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*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

THE PRODUCTION AND MARKETING OF SUPERPHOSPHORIC ACID FROM NORTH CAROLINA ORE

By B. M. Whitehurst

Texasgulf - U. S. A.

Introduction

The phosphate deposit in eastern North Carolina was deposited in the Miocene seas about 15 million years ago in an area as seen in Slide 1. The deposit is uniform over large distances (20,000 ha) and flat lying, with an average dip of 1.9 M per kilometer south-easterly. It is estimated that the deposit has an average P205 content of 12 to 14 % and contains about 2 billion tons of ore. Texasgulf has mining rights on more than 12,000 ha in the heart of this reserve.

The phosphorite probably originated in a marine environment in a large shallow lagoon or estuary with restricted circulation under reducing conditions (1). The phosphate has a composition similar to françolite or carbonate-apatite. The pellets are about 1 to 3 mm in diameter and contain organic matter throughout. A cross section of the mine area is shown in Slide 2.

Mining is by conventional dragline in an open pit. The ore is from 27 to 40 M below sea level. To maintain dry conditions it is necessary to depressure a large fresh water aquifer which underlays the ore.

The sand is removed from the ore by flotation. The beneficiated phosphate pellet is then calcined in a fluid bed calciner to remove the carbonate and organic matter which results in an upgraded product with a grade improvement from 30.6% to 33% P_2O_5 . This material has a median particle size of 180 to 200 microns, and range from 420 microns to 70 microns. The unground calcined phosphate is then acidulated in a conventional Prayon dihydrate process plant producing a filtrate of about 27% P_2O_5 . Because of the high organic content and carbonate content, acidulation of the uncalcined phosphate was not possible. The filter cake consists of gypsum crystals about 30 microns wide and 250 microns long which are a textbook example of an orthorhombic gypsum crystal which occurs in nature. The purity of the gypsum is such that it can be converted to wallboard The 27% P_2O_5 filtrate is concentrated to 54% P_2O_5 acid in Swenson evaporators.

The evaporator product contains about 2.5% solids which is a mixture of $CaSO_4$ and sodium and potassium silicofluorides. These solids are settled quickly to the 0.1 to 0.2% level in settling tanks. Post precipitation is not a significant problem with this acid. The clarified 54% P_2O_5 acid is then used as a feed stock to the Superacid plant.

Polyphosphates derived from superphosphoric acid play an important role in the manufacture of liquid fertilizer solutions. In 1971-72, 510,000 metric tons of P_2O_5 derived from superphosphoric acid were consumed in the United States in the liquid fertilizer industry (2). Liquid mixed fertilizers account for about 10% of the total fertilizer P_2O_5 consumed in the United States and during the past ten years fluid fertilizer usage has grown at a rate of about 14% per year.

Superphosphoric acid is used to produce an ammonium polyphosphate base solution by the customer (10-34-0). The term "fluid fertilizer" includes both suspensions and clear N-P-K liquids. For the past seven years the Technical Services Department at our North Carolina phosphate facility has conducted development work on superacid manufacture, ammonium polyphosphate base solutions, or N-P-K clear liquid systems, and on suspensions manufactured from Texasgulf super and orthophosphoric acids.

When wet process orthophosphoric acid (54% P₂O₅) is used to manufacture liquid fertilizer solutions, the impurities present in the acid tend to form crystals of phosphate salts that precipitate as bothersome sludges in storage tanks and applicator equipment. Polyphosphates tend to sequester or solubilize these impurities, thus keeping them in solution. The increased solubility of polyphosphates over orthophosphates also allows the production of more concentrated liquids.

In the manufacture of polyphosphates, orthophosphoric acid is polymerized. Polyphosphates are chains of orthophosphate units linked together (3). Much like making a chain, heat is used to "link" these orthophosphate units, and to give off water from the linking process. This is pictured in Figure 3.

PRODUCTION OF SUPER ACID

One of the key factors in the production of superacid is the quality of the orthophosphoric 54% P $_2$ O $_5$ acid feedstock. The aluminium content of super acid is critical to the viscosity of the acid. The North Carolina ore is characteristically low in aluminium as compared to Florida or some Western US ores. With an Al $_2$ O $_3$ concentration of 1.4% the viscosity of the super acid for a 30% polysphosphate content would be 600 centipoise at 38° C, whereas a 1% increase to 2.4% Al $_2$ O $_3$ would increase the viscosity to 1000 centipoise or a 67% increase The viscosity of a fluid has a major effect on the heat transfer capability of the superacid evaporator. The low viscosity of Tg acid makes it quite simple to concentrate to levels of 50% polyphosphate using a wetted surface heat exchanger. Submerged combustion is often required to attain the necessary poly level in higher alumina acids. An increase in the Fe $_2$ O $_3$ content has a tendency to lower the viscosity slightly.

