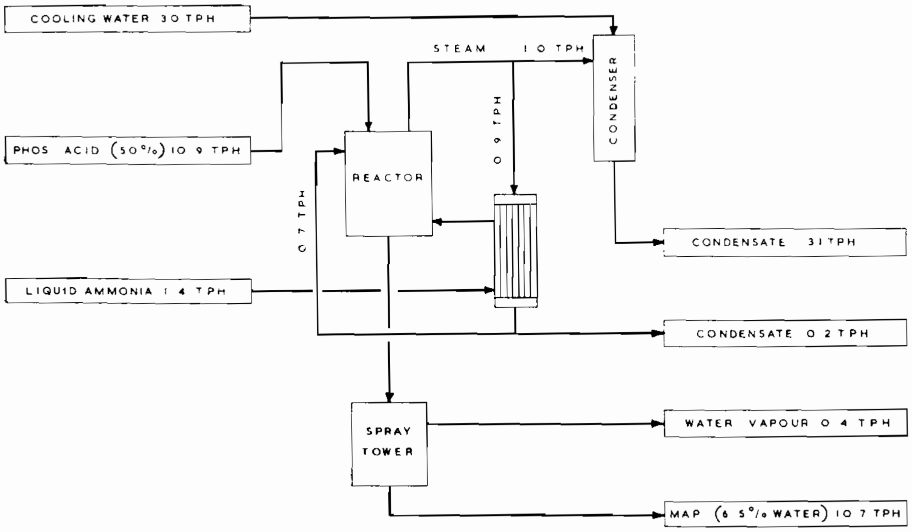

FIGURE IV

'MINIFOS' PROCESS – MATERIAL BALANCE

be entirely compatible with all conventional liquid and solid components such as urea, ammonium nitrate solution, ammonium sulphate, superphosphates and potash. A typical range of fertilizers would be:

19-19-19	20-10-10
17-17-17	10-15-20
15-15-15	8-20-16
14-14-14	13-13-20
12-24-12	16-18-14

The use of MINIFOS plays an important role in ensuring the maximum output from the granulation plant. This is particularly so where the granulation step is liquid phase controlled, due to the presence of other raw materials containing significant levels of water, for example ammonium nitrate solution. In this respect powder MAP has a significant advantage over MAP provided in the form of slurry from pre-neutralization facilities. The conventional Fisons granulation plant is capable of manufacturing the higher analysis fertilizers at fines recycle ratios no higher than 2:1 whilst grades such as 15-15-15 and 13-13-20 require recycle ratios in the range of 1-1.3:1. In all cases, the size distribution of fertilizers made on Fisons ten granulation plants is substantially within the range 1.6-3.4 mm.

Perhaps one of the most important considerations which enhances the attractiveness of solid mono-ammonium phosphate intermediate is the simple nature of the consumer granulation plant. It has already been said that the MAP manufacturing process does not need expensive ammonia recovery equipment. This also applies to the NPK granulation process. Furthermore, the use of MAP does not limit drying temperatures so that lower product water contents can be obtained much more readily than with fertilizers containing diammonium phosphate. This is becoming an extremely important consideration as the increasingly high standards for product storage became prevalent. In the UK, for instance, it has become necessary for granular fertilizers to be stored for periods up to nine months before use due to the very uneven market conditions. Fertilizers such as 17-17-17 for example need to be dried to less than 0.3 per cent in order to obtain satisfactory storage properties.

One of the most important groups of fertilizers during the next few years, especially in the Middle and Far Eastern areas, is likely to be the urea-ammonium phosphate and urea-ammonium phosphate-potash system. Hignett[3] and others have urged this prob-

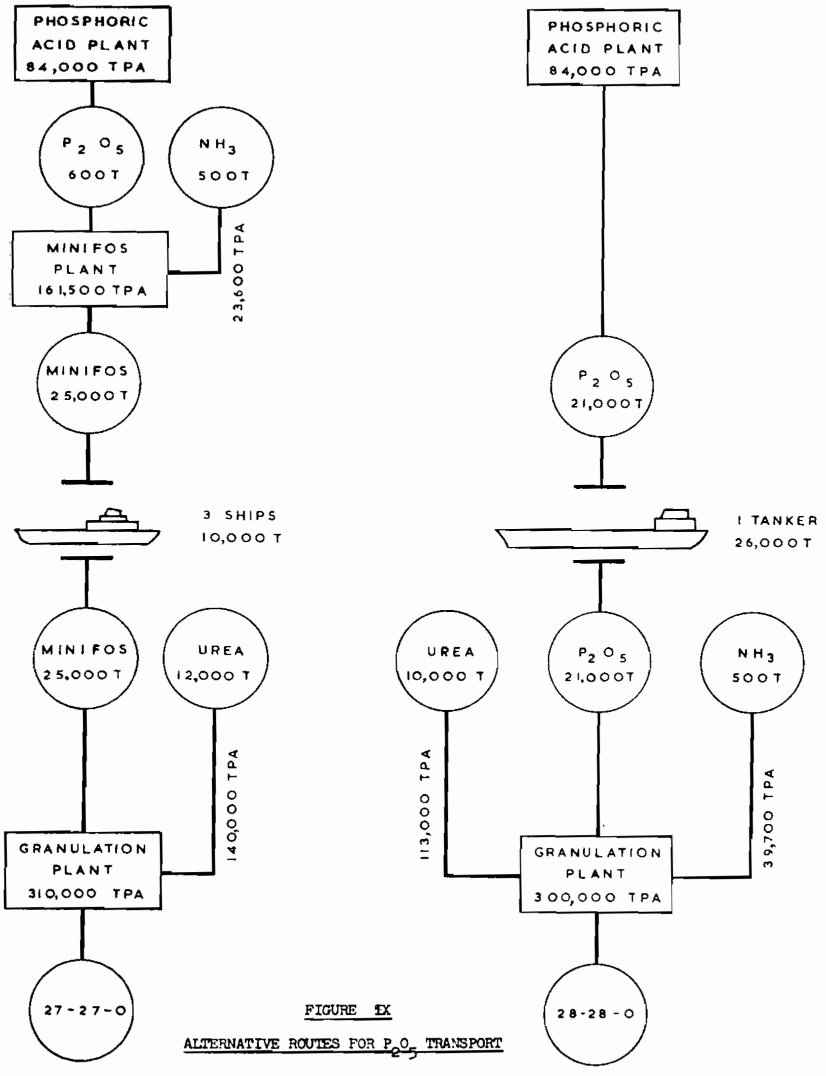

FIGURE IX

ALTERNATIVE ROUTES FOR P_2O_5 TRANSPORT

FISONS MINIFOS ROUTE

CONVENTIONAL ROUTE

Table II
Comparative Costs for Alternative Routes

	Minifos Route	Conventional Route
Capital Costs	£1,600,000	£2,300,000
Raw Material Costs	£8,700,000	£8,500,000
Operating Costs	£ 125,000	£ 250,000

ability for some time on the broad bases that these products have an exceptionally high nutrient content, are agronomically acceptable in these particular areas, and are free from burning or explosion hazards. There are however two other factors which are significant but do not appear to have been developed seriously as yet.

Firstly, there already exists in the "emergent" areas of the world a considerable internal urea capacity. This capacity will be augmented within the next few years by plants already under construction or in the last stages of planning. Urea has become and will continue to be a principal form of nitrogen plant food. The reasons for this are clear: urea is the cheapest and most concentrated form of solid nitrogen available, it is agronomically effective, and the basic raw material is frequently indigenous.

Secondly, the manufacture and use of phosphatic fertilizers has lagged behind that of nitrogenous fertilizers. There is now a growing understanding that properly balanced complete fertilizers are essential to the proper exploitation of the soil and the new high yield seed varieties. Some urgency now exists to redress the balance. In this respect the evaluation of the most appropriate process routes for compound NP and NPK fertilizers should take account of the existing or planned nitrogenous fertilizer capacity. As an illustrative example it is useful to consider the fertilizer industry in Pakistan. After the completion of the third five year plan proposals, which involve a very considerable nitrogen expansion, the country's requirements will be essentially satisfied for some years to come, with the exception of the requirements for phosphate. This need has now become fully realized by the relevant Organizations and Agencies within and without Pakistan, and various basic schemes for at least minimising the phosphate deficiency by means other than import of finished fertilizers are being discussed. Analogy with European history shows that the most viable and useful routes will be those which offer the phosphate plant food in combination with nitrogen and, later on, potash.

Of the various routes available, the urea-ammonium phosphate system appears to have the most attractive advantages. The urea-superphosphate system suffers from the fact that the two components are basically incompatible and it does not appear to be a practical process route particularly when high levels of urea are used. The nitro-phosphate route requires additional installation of nitrogen capacity and therefore cannot assist the basic problem of nitrogen-phosphate imbalance. Apart from this, there are other serious disadvantages of the process.

TVA has carried out extensive development work on methods for producing urea-ammonium phosphate fertilizers and much of this has been published[4]. Fisons Limited has also carried out research and pilot plant work on this system with particular reference to the use of MINIFOS as the phos-

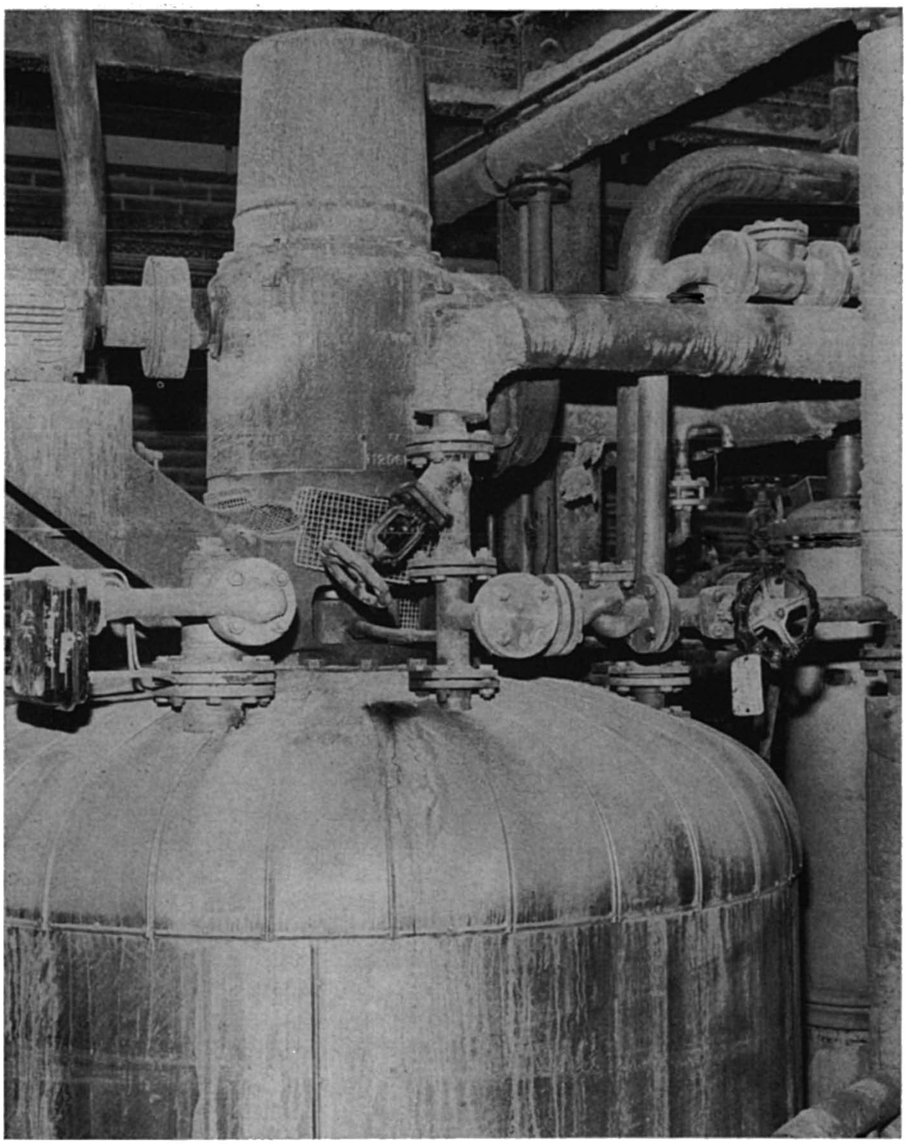

Figure 5
Top of Pressure Reactor with Agitator Drive

phate donor. Briefly, this work has shown that the granulation of solid urea with MINIFOS and, as required, potash can be carried out in the Fisons conventional granulation process with only modest alteration. The granulation step can be operated at a recycle ratio in the range 1.5-2:1. Drying rate experiments have shown that this step in the process is easier to accomplish than with ammonium nitrate based fertilizers even though reduced temperatures have to be used because of the lower melting point of the urea-ammonium phosphate system. Product storage and hardness properties are as good as those of equivalent fertilizers based on the ammonium nitrate-ammonium phosphate system. When MINIFOS is used, there is no measurable ammonia loss and the process is therefore much simplified by the absence of ammonia recovery equipment.