Tg has two identical superacid plants which produce about 275 metric tons day of P_2O_5 , and currently a 3rd plant is under construction. When this unit is complete we will have a superacid production capability of 825 metric tons per day of P_2O_5 . The first two plants incorporate two stage falling film evaporators. The first stage is heated by steam and the 2nd stage by Dowtherm. The design of the third plant will be based on the use of a forced circulation evaporator.

The reason for the two stages of evaporation was economic rather than process factors. The first stage unit which carries 60% of the evaporation load is heated by waste steam from the sulfuric acid plant, whereas the second stage is heated by vaporized Dowtherm from an oil fired boiler. The absolute pressure in both stages is maintained at 20 to 30 mm of Hg. The tubes in the second stage evaporator are made of Inconel 625, a nickel-moly-chromium alloy which has a higher temperature limit than Carpenter 20. The heat transfer coefficient for our falling film unit varies between 440 and 590 Kg-Cal/Hr/m2/° C dependent on the cleanliness of the tube wall. Carpenter 20 alloy is very satisfactory for construction of the steam heated first stage evaporator. The tubes have a life in excess of seven years in the first stage unit. The corrosion of the evaporator tubes is significantly less when a thin layer of scale is allowed to form. Some years ago we attempted to concentrate a more purified acid in the 2nd stage evaporator in which a scale did not form on the tube walls. We dissolved the second stage unit in 30 days. Therefore, I must conclude that impurities in the superacid are necessary for plant survival. Based on our experience, the conversion of a purified acid to polyphosphoric acid with a metal walled heat exchanger is not practical.

ACID PURIFICATION

The superacid evaporators concentrate the orthophosphoric 54% P_2O_5 to about 70% P_2O_5 and 35% polyphosphate. At this point the acid contains about 7% solids as measured by a methanol extraction. These solids are essentially an iron magnesium pyrophosphate. Thus when they are removed from the superacid, the resultant clarified acid has a lower iron and magnesium content. We are not sure whether this is a single compound or a co-precipitate of ferrous pyrophosphate and magnesium pyrophosphate. We estimate that this solid has a composition similar to 2 Fe $(H_2PO_4)_2$. 3 Mg $(H_2PO_4)_2$. Under certain conditions the ratio of Fe to Mg will vary. We are able to remove about 60% of the MgO and 40% of the iron via precipitation followed by clarification. A comparative analysis of the acids before and after purification is shown in Slide 4.

The solids in the acid can be removed by centrifugation and/or filtration. The particle size of the solids ranges from 20 microns to 30 microns. We have a centrifuge and rotary vacuum precoat filters to remove the solids.

One of the factors which affects the amount of precipitation of the 1ron magnesium pyrophosphate is the amount of free $\rm H_2SO_4$ in the 54% $\rm P_2O_5$ feed acid. The control of the phosphoric acid plant is such that the free $\rm H_2SO_4$ content is essentially zero. If the free sulfate level increases, the amount of precipitation decreases and thus the iron and magnesium removal is reduced.

MARKETING

The primary market for superacid is in the liquid fertilizer industry of the middle Western U.S. The acid is shipped in 91 metric ton insulated tank cars. It is loaded at 82° C and with normal delivery time reaches the customer with a temperature of 52° C. The viscosity of this acid is 175 centipoise at 52° C which is sufficiently low to use either a simple gear pump or a centrifugal pump for unloading.

The Texasgulf superacid product called Super 49 is typically 69% P_2D_5 with a 20-30% conversion of the phosphate to the non-ortho or poly form. Until the concomitant development of Super 49 and the TVA pipe reactor process, the polyphosphate level of our super acid was maintained at about 50% to insure sufficient sequestering ability when mixed with ammonia.

There are two basic methods for manufacturing ammonium polyphosphate solutions from superphosphoric acid:(1) neutralization of anhydrous or aqua ammonia with superphosphoric acid containing a minimum of 45-55% polyphosphate (conventional process) or (2) reaction of low poly superphosphoric acid containing 20-30% poly P_2O_5 with anhydrous ammonia in the TVA pipe reactor system.