A typical scheme showing how MINIFOS could be used to build up the granular N-P requirement for a country such as India where phosphate in one form or another has to be imported is shown in Figure IX. For comparative purposes a scheme representing a somewhat different but frequently discussed route involving phosphoric acid transport is also shown.

In both cases it is assumed that a phosphoric acid manufacturing unit is situated at a large phosphate rock mining area such as Florida or Morocco. In the MINIFOS route there is no extensive phosphoric acid storage, since the wet process acid is immediately converted to powder intermediate without the need for clarification and shipped by conventional sea transport to the consumer country where it is incorporated with urea and perhaps potash in a simple granulation plant such as that operated by Fisons. The alternative route necessitates the transport of phosphoric acid in specially constructed ships with little likelihood of suitable return cargoes being available. This form of transport has not yet been carried out on the scale needed for the size of consumer factories now envisaged. It would certainly be necessary to utilize clarified acid in order to minimise settling during transport. Large and expensive phosphoric acid storage facilities are required at both terminals. Furthermore, the consumer granulation plant needs phosphoric acid neutralization facilities and extensive ammonia recovery equipment which are expensive. The operation of this type of plant is also more complex.

Capital, raw material and operating costs have been calculated for these two routes and a summary is shown in Table II.

Notes:

1. Capital costs are based on battery limit process units and storage facilities but excluding the phosphoric acid plant, ammonia storage and granular product storage, these being common to both routes.
2. National capital costs are included for terminal facilities.
3. Costs for general off-site facilities are excluded.
4. Raw material and intermediate costs are those payable by the granulation plant operator.
5. It is assumed that the granulation plant site is at or close to the urea plant facilities.
6. Variable operating costs only are indicated.

The raw material costings have been based on current data available to Fisons. The difference in capital cost is particularly noteworthy and this is due mainly to the lower investment required for storage of P_2O_5 as solid ammonium phosphate. The increase in the raw material cost for the MINIFOS

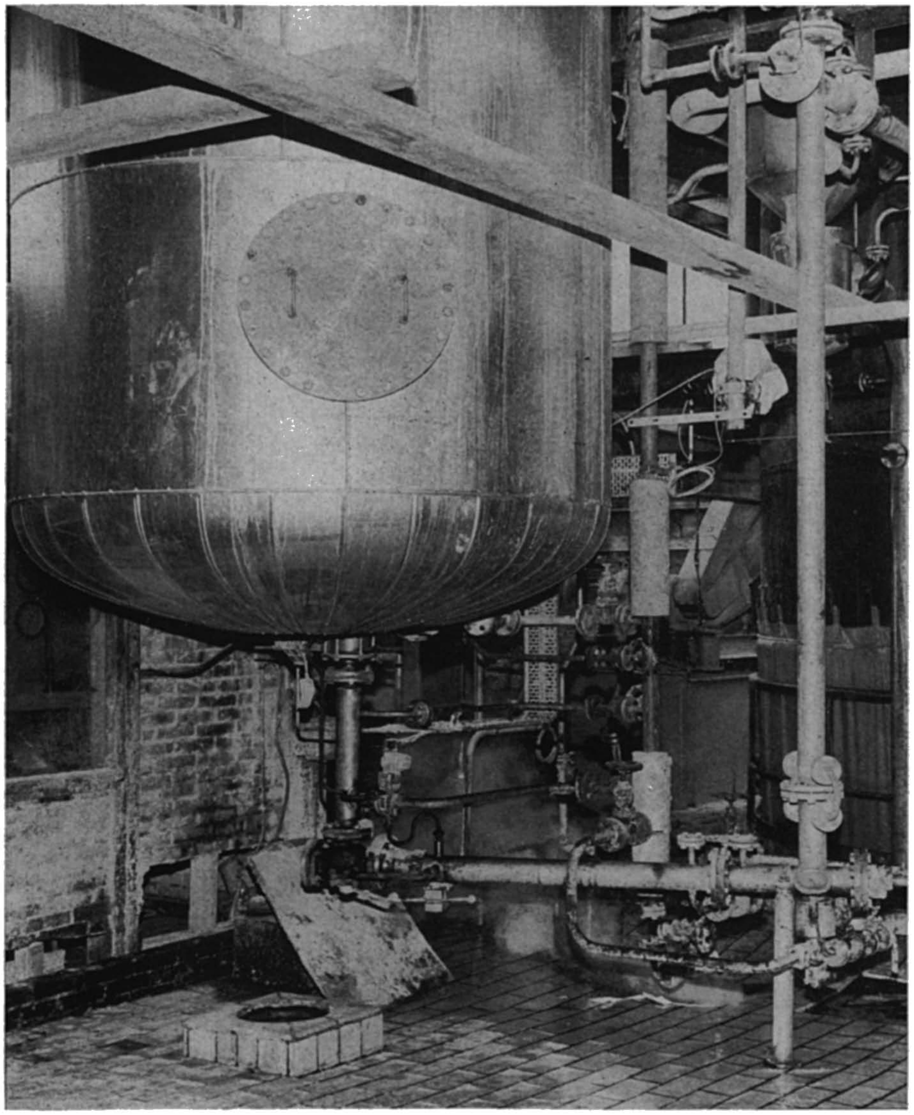

Figure 6
Bottom of Pressure Reactor Showing Solution Pipework

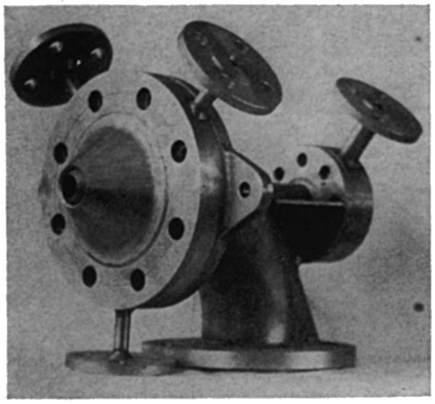

Figure 7
Special Nozzel Used for Ammonium Phosphate Solution

route follows from the higher urea requirement, although the P_2O_5 cost at the consumer factory is significantly cheaper.

If we assume however that the cost of servicing the additional capital in the form of maintenance, depreciation and return on capital is equivalent to about 30 per cent of the capital savings it can be seen that the net result of operating, materials and capital cost requirements is in favour of the MINIFOS route.

For areas where ammonium phosphate is clearly agronomically more satisfactory in the form of the mono salt, then the MINIFOS route becomes even more attractive since the raw material consumption for the additional nitrogen is then the same for both routes.

Patents

The MINIFOS process, and its apparatus, together with processes using MINIFOS described in the present paper form the subject matter of applications for patents and accepted patents in the name of Fisons Limited in the principal countries of the world.

Acknowledgements

The Author wishes to thank the Board of Fisons Limited, Fertilizer Division, for permission to publish this paper. Thanks are also due to Windmill Fertilizer Works, Holland, for permission to publish Figures V, VI, VII and VIII.

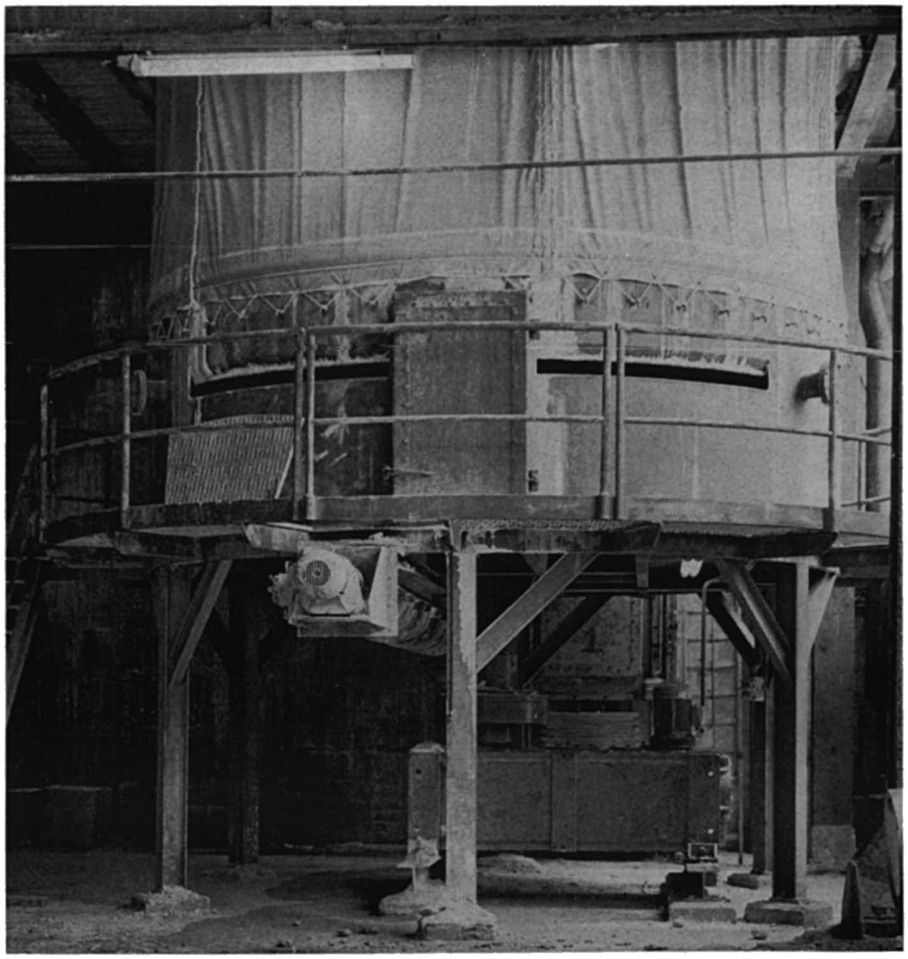

Figure 8
Base of the Spray Tower with Motor and Gear Box Drive to the Rotary Scraper

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MODERATOR SAUCHELLI: Thank you, Mr. Hemsley, for an excellent paper and very ably presented. We have time for one or two questions.

MR. WILLIAM MCGRATH (Gulf Oil): What do you feel for additional ammoniation as far as the monophosphate is concerned when you are using a granulation plant. Can you put more ammonia in?

MR. HEMSLEY: We have found that "Minifos" can be readily ammoniated in rotary drum granulator equipment. One of the problems, of course, in doing this is that there is some slip of ammonia from the granulator which has to be recovered by scrubbing equipment.

The sort of future we see for "Minifos" is as a carrier of P_2O_5 with its manufacture at a central site and subsequent transportation across the oceans of the world. Without phosphoric acid being available there is a problem in picking this ammonia up but we feel that the simplification of the granulation plant and the overall economy of the route described in the paper more than outweigh this particular point.

A MEMBER: Did you tell me that you actually can't figure on any additional ammonia, is that what you said?

MR. HEMSLEY: No, the material will absorb ammonia very readily. There is no problem from this standpoint. However, as you know, in the conventional TVA type ammoniation system there is some ammonia slip which has to be recovered and, if phosphoric acid isn't available at the particular site, there could be a problem in doing this.

SAME MEMBER: My question is what do you figure as far as the degree of ammoniation for this product when used in a conventional TVA type granulation plant?

MR. HEMSLEY: We have ammoniated this material up to the DAP level, with analysis of the order of 19-50-0.

SAME MEMBER: But that's with recovery of ammonia, right?

MR. HEMSLEY: Yes.

SAME MEMBER: I'm talking about conventional ammoniation.

MR. HEMSLEY: In conventional ammoniation, I would say we could go to perhaps about a mole ratio NH_3 to H_3PO_4 of 1.3 to 1 in the granulator without significant ammonia loss.

SAME MEMBER: Thank you.

ANOTHER MEMBER: In your ammoniation, have you had any evidence of conversion to non-ortho products?

MR. HEMSLEY: We haven't examined this problem in any detail but I can't imagine that this would occur to any significant extent.