In a conventional liquid fertilizer plant, N-P base solutions such as 10-34-0 are produced by reacting aqua or enydrous ammonia with superphosphoric acid using a large recycle stream of 10-34-0 liquid. The liquids produced by this method are limited in poly level to the maximum poly level present in the superacid used (typically 45-55%). The temperature of the 10-34-0 product has to be rigidly controlled below 32° C or hydrolysis of the polyphosphates to orthophosphate will occur at an unacceptably high rate.

The TVA pipe reactor process permits production of 10-34-0/11-37-0 (N-P) solutions with a polyphosphate level of 70 to 80% using an acid containing only 20-30% (3). Such solutions when stored at temperatures of less than 32° C have increased storage life as compared to N-P solutions made from superacid with a poly level of 45 to 50%. A typical pipe reactor plant is shown in Figure 5.

In the pipe reactor, the heat of reaction of vaporous anhydrous ammonia and superphosphoric acid causes extensive polymerization and yields large quantities of tri, tetra, penta, and higher polyphosphate species. The temperature attained in the pipe reactor is approximately 340° C, or 120° C higher than temperatures attainable in a superacid falling film evaporator. Since this process generates polyphosphates, an acid of low poly content is suitable as a feedstock (3). Some ammonium polyphosphate analyses from commercial production are shown in Figure 6.

A comparison of poly distribution is shown in Figure 7 for conventional, high-poly, and furnace ammonium polyphosphate solutions. It indicates that high-poly wet process 10-34-0 is comparable to furnace grade 11-37-0. As you can see, the conventional 10-34-0 has only 10% of its P_2O_5 above the pyro level.

It is generally accepted that the pyrophosphate do an excellent job of sequestration on valence + 3 metals such as iron and aluminium. However, for valence + 2 metals such as calcium and magnesium, it is generally agreed that polyphosphates above the pyro level are required. The more the better up to about the 81% poly level. Solubility problems can occur above this level. You will note that with the high poly 10-34-0 made from the pipe reactor, 56% of the polyphosphate is above the pyro level.

The first phase of fluid fertilizer manufacture is concerned with the production of superacid and the second phase with the production of the 10-34-0/11-37-0 base solution.

CONCLUSION

The purity of the North Carolina phosphate makes it uniquely suited for the production of superacid. The magnesium impurity in the ore can be substantially reduced by careful control of process conditions such as the free sulfuric acid content of the feedstock. Because of these factors it has been possible to produce a superacid with a quality comparable or exceeding the quality attainable by some solvent extraction processes. The liquid fertilizer base solution produced from this superacid (10-34-0) has a storage life in excess of 1 year. Because of these unique qualities and techniques, Texasgulf has become a major supplier of phosphoric acids for fluid fertilizer. Further expansion of superacid production capacity is planned. Research and development is continuing on the further development of fluid fertilizers, and on the production of a more highly purified acid for non-agricultural uses.

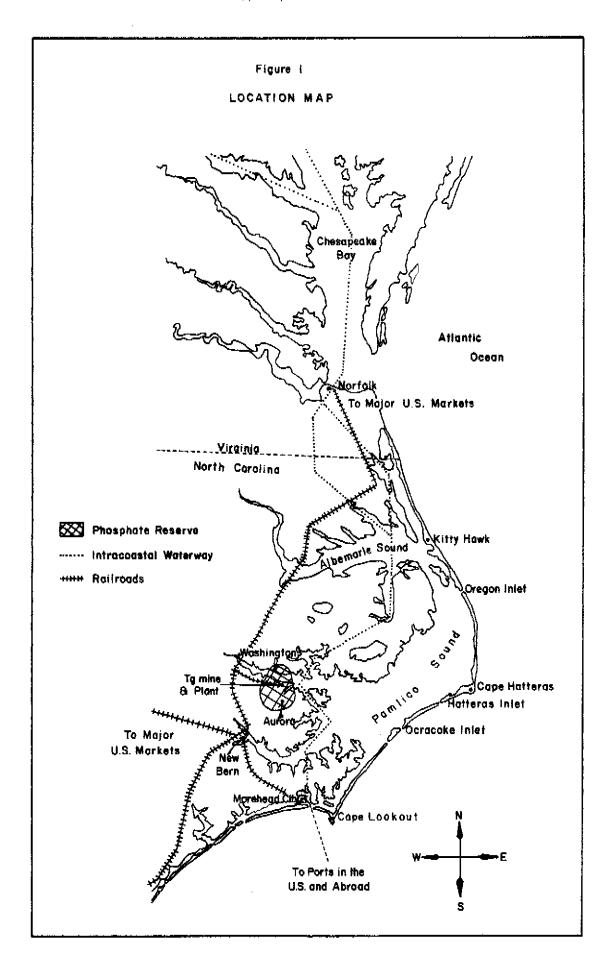
A thorough description of the pipe reactor process used to produce the base solutions has been given in papers by R.S. Meline, <u>et al.</u> (4) F.P. Achorn, <u>et al.</u> (5) and A.O. Harwell and L. Hopwood (6). Mr Meline is presenting a paper on his process before this conference.