MODERATOR SAUCHELLI: I shall now return the meeting to Billy Adams of our Executive Committee.

MODERATOR ADAMS: I hope that our program continues to be as lively as we switch to some other subjects. Of course, we have been talking about water soluble P_2O_5, citrate soluble and now we move along into polyphosphates.

Our next paper by Mr. Frank P. Achorn, Head of Product Improvement and J. S. Lewis, Jr., Chemical Engineer, TVA, Muscle Shoals, Alabama covers "Uses for Solid Ammonium Polyphosphate In Bulk Blending, Granulation, and Fluid Fertilizers". Mr. Frank Achorn, no stranger to the Round Table, will discuss the paper. Frank, please.

Uses for Solid Ammonium Polyphosphate in Bulk Blending, Granulation and Fluid Fertilizers

Frank P. Achorn* and J. S. Lewis, Jr.**

TVA started demonstration-scale production of solid ammonium polyphosphate (APP) in 1966 at Muscle Shoals. This material has the highest analysis (77 units of plant food) of any solid material now in the production stage. This paper will describe the product in detail, point out its usefulness in the production of clear liquid, suspension, and bulk-blended fertilizers, and briefly discuss its use as a granulation aid.

Solid ammonium polyphosphate is a completely water-soluble material with all the nitrogen in the ammonium form and about 45 percent of the phosphorus in the ortho form as monoammonium phosphate, about 51 percent as ammonium pyrophosphate, and the remaining 4 percent as more condensed phosphates. Figure 1 is a sketch of a TVA process for the production of solid ammonium polyphosphate from superphosphoric acid and ammonia. In this process the furnace superphosphoric acid, 77 percent P_2O_5, is reacted with ammonia under moderate pressure and at elevated temperatures. The resulting melt is granulated with recycle fines in a pug mill, and the product from the pug mill is screened and cooled.

Granular ammonium polyphosphate is free flowing. Results of storage tests indicate that it stores well in bulk. Bulk storage tests in Hawaii indicate that this material will store as well as diammonium phosphate 18-46-0 under humid conditions. Incidentally, the material shipped to Hawaii was barged in bulk to New Orleans, transferred to a steamer, and shipped in bulk to Hawaii. The company that used the 15-62-0 reported no difficulty in the bulk handling of the material. In solution polyphosphates of 15-62-0 can complex certain metallic elements such as iron, zinc, and manganese which would otherwise precipitate and settle out of solution. This property, commonly referred to as sequestration, results in advantages for the use of ammonium polyphosphate in the production of liquid fertilizers.

Some of the chemical and physical characteristics of 15-62-0 are shown in the following tabulation:

Approximate chemical contents	
Ammonium polyphosphates, %	55
Monoammonium orthophosphate, %	45
Total nitrogen, % N	15
Ammonium nitrogen (NH_4^+), % of total N	100
Total phosphorus, % P_2O_5	62
Available phosphorus, as % P_2O_5	62
Available phosphorus, as % P	27
Water-soluble P_2O_5, %	100
Orthophosphate P_2O_5, % of available P_2O_5	45
Polyphosphate P_2O_5, % of available P_2O_5	55
pH of saturated solution at 80°F.	5.6
Acid-forming potential, lbs. $CaCO_3$ per ton	1,400
Moisture content, %	nil
Bulk density (loose pour), lbs. per cu. ft.	60
Size distribution (Tyler screen), mesh	−6 +16

The product size is comparable to that of any well granulated material, and its product moisture is nil.

Clear Liquid Fertilizers

Solid ammonium polyphosphate can be used to produce 10-

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[**] Chemical Engineer, Tennessee Valley Authority, Muscle Shoals, Ala.

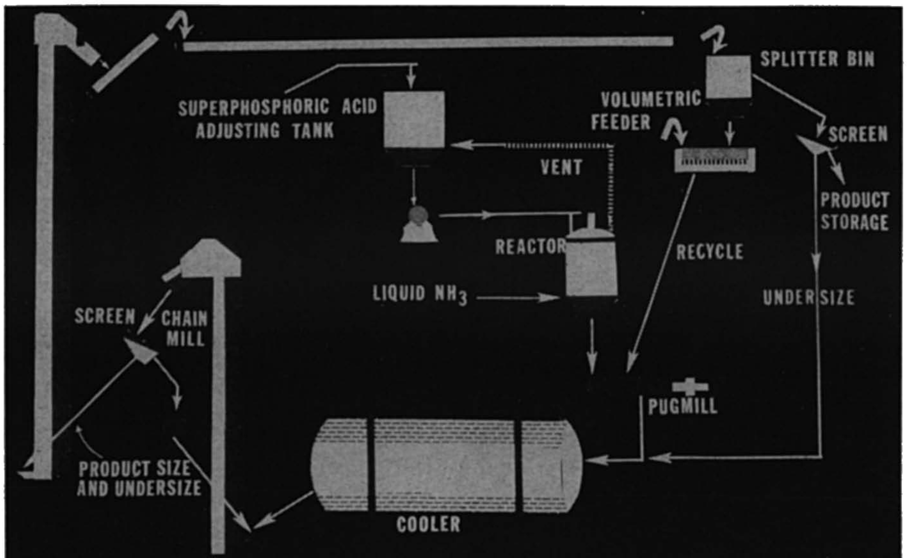
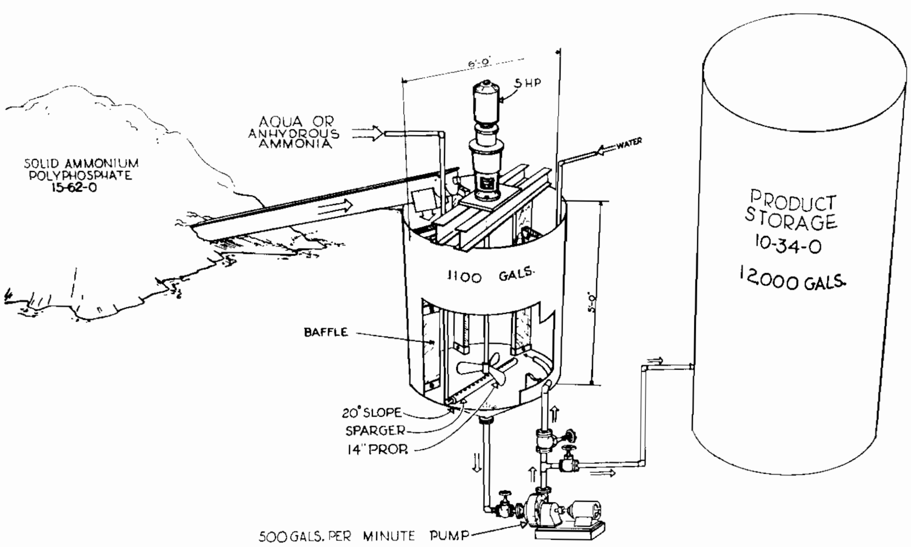


FIGURE I
AMMONIUM POLYPHOSPHATE PROCESS

34-0 and other clear liquids which are normally produced from 10-34-0 solution and potash. The production of 10-34-0 from ammonium polyphosphate should prove to be one of the most popular uses for this material. The 10-34-0 is produced by reacting 1,097 pounds of ammonium polyphosphate with 43 pounds of ammonia and 860 pounds of water. Vigorous agitation is required to dissolve the material in a reasonable length of time. A suitable mix tank with the necessary appurtenances for carrying out the reaction is shown in Figure 2. The three main features of this mix tank are a cone bottom, a 500-gallon-per-minute recirculation pump, and a 5-horsepower agitator which has a propeller 14 inches in diameter. The tank and piping may be fabricated from mild steel. The tank should be mounted on scales so that raw materials may be weighed in it; however, some operators may prefer to meter the liquid materials to the mix tank.

The best mixing procedure for producing 10-34-0 is to add water to the mix tank, follow it with solid ammonium polyphosphate, and then immediately add the aqua or anhydrous ammonia. After dissolution and ammoniation of the ammonium polyphosphate, the 10-34-0 solution should have a pH of about 5.8, a specific gravity of about 1.37, and a viscosity of 60 centipoises at 80°F. This pH and specific gravity can be used as an alternate control of the production of the 10-34-0 solution. The 10-34-0 material produced from ammonium polyphosphate is as clear as water, and it can be stored at temperatures below 0°F. without crystallization difficulty. It also has excellent prolonged storage characteristics.



PRODUCTION OF CLEAR 10-34-0 FROM SOLID AMMONIUM POLYPHOSPHATE
FIGURE 2

One company has recently used 15-62-0 to produce an 11-37-0 grade which stored without salting out at 20°F.

Several cold-mix operators have found it convenient to produce N-P-K mixtures directly from ammonium polyphosphate, aqua or anhydrous ammonia, urea-ammonium nitrate solution, and potash. Some of the grades which they have produced in this manner are 16-16-0, 7-21-7, 5-10-10, 20-10-0, 8-8-8, 8-16-8, and 10-15-5. In each of these grades the P_2O_5 was ammoniated to an $N:P_2O_5$ weight ratio of 1:3.4. This is a ratio of maximum solubility for ammonium polyphosphate solutions.

Many companies that have bulk blending plants would like to have facilities for the production of liquid starter grades. However, they do not want to invest in a complete liquid cold-mix facility. Ammonium polyphosphate fills the needs of these blenders quite well, because the only equipment needed to produce liquid starter grades is a mix tank and perhaps one or two storage tanks. Such companies already have solid storage space for the 15-62-0 and potash. The cost of the additional equipment for manufacturing liquids is estimated to be less than $9,000. Some blenders have already installed these facilities and are producing a 7-21-7 starter grade.

Ammonium polyphosphate can be combined with wet-process or spent phosphoric acid to produce clear liquid fertilizers. It can be used in this manner, because the pyrophosphates in 15-62-0 sequester or dissolve the impurities which would normally precipitate from wet-process and spent phosphoric acids when they are ammoniated.

Ammonium polyphosphate is particularly adapted to this process, because it has the highest pyrophosphate content of all the polyphosphate products which are being produced for the fertilizer market. In most instances the wet-process acid—and in all instances the spent phosphoric acid—is more economical than furnace phosphoric acid. Therefore, use of 15-62-0 in combination with the less pure acids usually provides some saving to the liquid fertilizer producer.

Field tests have shown that in the production of nonpotash grades adequate sequestration is obtained by supplying 20 percent of the total P_2O_5 in the form of 15-62-0. In grades containing potash 30 percent of the P_2O_5 usually must be supplied by 15-62-0.

A large percentage of the plants which now produce liquid fertilizers are of the hot-mix type. The hot-mix plants involves the neutralization of phosphoric acid with ammonia and the addition of supplemental materials to give the desired formula. The heat of neutralization gives a hot mix. These plants usually have coolers to prevent excessive boiling in the mix tanks. With the use of 15-62-0 it is possible to produce N-P-K mixtures by the hot-mix method without a cooler. Figure 3 is a sketch of such a plant which would use wet-process phosphoric acid, 15-62-0, urea-ammonium nitrate solution, and potash. The investment for a plant of this type should be about $25,000. The investment for a conventional hot-mix plant would be about twice this cost. The need for a cooler is eliminated by the use of the proper quantities of ammonium polyphosphate, phosphoric acid, and ammonia to prevent the release of enough heat to cause excessive boiling in the mix tank.

Some companies find that it is possible for the semihot-mix plant to use phosphoric acids of lower concentrations — such as spent phosphoric acid with 22 to 24 percent P_2O_5—and still produce high-analysis liquids or suspensions. Tests indicate that when N-P-K mixtures are produced by formulations in which 50 percent of the needed P_2O_5 is supplied by 15-62-0 and the remainder by wet-process or spent acid the resulting product temperature is in most instances less than 160°F. Therefore, when 15-62-0 is used, it is possible to produce clear liquid grades from low-cost raw materials (wet-process or spent phosphoric acid) in a mix plant having a low capital investment.

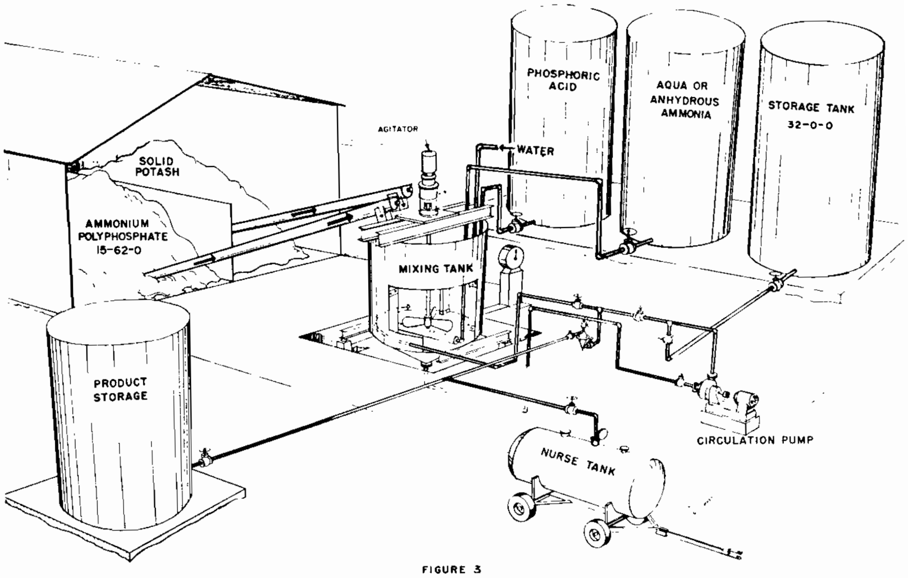


FIGURE 3

SEMI-HOT MIX PLANT

FOR PRODUCTION OF CLEAR LIQUIDS OR SUSPENSIONS FROM 15-62-0, PHOSPHORIC ACID AND AMMONIA

Suspension Fertilizers

The plant shown in Figure 3 has also been used for the production of suspension grades. One company in the Mid-West is now using spent phosphoric acid in a semihot-mix plant of this type to produce a 5-15-30 potash base suspension grade. The base suspension has been used to produce other high-analysis suspension grades. Other companies have used conventional cold-mix plants such as the one shown in Figure 4 for the production of suspension mixtures. When suspensions are produced in either a semihot-mix or a cold-mix plant, it is advisable for the plant to be equipped with a mix tank which has violent agitation and a cone bottom. It is also advisable that the potash be screened prior to its use in the mixture and that the product from the mix tank be strained. The ammonium polyphosphate which was shipped to Hawaii was converted to suspensions in a cold-mix plant. Some grades produced in this plant from 15-62-0 were 8-32-5, 11-28-11,

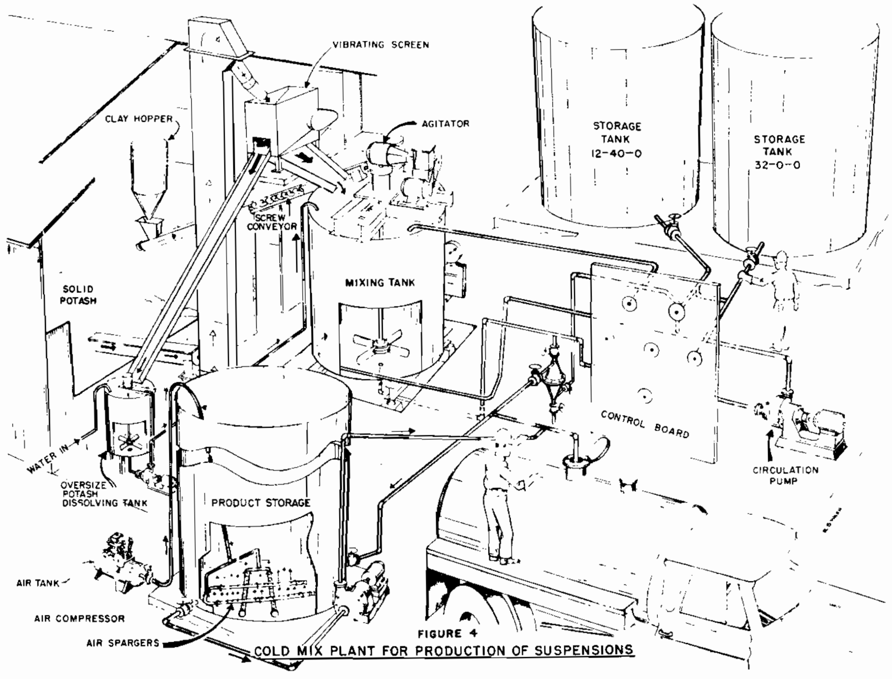


FIGURE 4

COLD MIX PLANT FOR PRODUCTION OF SUSPENSIONS

12-24-15, and 8-14-6-4MgO. Some companies in the continental United States have used 15-62-0 in conventional cold-mix plants to produce grades such as 14-14-14, 11-22-11, 9-18-18, 3-10-30, and 7-21-21. One particular advantage in using 15-62-0 in the production of suspensions is in the manufacture of fertilizers for tobacco. Bench scale tests have shown that 15-62-0 can be used with potassium nitrate, magnesium silicate, clay, and water in the production of a 6-12-18-2Mg tobacco-grade fertilizer. This suspension probably would not have satisfactory prolonged storage characteristics; however, bench scale tests indicate that if it is applied shortly after it is produced no difficulties are encountered in its application.

Some companies have used low-pressure ammonia-ammonium nitrate-urea solutions, together with 15-62-0 and potash, in the production of clear liquid or suspension mixtures. Since only a small amount of ammonia is required, the ammonia used in these solutions may be used to bring the 15-62-0 to the proper ammonia-nitrogen-to-P_2O_5 ratio without seriously affecting the salting-out temperature of the clear liquid grades or the viscosity of the suspensions. Since many ammoniating low-pressure direct-application nitrogen solutions are available and their production cost is less than that of urea-ammonium nitrate solutions, perhaps these nitrogen solutions can be used now in conventional cold-mix plants with 15-62-0 to produce fluid fertilizers by the cold-mix process.

Bulk Blends

The high plant-nutrient content of ammonium polyphosphate aids in the production of high-analysis bulk blend grades such as 12-24-24, 10-20-30, and 9-27-27. Urea is compatible with ammonium polyphosphate, and when it is used with 15-62-0 in dry blending, grades such as 20-20-20 and 36-12-0 can be produced. Since nitrogen and phosphorus are chemically bound in the same granule, a more homogeneous bulk blend can be prepared. No difficulty should arise in blending ammonium polyphosphate with other fertilizer materials. Only one company—located in Alaska—has used solid ammonium polyphosphate in bulk blending. This company reports no difficulty in the use of this material in blending.

Granulation

TVA has conducted a limited number of granulation tests in continuous and batch ammoniator-granulators. Tests indicate that ammonium polyphosphate is valuable as a granulation aid. When 50 to 200 pounds of 15-62-0 was added per ton of granular fertilizer, hard well formed granules were produced. Tests show that a hard well formed 6-24-24 grade and similar hard-to-granulate grades can be produced when 15-62-0 is incorporated into the mixture.

Limited quantities of ammonium polyphosphate micronutrient carriers have been produced by coating solid ammonium polyphosphate with micronutrient materials. A 14-59-0-4Zn has been produced by coating zinc oxide onto solid ammonium polyphosphate.

Table 1

Estimated Cost of Producing Ammonium Polyphosphate (15-62-0)

Plant capacity:	400 tons/day (330 days/year = 132,000 tons/ year)	
Fixed investments:	Battery limits plant	$1,000,000
	Off sites	400,000
	Total	$1,400,000
Working capital:[a]		$3,700,000

Variable Costs	Quantity/Ton of Product	$/Unit	$/Ton of Product
Superphosphoric acid (77% P_2O_5)	0.805 ton	88.40[b]	71.16
Ammonia (82.3% N)	0.182 ton	35.00	6.37
Product loss	0.013 ton	77.53	1.01
Power	25.000 kwh.	0.00445	0.11
Cooling water	2.000 M gal.	0.02	0.04
Supplies			0.10
Subtotal			78.79
Semivariable Costs			
Operating labor and supervision (2 men/shift and 1 foreman) (0.295 man-hour/ton at $4)[c]			1.18
Maintenance (6% of investment/year)			0.64
Labor overhead (30% of operating labor and supervision)			0.35
Subtotal			2.17
Fixed Costs			
Plant overhead (70% of operating labor and supervision)			0.83
Depreciation (15-year straight-line depreciation)			0.71
Local taxes and insurance (2% of plant investment/year)			0.21
Interest on working capital (7% of ½ of investment and working capital)			1.35
Subtotal			3.10
Total manufacturing cost (0% return on investment)			84.06
Sales and administrative expense (10% of total manufacturing cost)			8.41
Average out freight			10.00
Total delivered cost			102.47
Delivered cost considering 10% return on investment and working capital			106.33
Delivered cost considering 20% return on investment and working capital			110.20

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[a] Working capital is estimated to be 30 days of raw-material cost plus estimated production cost of 3 months end product.

[b] Unit cost of superphosphoric acid was based on a cost of $0.12 per pound for phosphorus and a cost of $10 for converting a ton of P_2O_5 to superphosphoric acid.

[c] Includes benefits $\frac{3 \times 24 \times 365 \times 1.48}{132{,}000} = 0.295$ man-hour/ton.
The 1.48 factor is to correct man working only 40-hour week.

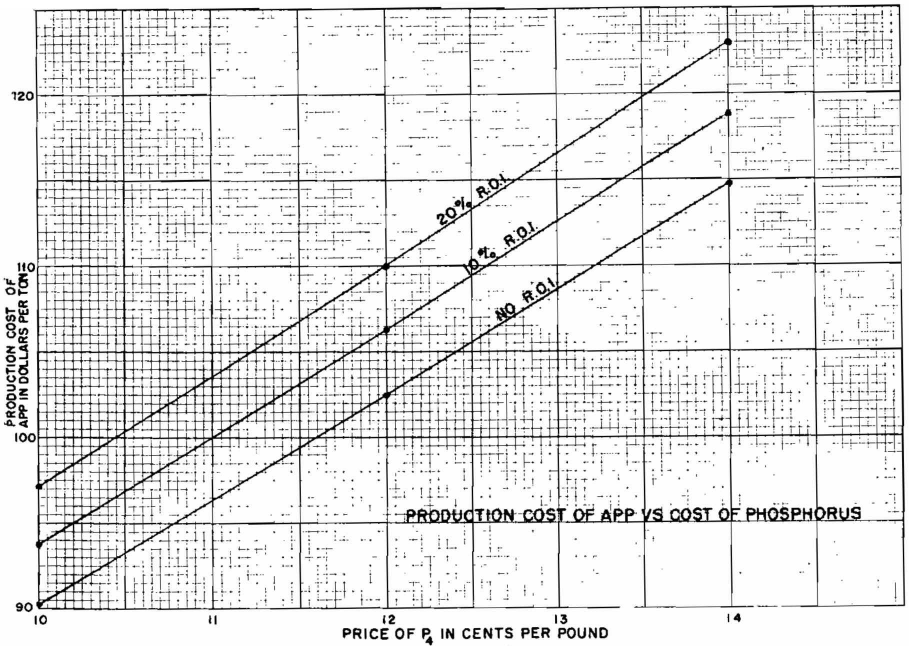

FIGURE 5

This material can be used as a zinc carrier for bulk blends or for the production of fluid fertilizers.

TVA has also produced a nominal 12-52-0-15S by spraying molten sulfur onto a rolling bed of granular ammonium polyphosphate. This material will be used primarily in direct-application programs; however, it could be used as a source of sulfur in the production of bulk blends.

Agronomic Characteristics

Field and greenhouse tests show that ammonium polyphosphate is an effective source of nitrogen and phosphorus on acid, neutral, and basic soils. Since all its nitrogen is in the ammonium form, it is as effective as any of the commonly used ammonium nitrogen sources. As a source of phosphorus ammonium polyphosphate is as effective as monoammonium and diammonium phosphates. In greenhouse tests APP has usually been more effective than superphosphate in terms of dry-matter yield and phosphorus uptake — probably because of the beneficial effect of having nitrogen and phosphorus in the same granule.

The material is suitable for either broadcast application or band placement to the side and below the seed. Ammonium polyphosphate can serve as an effective carrier of some micronutrients. For example, granular ammonium polyphosphate is a more effective carrier of zinc (as zinc oxide) than granular monoammonium phosphate. When used to produce fluid fertilizers containing micronutrients, ammonium polyphosphate has the advantage over ammonium orthophosphate, because larger amounts of zinc, copper, iron, and manganese can be dissolved in the polyphosphate material.