ACKNOWLEDGMENTS

Acknowledgment is made to co-workers at TVA, Mapco, and Texasgulf for contributions in the development of superacid from a speciality chemical to a product of wide use and utility. Special acknowledgment is made of the work of my Tg associates John Jernigan, John Boyd, Eric Kelder, and Andy Harwell.

REFERENCES

- Caldwell, A. Blake, "TGS Ledd Creek Complex A New Dimension
 in Phosphate Mining and Processing," <u>Engineering and
 Mining Journal</u>, January, 1969.
- 2. (a) Donohoo, H.V.W., "Phosphorus", <u>Fertilizer Solution</u>, 10 No.5, 42-46 (1973).
 - (b) Blue, Thomas A., "Superphosphoric Acid". Chemical Economics Handbook, November (1973).
 - (c) Achorn, F.P., and Hubert L. Balay, "Phosphoric Acid: Shipment, Storage, and Use in Fertilizers." <u>Fertilizer Solution</u>, 17. No. 5, 54-68 (1973).
- 3. Boyd J.B., and J.D. Jernigan, "Use of Superphosphoric Acid in Fluid Fertilizer," Presented to the Fertilizer Institute Round-Table, November 6, 1973.
- 4. Meline, R.S., R.G. Lee , and W.C. Scott, Jr., "Use of A Pipe Reactor in Production of Liquid Fertilizers With Ver. High Polyphosphate Content." <u>Fertilizer Solution</u>, 16, No. 2, 32–45 (1972).
- 5. Achorn, F.P., H.L. Balay, and H.L. Kimborough, "Commercial Uses
 Of The Pipe Reactor Process For Production Of High
 Polyphosphate Liquids." <u>Fertilizer Solution</u>, 17,
 No. 2, 44-54 (1973).
- 6. Harwell, A.O., and L. Hopwood, "Superphosphoric Acid And The Pipe Reactor." Presented to The American Chemical Society National Meeting, Chicago (August 28, 1973).



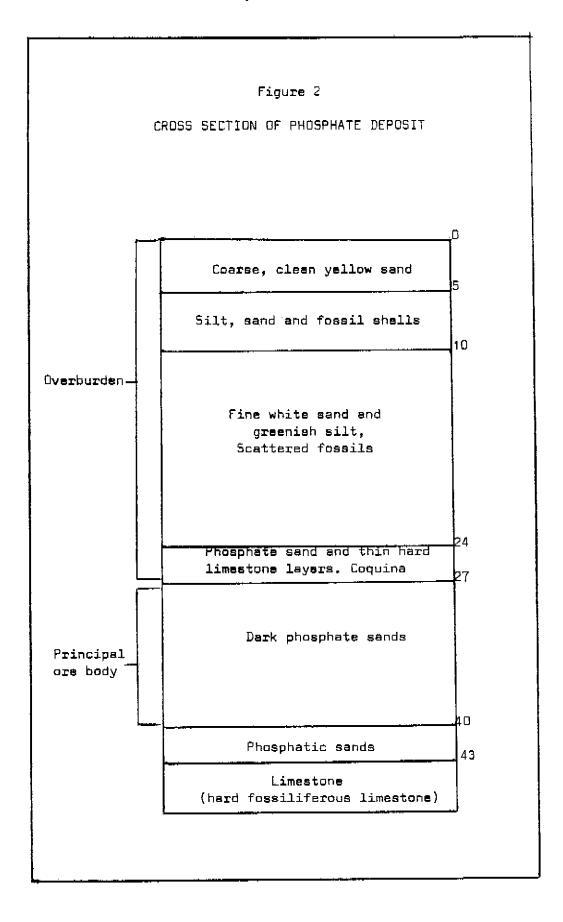
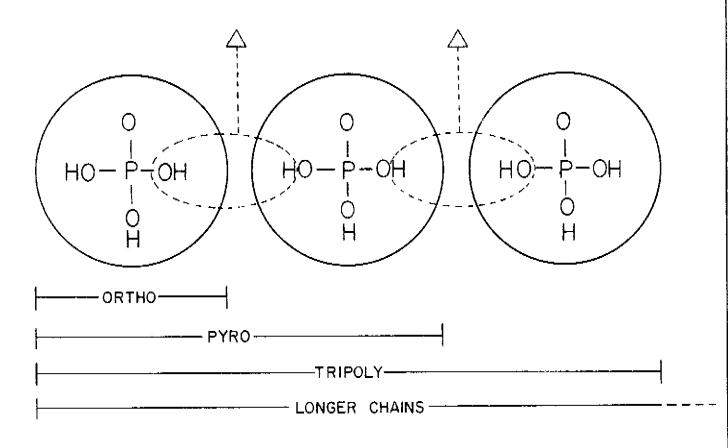