Production Costs

An estimated toal production cost of 15-62-0 is shown in Table 1. It was assumed that electrical power would cost 4.45 mills per kwh. The calculated cost of phosphorus for this estimate was about $0.12 per pound. It was recognized that the cost of phosphorus may vary from $0.10 to $0.14 per pound. In the estimate $0.12 was used as shown in Table 1. Figure 5 shows how much the cost of ammonium polyphosphate would vary with this variation in the cost of phosphorus. It was assumed that the ammonium polyphosphate would be produced in a 400-ton-per-day plant. The cost of ammonia was assumed to be $35 per ton. Its total delivered cost, considering no return, a 10 percent return, and a 20 percent return on investment, was calculated to be $102.47, $106.33, and $110.20 respectively.

Solid ammonium polyphosphate is a multipurpose product which can be used in all segments of the fertilizer market. Because of its multiple use, we expect others to produce this material in the near future.

MODERATOR ADAMS: Thank you, Frank. We have a few minutes for questions.

A MEMBER: Frank, under extended storage conditions, hot, humid weather, have you any data on the loss of poly due to hydrolysis?

MR. ACHORN: We haven't had that problem with ammonium poly produced from furnace superphosphoric acid. Now, I understand that some of the 12-59-0 produced by a commercial firm are having some problem along that line. We have not been able to prove it ourselves and we have had no hydrolysis whatsoever. In fact, one of the advantages for the product is that it does not hydrolize.

SAME MEMBER: Are you saying then with wet acid this can be experienced?

MR. ACHORN: No. We haven't been able to prove it one way or the other. The 12-59-0 is at a lower pH than 15-62-0 and there may be the possibility of some hydrolysis there but it hasn't been proven yet.

A MEMBER: Could the suspension type based on polyphosphate liquid fertilizer, the fluid, can it be sprayed on or broadcast from an airplane?

MR. ACHORN: We have been applying suspensions for, I guess, three years now in Louisiana from an Ag Cat, if you know what I'm talking about when I say an Ag Cat.

The suspensions were produced from 12-40-0. They were not produced from ammonium poly but I think it would be the same thing and it's certainly practical to apply from an airplane.

SAME MEMBER: Okay. Thank you.

MODERATOR ADAMS: Our next discussion "Ammonium Polyphosphate Materials for Use in Fluid Fertilizer Formulations" prepared by Dr. Ronald D. Young, William C. Scott and R. S. Meline, TVA, Muscle Shoals, Alabama. Mr. Young will give the paper.

Alternatives in Production of Ammonium Polyphosphate Materials for Use in Fluid Fertilizer Formulations

R. D. Young*, W. C. Scott* and R. S. Meline*

Introduction

Beginning in the middle fifties with the introduction of furnace superphosphoric acid, TVA research and development has emphasized polyphosphate-based fertilizers.[19,14,17] Fluid products, such as 10-34-0 and 11-37-0 clear liquids and 12-40-0 suspensions, have been of particular interest. These ammonium polyphosphate materials supplied to the industry made possible the production of higher analysis N-P-K fluid products than were possible with orthophosphates. Savings in freight, storage, and handling were realized because of their higher nutrient content. In 1966 TVA introduced granular ammonium polyphosphate produced from electric-furnace superphosphoric acid in demonstration-plant facilities.[12]

Research and development work by TVA and others, and subsequent commercial experience in the field of polyphosphate intermediates, have provided a choice of means by which the final fertilizer products may be obtained. For instance, the successful development of a process for production of wet-process superphosphoric acid provided an alternative to the elemental phosphorus route for obtaining superphosphoric acid. Also, a more recent development was successful in providing a way to produce ammonium polyphosphate granular or fluid fertilizers directly from orthophosphoric acid. This is done by effectively taking advantage of the heat of ammoniation of the acid to evaporate water from the orthophosphoric acid.

The purpose of the present paper is to describe and compare several alternative schemes for production of ammonium polyphosphate materials of various types for use in fluid fertilizer formulations. A comprehensive description of properties, production methods, and uses of ammonium polyphosphate fertilizers has been published.[15]

Elemental Phosphorus-Based Products

The production of elemental phosphorus in an electric reduction furnace operation is illustrated in Figure 1. The phosphate charge after agglomeration or size preparation is calcined and blended with coke and supplemental silica (if required) to provide the charge or "burden" for the furnace. The smelted phosphorus is evolved as a vapor and recovered by cooling in a condenser. It is collected in a sump under water. By-product carbon monoxide gas is evolved from the furnace and can be used to provide most or all of the fuel for the calcination step. Ferrophosphorus and calcium silicate slag byproducts are tapped from the furnace periodically.[18,20]

Phosphorus can be safely stored and shipped in plain steel tanks under a layer of water. It can be pumped readily as a fluid by supplying enough heat by hot water jacket or coils to keep the material molten at a temperature of 120° to 130°F.

Electric-Furnace Superphosphoric Acid

Elemental phosphorus can be readily converted to superphosphoric acid with polyphosphate content ranging up to 85% of the total P_2O_5. The production of acid is simple and straightforward, investment and operating costs for the acid plant are reasonably low, and the product acid is of very good quality.

A diagram of a stainless steel acid plant of the type developed and used by TVA is shown in Figure 2. Production of acid by the thermal process involves (1) oxidizing (burning) elemental phosphorus with air in a combustion chamber to produce P_2O_5, (2) hydrating the P_2O_5 with dilute acid or water to produce phosphoric acid, and (3) recovering the acid from the vapor stream in a venturi scrubber and separator. In an acid unit made of stainless steel, effective cooling of equipment in contact with the hot gases and acid streams is essential to minimize corrosion. Complete jacketing of the equipment and adequate flow of cooling water are required.[2]

Superphosphoric acid with concentration ranging from 75 to 83% P_2O_5 (equivalent to 105 to 115% H_3PO_4) can be readily produced by appropriate changes in operating conditions. The high polyphosphate content (60 to 85% of the total P_2O_5) and comparative purity of the electric furnace acid offer attractive advantages for use in the preparation of fluid fertilizers. The high concentration

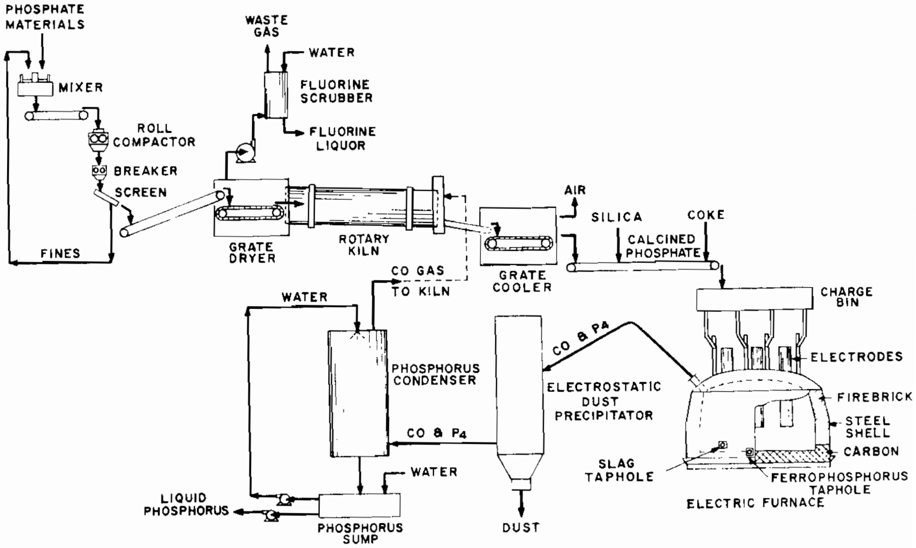

Figure 1
Manufacture of Elemental Phosphorus

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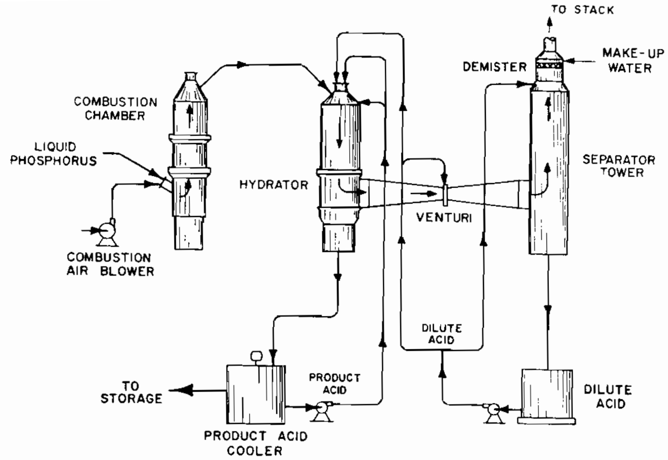

Figure 2

Manufacture of Superphosphoric Acid from Elemental Phosphorus

allows savings in shipping and handling costs.

Properties of electric-furnace superphosphoric acids with 76 and 80% P_2O_5 contents are given below.

Concentration, % P_2O_5	76	80
Specific gravity		
At 75°F.	1.921	1.986
At 170°F.	1.885	1.952
Viscosity, centipoises		
At 75°F.	800	—
At 170°F.	80	250
Crystallization temperature,[a] °F.	70	130
Distribution of species, % of total P_2O_5		
Ortho	49	15
Pyro	42	39
Tripoly	8	24
Tetrapoly	1	12
Other	0	10

[a] Approximate (76% P_2O_5 acid usually is fluid below 70°F. because of supercooling tendencies).

The essentially pure (normally less than 0.1% total impurities) electric-furnace superphosphoric acid can be easily ammoniated to produce a variety of polyphosphate-base fluid products such a 11-37-0 liquid and 12-40-0 suspension. Higher analysis suspensions are under development. These liquid and suspension-base materials can be used to prepare a variety of N-P-K final products by mixing with supplemental nitrogen and potash in simple and inexpensive local plants. The polyphosphate intermediates can be used to provide all of the phosphate or supplied only in a proportion sufficient to sequester impurities in ammoniated wet-process orthophosphoric acid used as the major source of P_2O_5.

Granular Ammonium Polyphosphate

The granular ammonium polyphosphate introduced by TVA from demonstration-plant facilities in 1966 is produced by ammoniating electric-furnace superphosphoric acid in a pressure reactor. Grade of the product is 15-61-0 or 15-62-0. The melt prepared in the reactor is granulated with recycle in a pug mill and the product is cooled and screened. No drying step is required since the feed materials are anhydrous; this simplifies the equipment and makes operation more convenient. Experience in production and in use of the granular ammonium polyphosphate as an intermediate in preparation of liquid and suspension products has been very good. This is covered in detail by F. P. Achorn in another presentation at this Round Table.

Typical chemical analysis for granular ammonium polyphosphate is:

	P_2O_5		
N	Total	Ortho	H_2O
15.0	62.2	25.6	0.03

Particle size of the uniform, closely sized granular product is minus 6 plus 12 mesh. It is stored and shipped in bulk without a conditioner.

Wet-Process Acid-Based Products

Wet-Process Superphosphoric Acid

Because of the many advantages gained in using the ammonium polyphosphate liquids and suspensions produced from electric-furnace superphosphoric acid, their popularity increased and they became the backbone of the fluid fertilizer industry. As a result of this popularity, research and development activities by TVA and others were directed toward processes and equipment for concentrating wet-process acid to the superphosphoric acid range.[4] A modified submerged combustion-type evaporator was developed by TVA in pilot-plant studies.[13] In this type of concentrator the feed acid of about 54% P_2O_5 content is fed at a controlled rate continuously to the small pool of acid in the concentrator. Hot combustion gases at a temperature of about 1700°F. are released from a dip pipe beneath the surface of the acid pool. The considerable turbulence and direct contact of acid and hot gases result in efficient evaporation. Product acid is withdrawn at a temperature of about 550°F. and concentration of about 70 to 74% P_2O_5. Polyphosphate content of the product acid is about 50% of the total P_2O_5. Exhaust gases pass through a scrubber and mist eliminator.

Other evaporators are operated under vacuum and include the forced circulation tubular type and the falling film type. The various designs have been developed or modified for this use. All of these types of concentrators are being used in commercial systems now in operation. Descriptions and diagrams of the various types of concentrators in use for preparation of wet-process superphosphoric acid have been published.[11]

The impurities in typical wet-process acid cause some difficulties in concentration which limits the product acid concentration to 70 to 74% P_2O_5 and the polyphosphate content to about 50%. With this polyphosphate content, the concentration of the base ammoniated fluids produced from it is limited to a maximum of 10-34-0 for the liquid and 11-37-0 for the suspension.

Chemical analyses of some wet-process superphosphoric acids produced with rock from various sources are given below.

Percent by weight							
P_2O_5							
Total	Ortho	Fe_2O_3	Al_2O_3	F	SO_3	MgO	W. I. solids
(Acid made with uncalcined Florida phosphate rock)							
72.9	31.8	2.2	1.8	0.3	2.0	0.3	0.4
(Acid made with calcined western phosphate)							
72.5	34.0	1.2	3.0	0.3	2.1	0.8	0.3
(Acid made with uncalcined North African phosphate rock)							
72.4	25.1	0.6	0.4	0.12	2.7	1.1	0.4

Direct Process for Ammonium Polyphosphates

Recent pilot-plant development work has led to a process for production of ammonium polyphosphate products directly from the usual merchant-grade wet-process acid.[3,9] In this process, acid containing about 54% P_2O_5 is ammoniated in a two-stage reaction system. The heat of reaction of anhydrous ammonia and the acid is utilized effectively to evaporate water. Essentially all of the free water and part of the chemically combined water are removed, resulting in an essentially anhydrous melt of about a 12-58-0 grade with up to 50% of the P_2O_5 condensed to a non-ortho form. A flowsheet of the reaction system is shown in Figure 3.

Acid is fed to the first stage and gaseous ammonia is fed countercurrently to the mixing tee where part of the ammonia reacts with the flow of partially neutralized acid from the first stage to form the polyphosphate melt. The melt, excess ammonia, and water vapor flow to the disengaging chamber where the ammonia and water vapor separate from the product melt. The ammonia and water vapor from the disengaging chamber are directed to the first stage where the ammonia is recovered by reaction with the feed acid. The water vapor from the second stage plus that generated in the first stage is vented.

To produce the products with about 50% of the P_2O_5 in a non-ortho form, it is advantageous to use acid produced from calcined rock to avoid the difficulties of the very viscous foamy melts that result when acid made from uncalcined rock is used. Acids produced from uncalcined rock can be satisfactorily utilized in production of melts with up to about 30% of the P_2O_5 as polyphosphate.

The ammonium polyphosphate melts may be converted directly to a fluid fertilizer or may be converted to a solid granular product. A flowsheet of the fluid system is shown in Figure 4.

With this system, either a 10-34-0 grade solution or 11-37-0 grade suspension may be made. To produce fluids directly, the polyphosphate melt from the disengaging chamber flows directly to a stream of base solution circulating from the fluid fertilizer reactor. Supplemental ammonia and water are added to the fluid fertilizer reactor to maintain the desired grade. Indirect cooling is used to remove heat generated in this system and maintain a temperature of about 180°F. in the reactor. If 10-34-0 liquid fertilizer is being made, the material is pumped through a secondary cooler directly to product storage at a temperature of about 100°F. If 11-37-0 suspension fertilizer is being made, the solution flows from the secondary cooler through a mixing tank where 3% by weight of suspending clay is added prior to going to storage.

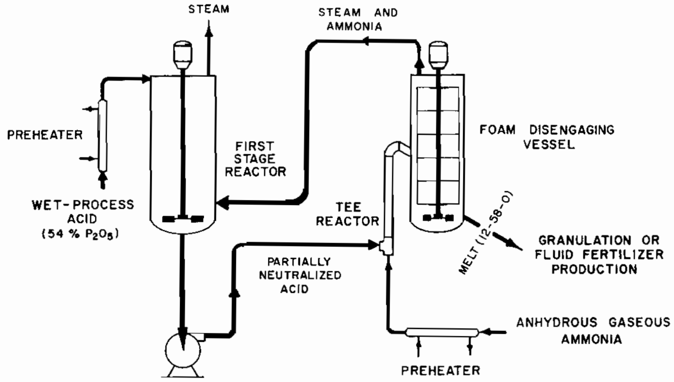

Figure 3
Reaction System for Direct Production of Ammonium Polyphosphate Melt from Wet-Process Phosporic Acid

When producing a 12-58-0 grade granular product, the melt from the disengaging chamber is fed directly onto a bed of recycle in a pug mill where granulation is accomplished. The pug mill provides some degree of working to the melt so that partial crystallization of the melt occurs. The material discharges from the pug mill to a rotary cooler followed by screening and crushing equipment. The crushed oversize, the undersize, and a large portion of the product size are recycled to the pug mill. A flowsheet of the granulation system is shown in Figure 5. The retention time and additional working provided in the cooler result in further crystallization of the melt so that the material discharging from the cooler is only slightly sticky and can be screened and crushed without undue difficulty. About 15 pounds of recycle per pound of product is usually required. The high recycle ratio is required so that the entire bed of material in the pug mill will remain relatively free flowing, thus preventing buildup of material on the rotating shafts and the walls of the mill and overloading of the drive motor. Studies of methods for improving the rather cumbersome granulation operation are under way.

The granular 12-58-0 grade product would be suitable for shipment and conversion to solution and suspension fertilizers; it also should be suitable for direct application, bulk blending, or granulation with other materials.

Importance of Polyphosphate in Fluid Fertilizers

Polyphosphates offer significant advantages in the production

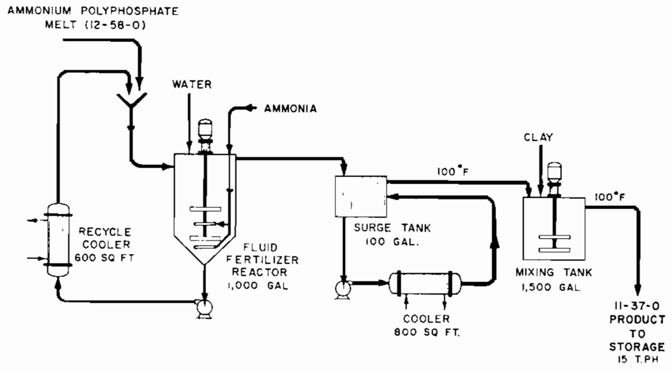

Figure 4
Conversion of Ammonium Polyphosphate Melt Produced by Direct Process to Base Suspension

of both liquid and suspension fertilizers. These advantages are so well established now that the industry is dependent upon reliable economic sources of supply. The main advantage is the significantly higher concentration of N-P products that can be produced because of increased solubility in the polyphosphate system. This is shown in Figure 6 where the total units of plant food ($N + P_2O_5$) over a range of $N:P_2O_5$ weight ratios is compared for 0, 45, and 70% levels of polyphosphate in the parent acid. An increase of 6 units is shown in the maximum solubility for 50% polyphosphate over that obtained when no polyphosphate is present and an additional 2 units if the polyphosphate level is increased to 70%.[16]

The polyphosphate materials can also be used effectively to sequester the impurities in wet-process acid to allow substantial use of the regular 54% P_2O_5 orthophosphoric acid for fluid fertilizer production. In producing liquid nonpotash grades, adequate sequestration usually is obtained by supplying 10 to 20% of the total P_2O_5 in the form of 11-37-0. In grades containing potash, 30 to 40% of the P_2O_5 usually must be supplied as 11-37-0.

Procedures for sequestration have been described.[9] Typical formulations for liquid fertilizers that include 11-37-0 as a sequestrant for wet-process phosphoric acid are shown in the following tabulation.

		Pounds per ton						
Ratio	Grade	TVA 11-37-0	Wet-process ortho acid (0-54-0)	Aqua ammonia (20-0-0)	UAN solution (32-0-0)	KCl (0-0-62)	Water	Est. salt-out temp., °F.
1:1:0	14-14-0	151	415	375	589	—	470	32
1:2:0	10-20-0	216	593	533	218	—	440	25
1:3:0	8-24-0	260	711	657	—	—	372	19
1:1:1	8-8-8	130	207	186	339	258	880	48
1:2:1	8-16-8	259	415	373	178	258	517	44
1:3:1	6-18-6	292	467	440	—	194	607	3
1:2:3	4-8-12	130	207	185	91	387	1000	46

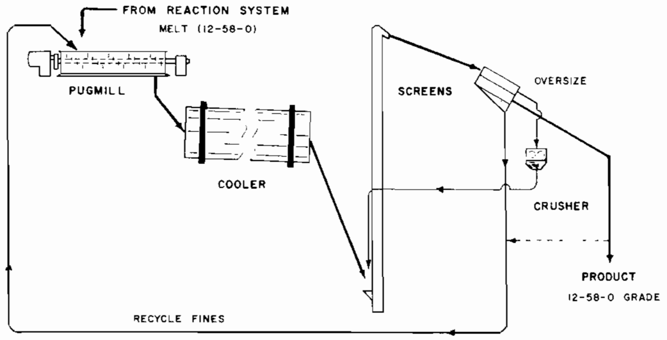

Figure 5
Granulation of Ammonium Polyphosphate Produced by the Direct Process

When producing clear liquid $N:P_2O_5:K_2O$ final products, the advantage of polyphosphates is less pronounced because the potassium salts control the solubility of the other salts in solution. As the potash content of liquid is increased, the total nutrient content that can be maintained in solution decreases.

The polyphosphate may be present as pyro, tripoly, tetra, and higher poly species. The pyrophosphate has been found to be the most effective component for increasing the concentration of liquid products and for sequestration.

The polyphosphate content of electric-furnace superphosphoric acid and its ammoniated products is considerably higher than for similar products made by the wet-process acid route. A comparison of grades and typical polyphosphate contents is shown on p. 132.

A 12-40-0 suspension or an 11-37-0 liquid made by ammoniating furnace superphosphoric acid normally has polyphosphate content amounting to 65% or more of the total phosphate. The 10-34-0 liquid and 11-37-0 suspension made with wet-process acid, either by the direct process or with superphosphoric acid, have polyphosphate contents of about 50%.

Recent research at TVA has resulted in experimental production of suspensions higher in grade than the typical 12-40-0 made by ammoniating furnace superphosphoric acid. The grades of these experimental materials are 13-41-0 (2% clay), 14-44-0 (0.5% clay), and 14-47-0 (no clay). Development work on production of these higher analysis materials is in progress.[10]

Because of the impurities in wet-process acids, and particularly those with high magnesium contents, interest and activity in suspension fertilizers made from wet-process acid are increasing. Generally, the storage properties of all fluid products made with furnace superphosphoric acid have been superior to those derived from wet-process acid where storage periods exceed about 1 month. Although this difference seems to favor furnace acid, practical experience has shown that producers are able to use fluids made with wet-process

	Polyphosphate content, % of total phosphate
Electric-furnace superphosphoric acid (76-80% P_2O_5)	50-85
Ammoniated products	
10-34-0 liquid	50-80
11-37-0 liquid	65-80
12-40-0 suspension	65-80
15-61-0 granular ammonium polyphosphate	54-60
Wet-process superphosphoric acid (70-74% P_2O_5)	50-55
Ammoniated products	
10-34-0 liquid	50-50
11-37-0 suspension	50-55
13-58-0 granular ammonium polyphosphate	50-55
Direct-process ammonium polyphosphate	
10-34-0 liquid	40-50
11-37-0 suspension	40-50
12-58-0 granular ammonium polyphosphate	40-50

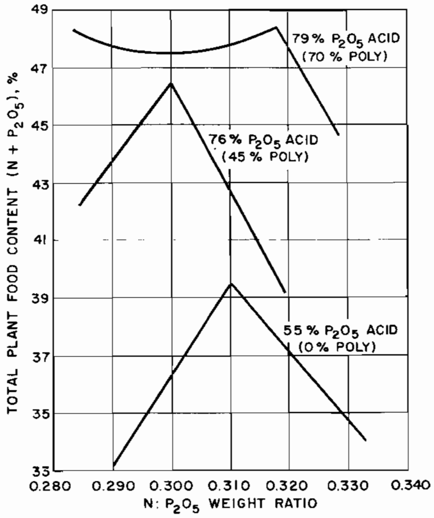

Figure 6

Effect of Polyphosphate Level and N:P_2O_5 Weight Ratio on Solubility of Ammoniated Electric-Furnace Acids, 32°F. (0°C.)

acid effectively. Consequently, most fluid mixed products marketed today are derived all or in part from wet-process acid.

Successful application of liquids and suspensions requires differences in equipment and procedure. For broadcast application, it is necessary to provide flooding-type nozzles for suspensions because these materials contain some solid nutrient. Also, it is desirable to provide means for agitating suspensions in applicator tanks to prevent settling and to ensure homogeniety. This is usually done with a recirculation pump or, in some cases, with a simple air sparger.[8] On the other hand, most liquids contain little, if any, particulate matter and can be applied with smaller nozzles and do not require agitation.