Figure 3
POLYPHOSPHATE S⁽³⁾



Example of forming Tripolyphosphate

Orthophosphate Units

Tripolyphosphate

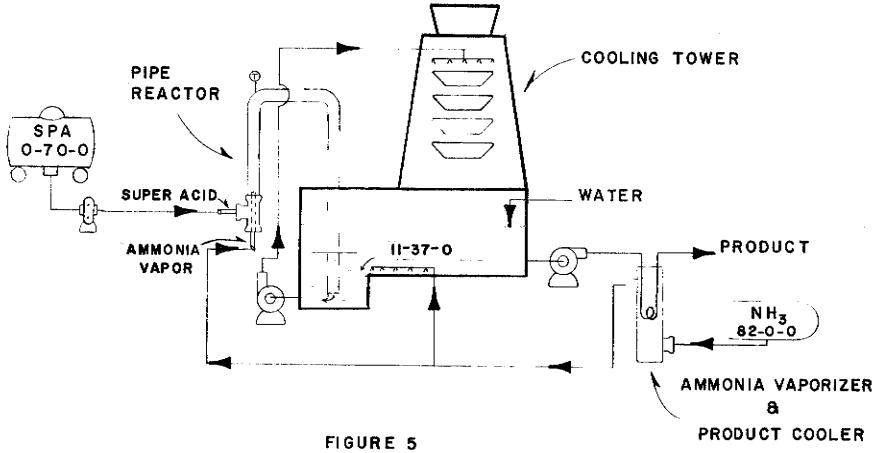
Water

Figure 4

COMPARATIVE ANALYSIS

Tg Superphosphoric Acid

	PRODUCT NAME		
	SUPER 49	SUPER 45	
COMPONENT	PURIFIED	<u>UNPURIFIED</u>	
Total P ₂ O ₅	70.0	69.8	
% Polyphosphate	30.0	36.8	
Sulfate (SO ₄)	3.8	3.4	
Aluminum (Al203)	1.1	0.9	
Iron (Fe ₂ O ₃)	1.0	1.8	
Magnesium (MgO)	0.4	1.3	
Fluorine (F)	0.27	0.26	
Solids (Insol. in CH3OH)	0.15	8.0	
Solids (Insol. in H ₂ O)	0.01	0.20	
Sp. Gr. at 24°C	1.96	2.00	
Viscosity, Centipoise at 52°C	175	450	



DIRECT AMMONIATION PLANT USING A RECYCLE PUMP FOR MIXING AMMONIUM POLYPHOSPHATE MELT

FIGURE 6

COMMERCIAL PRODUCTION OF HIGH-POLY 10-34-0 FROM Tg SUPER 49 SPA

Component, %	Company			
	A	В	С	D
Nitrogen	9.74	10.08	10.09	10.02
-	33.95	33.71	33.57	34.08
P ₂ 0 ₅ Poly P ₂ 0 ₅	75.94	76.02	76.46	74.91
pH 2 5	5.85	6.04	5.90	5.97

D 37 A

Figure 7
POLYMER PROFILE 10-34-0/11-37-0

	Conventional	Tg Pilot Plant	Commercial Plant	II-37-0 Electric Furnace	
	50% P ₂ O ₅ Feed	TVA Pipe Reactor & Super 49	TVA Pipe Reactor 8 Super 49	Electric Furnace Acid	
% Poly	47	83	79	81	
Species, %					
Ortho	53	17	21	19	
Pyro	37	27	35	37	
Tri	8	21	23	24	
Tetra	-	13	П	11	
Penta	-	9	6	-	
Hexa	-	5	2	-	
Hepta	-	3	2	-	
Octa	-	3	-	-	
Other	2ª	2	1	9 p	
Above Pyro	10	56	44	43	

- a. includes tetra
- b. includes penta

COMMUNICATION Nº11

Mr.WHITEHURST (Texasgulf, U.S.A.)