Comparison of Design and Operating Factors for Fluid Fertilizer Plants

Typical designs of fluid fertilizer plants may be divided into three main categories. These are (1) hot-mix continuous plants, (2) hot-mix batch plants, and (3) cold-mix plants. Each of these can make use of some types of polyphosphate materials.

The hot-mix continuous plant is designed for the reaction of furnace or wet-process superphosphoric acid with ammonia to produce base liquids such as 10-34-0 and 11-37-0 or base suspensions such as 12-40-0. Potash and supplemental nitrogen (usually urea — ammonium nitrate solution) then may be added to produce three-component solutions or suspensions. Typically, this type of plant has a capacity of about 15 tons per hour of the N-P intermediate.

Either furnace or wet-process superphosphoric acid may be ammoniated in a plant of this design; requirements for satisfactory design and operation are the same for both acids with the exception that the wet-process acid is more viscous and must be heated to a slightly higher temperature for metering and handling.

The same equipment may be used effectively for the production of an 11-37-0 suspension with melt from a direct-process ammonium polyphosphate plant fed into the reactor instead of superphosphoric acid. However, the amount of heat to be removed when the direct-process melt is fed to the reactor is only about half that to be removed when superphosphoric acid is fed. For example, about 10 million Btu's per hour are removed when the acid is ammoniated at a rate required for production of 15 tons of 11-37-0 per hour as compared with only about 5 million Btu's for the melt.

Design features of the hot-mix batch plant and the continuous plant are similar. However, the usual function of the continuous plant is to provide base materials for shipment to small cold-mix plants; the function of the hot-mix batch plant is to produce N:P_2O_5:K_2O products tailored for local use.

The cold-mix plant uses a fluid-base ammonium phosphate which was produced in a hot-mix plant. Cold-mix plants are not designed for neutralization of acid with ammonia. Consequently, no stainless steel is required in construction of this plant. Nitrogen solutions are usually stored in aluminum tanks or mild steel protected by a coating or lining. Other equipment is mild steel. Investment for this type plant is very low, and operation is convenient and inexpensive.

The cold-mix plant is well suited to the use of granular ammonium polyphosphate in production of fluid fertilizers. The 15-62-0 dissolves readily in water if vigorous agitation is supplied in the mix tank. The additional ammonia that is added provides heat to aid dissolution of the granular ammonium polyphosphate. Some plants depend on a high-capacity pump for agitation; however, a turbine agitator in a tank equipped with properly designed baffles in superior. The presentation of F. P. Achorn, "Uses for Solid Ammonium Polyphosphate in Bulk Blending, Granulation, and Fluid Fertilizers," at this session gives more details on use of the granular ammonium polyphosphate.

Advantages and Disadvantages of Various Polyphosphate Materials

Electric - furnace superphosphoric acid and its ammoniated products 11-37-0 liquid and 12-40-0 or higher grade suspensions have significant advantages of comparative purity, higher grade, and high polyphosphate content than derivatives of wet-process acid. The absence of impurities that can be troublesome in wet-process acid products also ensures more consistent storage and application properties. The elemental phosphorus-based polyphosphate materials are proportionally more effective as a sequestrant since wet-process acid derivatives have utilized a large part of the polyphosphate potential in sequestering their own impurities. The granular ammonium polyphosphate made from electric-furnace superphosphoric acid has very good storage and handling properties. The relatively easy dissolution to produce fluid products and versatility for use in bulk-blended granular fertilizers are plus factors that enhance future prospects. The generally higher cost is the only apparent disadvantage for polyphosphates produced from elemental phosphorus.

Despite considerable problems in concentration and the need for added expense for clarification of the feed acid, wet-process superphosphoric acid has proved feasible for production and shipment. The comparative high viscosity and need for keeping this acid hot (about 150° F.) to allow effective unloading, pumping, and feeding have been coped with satisfactorily through use of suitable insulated tank cars. The ammoniated liquid 10-34-0 made from wet-process superphosphoric acid ranges in color from opaque dark to clear green, depending on whether raw or calcined rock is used to make the parent acid. The 10-34-0 may contain visible amounts of fine solid particles, but if properly prepared, no appreciable problems are experienced in storage or application. Some wet-process acids with higher magnesium content can result in precipitation problems on prolonged storage of ammoniated products. Suspensions made with wet-process acid have essentially the same appearance as those made with furnace acid. The main advantages of wet-process acid-based polyphosphates include the greater availability of this type of acid and likelihood of lower cost, especially if the direct process proves to be commercially feasible.

Future growth in production of both wet-process acid-based and elemental phosphorus-based polyphosphate materials is expected. Substantial increased production will be necessary to support the anticipated increase in popularity of fluid fertilizers.

At present the production of fluid fertilizers is of major importance only in the United States and France. There is some production in England and indication of substantial interest and planned activity in other European countries and in Australia and South Africa. A recent paper on the technology and economics of liquid mixed fertilizers[5] stirred considerable interest at the International Superphosphate Manufacturers' Association meeting in Brussels, Belgium, that likely will result in increased evaluation and activity.

Commercial Production of Polyphosphate Materials

The past 2 years has seen production of wet-process superphosphoric acid reach commercial reality, and it is now available in dependable supply. Of the approximately forty plants in the U. S. that manufacture wet-process acid, there are now reported to be at least eight that produce wet-process superphosphoric acid and market it or its ammoniated products. The "hot-dog" type of insulated railroad tank car has allowed shipment of the wet-process superphosphoric acid for long distances with temperature maintained satisfactorily high for handling and conveniently unloading the viscous acid.

In the U. S. there are thirty plants operated by ten companies that produce phosphoric acid from elemental phosphorus; nine of the plants are equipped to produce superphosphoric acid. At least one producer purchases elemental phosphorus and produces superphosphoric acid and 11-37-0 from it.

TVA is the only source at present of 15-61-0 granular ammonium polyphosphate; it is produced in demonstration-plant facilities and made available for testing as an intermediate in production of liquid and suspension fertilizers. It has been shipped in bulk by rail, barge, and ship with very good results. Interest that has developed rapidly in this versatile granular material indicates good prospects for commercial producers to enter production in the future.

A recent survey shows that more than seventy-five plants produce 10-34-0 liquid by various means. Most of these use wet-process superphosphoric acid. Several use electric-furnace superphosphoric acid of the 76% P_2O_5 shipping grade, and use of granular ammonium polyphosphate is increasing. Activity in production of base suspensions apparently is increasing substantially.

The direct process for production of ammonium polyphosphate fluid and granular products that has been developed on pilot-plant scale by TVA[3] is not known to be in use commercially. A number of firms are engaged in test work and appear to be evaluating the process and its potential in their planning activities.

Economics

Although it is generally recognized that wet-process phosphoric acid usually can be produced at lower cost than thermal acid from elemental phosphorus, recent evaluations (taking into account higher sulfur prices and prospects for lower electric power costs) indicate narrowing of the margin.[7] The investment in electric-furnace facilities is about double that for wet-process acid production and this has considerable impact on costs. Recent estimates[21] indicate production costs of about $118 per ton of P_2O_5 for 76% P_2O_5 electric-furnace superphosphoric acid and $109 per ton of P_2O_5 for 70% P_2O_5 wet-process superphosphoric acid (f.o.b. plant). These estimates are for facilities located in Florida with a 10% return on investment and producing 600 tons of P_2O_5 per day. The cost of wet-process superphosphor-

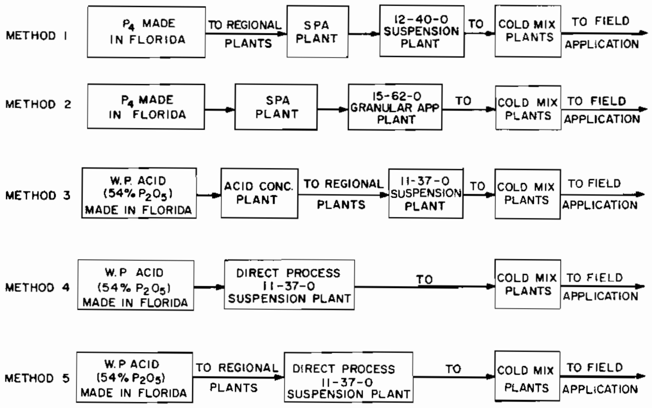

Figure 7
Alternatives for Producing Ammonium Polyphosphate Suspensions

ic acid is based on a sulfur cost of \$41 per ton and includes an estimated \$11 per ton for clarification of the feed acid and concentrating to 70% P_2O_5. The cost of electric-furnace superphosphoric acid is based on a power cost of 5 mills per kwh. Shipment of elemental phosphorus long distances could significantly offset the indicated difference in cost.

The present process technology provides a choice between at least five alternative routes to production of ammonium polyphosphate-base solutions and suspensions. These alternatives, shown diagrammatically in Figure 7 are:

1. Elemental phosphorus produced at, or near, a major phosphate deposit is shipped to a regional plant and converted to superphosphoric acid. This superphosphoric acid is ammoniated to produce 11-37-0 clear liquid or a suspension such as 12-40-0.
2. Furnace superphosphoric acid is ammoniated in a pressure reactor to produce 15-62-0 grade granular ammonium polyphosphate. The 15-62-0 is shipped to cold-mix fluid plants for dissolution in water to produce either liquids or suspensions. (Pilot-plant work has indicated feasibility of 13-59-0 grade granular ammonium polyphosphate acid.)
3. Wet-process superphosphoric acid is produced at, or near, a major phosphate deposit and shipped to a regional plant. This superphosphoric acid is ammoniated to produce 10-34-0 clear liquid or 11-37-0 suspension.
4. Wet-process orthophosphoric acid is produced at, or near, a major phosphate deposit. The acid is used at the plant site to produce a 12-58-0 grade melt by ammoniating wet-process orthophosphoric acid in the direct process at atmospheric pressure. The melt is dissolved in water and a small amount of ammonia is added to produce a 10-34-0 liquid. If a suspension is desired, the amount of water is slightly decreased to raise the grade to 11-37-0, and attapulgite clay is added.
5. Same as 4 except the 54% wet-process acid would be shipped to a regional plant for use in the direct process.

With the exception of the 12-58-0 material made by the direct process, these alternatives have been reduced to commercial practice. The direct process has not been carried beyond the pilot-plant stage to date.

For comparison, the delivered costs of base suspensions in Des Moines, Iowa, have been estimated and reported for four of the alternatives.[6] An estimate was made for Method 2 (production of granular ammonium polyphosphate from electric-furnace superphosphoric acid and shipment to Iowa for preparation of suspension in a simple cold mix-type operation). This estimate used a delivered cost of \$106 per ton of product for granular 15-62-0 in Iowa.[1] A phosphorus cost of \$240 per ton to the acid plant was used. Total cost of conversion of granular ammonium polyphosphate to 12-40-0 (not including raw materials) was estimated at \$6 per ton of 12-40-0 product. Results of the estimates are tabulated below.

Grade of base suspension	Delivered cost, \$/ton of material				
	Method 1	Method 2	Method 3	Method 4	Method 5
12-40-0	76.72 (147.54/T plant food)	78.01 (150.00/T plant food)			
11-37-0			71.49 148.94/T plant food)	70.13 (146.10/T plant food)	72.05 (150.10/T plant food)

These estimates indicate a slight economic advantage for method 4 which makes use of the direct process for ammonium polyphosphate made from wet-process orthophosphoric acid. In the estimates, a price of \$60 per ton for ammonia was assumed. Although lower prices that now are available would affect the results obtained in these estimates, the comparisons would not be affected significantly. The comparatively minor differences in delivered cost of the suspensions indicate that savings in shipping and handling costs for more concentrated materials, and higher grade of product, can offset substantially higher cost of starting material. These comparisons indicate that the elemental phosphorus and wet-process acid routes to polyphosphates are likely to be keenly competitive.

Summary and Conclusions

Alternative routes to production of ammonium polyphosphate-base solutions and suspensions have increased in recent years with the result that fluid fertilizer producers are in a much more flexible position to produce polyphosphate-based products. These developments should greatly aid the growth of the fluid fertilizer industry in the future. Because of the comparative ease with which fluids are handled, transported, and applied to the soil, continued growth of this industry is expected.

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MODERATOR ADAMS: Thank you for that excellent paper. Are there any questions?

It looks like you have covered your subject real well. Our chairman suggests that we all stand up and stretch for a minute.

Our program continues with Polyphosphates and Suspension or Fluid Fertilizers. We regret that Mr. Formaini was not able to attend to give the next talk. My associate, Mr. George R. Gilliam and I have agreed to give this talk and I hope you will bear with us.

Fluid Fertilizers Containing Polyphosphate and Micronutrients

R. E. Formaini*

Introduction

Significant quantities of inorganic micronutrients may be incorporated into liquid fertilizers when products contain polyphosphates.[1] The quantity of micronutrient soluble differs for each metal, and it is influenced by several factors.

Some information is available concerning micronutrient compatibility in solution[2,3] and salt-suspension[4] systems, particularly for zinc.[5] This paper presents micronutrient solubility data for boron, copper, iron, molybdenum, manganese and zinc in fluids containing wet-process 10-34-0, urea-ammonium nitrate solution 32 and muriate of potash. In addition, procedures for incorporating metals into cold-mixed, salt suspensions will be given. Discussion will be limited mainly to the metals which depend upon sequestration for dissolution.

Solubility Limits

The metals boron (B) and molybdenum (Mo) supplied as the usual commercial sodium salts are soluble to the extent of at least one percent in fluid fertilizers. Since sequestration is not involved

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* Contribution from Allied Chemical Corp., Agricultural Division, Research Department, Hopewell, Virginia.

Table 1

Solubility of Metals in Wet Process 10-34-0[1]

Metal[3]	P_2O_5 In Final Mix, %	Pounds Metal Per 100 Pounds P_2O_5[2]	
		Stable 1 Day[4]	Stable 1 Week[4]
Cu^{+2}	15 and above	10.0	8.0
	6 to 15	9.0	6.0
Fe^{+3}	6 and above	2.6[5]	2.6[5]
Mn^{+2}	30 and above	0.6	0.2
	15 to 30	0.4	0.2
Zn^{+2}	28 and above	10.0	6.0
	15 to 28	6.0	4.0

Notes:

[1] 10-34-0 Containing 1.8 pounds Fe per 100 pounds P_2O_5 initially.

[2] Can be used for solutions or suspensions.

[3] Supplied as sulfates, chlorides, carbonates and for ZnO.

[4] Time elapsed before a precipitate formed in solutions.

[5] Does not include Fe in 10-34-0.

in solubility and one percent is excessive to normal needs, we will turn our attention to the other micronutrients.

The solubility of copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) in N-P-K liquids is dependent upon the polyphosphate content in the system. However, product stability is determined by metal and P_2O_5 content. This is shown in Table 1 which gives data for metal sulfates, carbonates and chlorides, and for zinc oxide in 10-34-0 containing 0.6 percent iron and having at least 58 percent of its phosphate in the polyphosphate form. As shown, substantial amounts of Cu, Fe, and Zn are sequestered but Mn has limited solubility. In addition, metal content at saturation increases with P_2O_5 content, but product stability decreases with increase in metal content.

Micronutrient Mixtures

Maximum metal content of fertilizers containing micronutrient mixtures may be computed by using the weighted average method and the values in Table 1. The following solution grades are examples when 30 percent of the polyphosphate is used for Cu and the balance is used for Zn:

9-27-0-0.8Cu-0.5Fe-1.9Zn
8-8-8-0.2Cu-0.1Fe-0.3Zn
8-16-8-0.5Cu-0.3Fe-0.7Zn
5-10-10-0.3Cu-0.2Fe-0.4Zn

Metal Content of Suspensions

Since the problem of solubility is not involved with suspensions, more metal than that specified in Table 1 can be used. The limiting factor, in this case, is product viscosity which may be controlled by preparing lower grades.

In this respect, maximum plant food content was found to be related to the type and quantity of metal added and the P_2O_5 content of the suspension. Severity of thickening was in order Mn> Fe> Zn = Cu which is the reverse of the preferential order of sequestration. The influence of metal source on thickening was minor except for Cu and Zn. Suspensions with copper and zinc sulfates were more thixotropic than those with other salts. Selected grades given in Table 2 to 5 illustrate the preceding statements and show the highest metal contents attained for which no reduction in plant food due to thickening was required.

Table 2

Maximum Suspension Grades with Copper[1]

Grade Ratio	Metal to P_2O_5 Weight Ratio	
	10:100	20:100
1-1-1	13.6-13.6-13.6-1.4Cu	11-11-11-2.2Cu
1-2-1	10.2-20.4-10.2-2.0Cu	7-14-7-2.8Cu
1-2-4	6.7-13.4-26.8-1.4Cu	4-8-16-1.6Cu
1-3-1	8-24-8-2.4Cu	6-18-6-3.6Cu
1-3-3	6.6-19.8-19.8-2.0Cu	4-12-12-2.4Cu
1-3-6	4.6-13.8-8-27.6-1.4Cu	3-9-18-1.8Cu

Note:

[1] Prepared from urea-ammonium nitrate solution 32, 10-34-0, KCl (62% K_2O) and $CuSO_4$ (25.2% Cu) and stable for 24 hours.

Maximum Metal Content of Suspensions

Maximum grade for micronutrient mixtures may be computed using the data herein and assuming the preferential order of sequestration is Cu = Zn > Fe > Mn. However, N-P-K suspensions have been prepared and applied having the following metal contents:

1.0% B or Mo
(maximum tested)
4.0% Zn or Cu or Zn + Cu
1.5% Mn or Fe or Mn + Fe
3.0% Fe + Zn (Fe = 1.2%)
2.5% Mn + Cu or Fe + Cu
(Cu = 1.0%)
4.5% Total metals
(Fe + Mn = 1% max.)

These data are shown graphically in Figure 1. It should be mentioned that clay content was decreased as metal content was increased. At the maximums indicated, no clay was used. This was necessary to maintain viscosity below 700 centipoises.

Fig. 1, see page 138.

Mixing Procedures

Micronutrients are more efficiently added to suspensions in a batch mix tank rather than in applicators or nurse tanks. When the mixture is to contain up to one percent metal, the micronutrient may be added to the liquid used to develop clay pregel. Using large amounts of micronutrients, addition should be made just prior to potash addition, the final mixing step.

Micronutrients may be added as finely divided solids, water slurries, or preferably, as solutions. With each, the rate of addition must be slow to prevent agglomeration and avoid forming heavy gels which can occur while adding micronutrients.

Suspension Storage

In some cases, suspensions containing micronutrients will thicken to a slight degree after mixing. Thickening may result from downward temperature change but mostly to continuing chemical reactions. For this reason, we recommend applying the material as soon after mixing as possible. If application is delayed, mechanical agitation should be provided to prevent possible gelation.

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Table 3

Maximum Suspension Grades with Iron[1]

Grade Ratio	Metal to P_2O_5 Weight Ratio	
	5:100	10:100
1-1-1	14-14-14-0.7Fe	11.5-11.5-11.5-1.2Fe
1-2-1	10.5-21-10.5-1.0Fe	8-16-8-1.6Fe
1-2-4	7-14-28-0.7Fe	4.5-9-18-0.9Fe
1-3-1	8-24-8-1.2Fe	6-18-6-1.8Fe
1-3-3	6.8-20.6-20.6-1.0Fe	4.5-13.5-13.5-1.3Fe
1-3-6	5-15-30-0.75Fe	3-9-18-0.9Fe

[1] Prepared from urea-ammonium nitrate solution 32, 10-34-0, KCl (62% K_2O) and $Fe_2(SO_4)_3$ (27% Fe), and stable for 24 hours.

Table 4

Maximum Suspension Grades with Manganese[1]

Grade Ratio	Metal to P_2O_5 Weight Ratio	
	2:100	5:100
1-1-1	14-14-14-0.28Mn	12.5-12.5-12.5-0.6Mn
1-2-1	11-22-11-0.44Mn	10-20-10-1.0Mn
1-2-4	7-14-28-0.28Mn	6-12-24-0.6Mn
1-3-1	8-24-8-0.48Mn	7-21-7-1.0Mn
1-3-3	7-21-21-0.42Mn	6-18-18-0.9Mn
1-3-6	5-15-30-0.30Mn	4-12-24-0.6Mn

Note:

[1] Prepared from urea-ammonium nitrate solution 32, 10-34-0, KCl (62% K_2O) and $MnSO_4$ (27.3% Mn), and stable for 24 hours.

Table 5

Maximum Suspension Grades with Zinc[1]

Grade Ratio	Metal to P_2O_5 Weight Ratio	
	10:100	20:100
1-1-1	14-14-14-1.4Zn	11-11-11-2.2Zn
1-2-1	10.5-21-10.5-2.1Zn	8-16-8-3.2Zn
1-2-4	6.9-13.8-27.6-1.4Zn	4.5-9-18-1.8Zn
1-3-1	8-24-8-2.4Zn	6-18-6-3.6Zn
1-3-3	6.7-20.1-20.1-2.0Zn	4-12-12-2.4Zn
1-3-6	4.8-14.4-28.8-1.4Zn	3-9-18-1.8Zn

Note:

[1] Prepared from urea-ammonium nitrate solution 32, 10-34-0, KCl (62% K_2O) and $ZnSO_4$ (36% Zn), and stable for 24 hours.

MODERATOR ADAMS: We will move along with our program. Mr. Edward Platz will tell us a little bit about the manufacture of Liquid and Suspension Fertilizers, right from the plant.

Editor's Note: Sorry at time of printing we did not have the notes from Mr. Platz's discussion. Mr. Platz spoke from the cuff and our transcriber was not operating. We will try to include Mr. Platz's message in our 1969, Round Table Proceedings.

MODERATOR ADAMS: Thank you, Ed, for that personal testimony on your way of operating the liquid fertilizer operation.

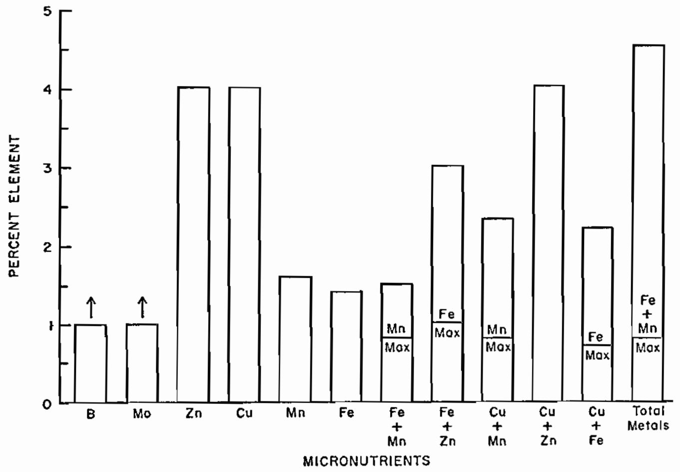
He personally runs the plant and knows all of the ins and outs. If you have any questions, he will be around and you can ask him later. I will turn the meeting back to our Chairman Dr. Sauchelli.

CHAIRMAN SAUCHELLI: Thank you, Billy.

That certainly was a refreshing experience to have Mr. Platz explain his method.

We are nearing the end of these present sessions and I take this opportunity to thank all of the speakers for their unstinted cooperation in making this meeting the success that it admittedly was. We should recognize the efforts

FIGURE I
COMPATIBILITY OF BORAX, SODIUM MOLYBDATE AND METAL SULFATES WITH SUSPENSIONS



of the speakers who generously give of their time and expenditures to share with us their knowledge and experience, and particularly those who come from overseas at great expense to be able to share with us their knowledge and experience. Also, we thank the employers who permit their men to participate in these meetings.

I thank my associates on the Executive Committee, and especially that tireless worker Dr. Marshall, for their loyal cooperation, and Miss Jo Ann Withers for her patient and alert recording of the talks and comments.

Thanks also to the personnel and management of the Mayflower Hotel for their courteous help and

I sincerely hope we have not neglected our foreign guests. We want to make sure at all of our sessions that our foreign guests have been well taken care of.

I do want to express our appreciation to the representatives of the trade press. At every meeting of the Round Table we have had the good fortune to get friendly, helpful publicity.

Our Secretary has arranged to have the next Annual Meeting held at this hotel on November 5, 6 and 7 of 1969. Please record the dates. Meanwhile, please remember to send us your suggestions. Don't wait until it is too late. We need your suggestions and problems for building up an interesting and helpful agenda for our next meeting.

Unless there is something else to be brought before the group, I want to declare that our meeting is adjourned until next November, about 50 weeks away.

(Applause.)

(The Meeting adjourned at eleven-fifty-two o'clock a.m.)

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Note: There were many more participants who did not announce their names when asking or answering questions.