Since points on the marketing have already been covered, I would try to confine my remarks to the production area. Polyphosphates derived from superphosphoric acid play an important role in the manufacture of liquid fertilizer solutions in the United States. 510 000 t of PpOs were consumed in the liquid In 1971-72, fertilizer industry in the United States. Liquid mixed fertilizers account for about 10 % of the total fertilizer P⊃Os comsumed in the United States and during the past ten years have grown at the rate of 14 % per year. Texasquif has two identical superacid plants which produce about 275 metric tons/day of P205, concurrently there is a third plant under construction of comparable capacity. When this unit is complete it will give us a production capacity of 825 metric tons per day of PpDq. The first two plants that we have, which were built in 1967 and 1978, incorporated two stage falling film evaporators. The first stage is heated by steam and the second stage by Dowtherm. The design of the third plant will be based on a forced circulation evaporator, because the market requirements have changed. The two stages would be needed if the market requires a 50 % polyphosphate level whereas a 35 % or a 30 % which is currently now what is on the U.S. market requires only about 25 - 30 % levels. You don't need the second stage for that kind of poly level. The superacid evaporators that we have concentrate our 54 % merchant grade acid to about 70 % P_2O_5 and 35 % polyphosphate. At this point the acid contains about 7 % solids as measured by methanol extraction and these solids are essentially an iron-magnesium pyrophosphate. And thus, when they are removed from the superacid, the resultant clarified acid has a lower iron and magnesium content. We are not sure at this point whether this is a single compound or a co-precipitate of ferrous pyrophosphate and magnesium pyrophosphate. We are able to remove about 60 % of the magnesium and about 40 % of the iron via precipitation followed by clarification. The purity of the North Carolina phosphate makes it uniquely suited for the production of superacid. The magnesium impurity in the ore can be substantially reduced by careful control of the process conditions such as the free sulphuric acid content of the feedstock. Because of these factors, it has been possible to produce a superacid with a quality comparable to furnace acids. The liquid fertilizer base solution produced from the superacid 10-34-0 has a storage life in excess of 1 year. Because of these unique qualities and techniques, Texasgulf has become a major supplier of phosphoric acids for liquid fertilizers. Further expansion of superacid is planned beyond the three plantlevels and we are certainly continding research and development in liquid fertilizers and we are also now working on purification of phosphoric acid for non-agricultural uses.

Slide 1.: This is a map of the Eastern part of North Carolina which shows the relative position of our plants with an area to the North. The phosphate deposit that we have is of Myocene type of about 15 million years old. It covers an area of something of the order of 20 000 ha. It is about 40 feet and there are between 2 and 10 billion

tons of this material in North Carolina, depending upon which geologist you might talk to. One of the unique characteristics of this phosphate deposit is that its composition is virtually constant and I know from many others who have used rocks from all around the world, this is quite a problem. The analysis that we are processing is the very same as 7 years ago when we first started.

Slide 2. : In the superacid production this is what we refer to as the unpurified or unfiltered material. The two primary things we are removing are magnesium and iron and when these things precipitate you get an idea about how much we are removing of those particular things there. Now, I do want to point out one thing here which is somewhat confusing. The fluorine level of this acid does have a ratio of P : F in excess of 100, which supposedly makes it suitable for feed grade animal feed uses. However, in the United States, the National Feed Ingredients Association has a scale of heavy metals which was established on furnace acid. Unfortunately, that procedure winds up precipitating most of these metals in the acid, so we currently do not market nor do we intend to market this material for that use because of this problem which we are unable to solve.

Slide 3. : Now I would like to give you an idea about what the colour of this acid is. This was an older product that we produced and this is our current product right here.

Mr.FRAITEUR (Société de Prayon, Belgium)

Most of you undoubtedly know for some time that Texasgulf was one of those who pioneered the production of low-conversion superphosphoric acid successfully used by the pipe reactor process developed on pilot scale by the experts of the Tennessee Valley Authority. This process for producing ammonium polyphosphates, described in M. MELINE's paper and, thanks to produces like Texasgulf, presently more and more widely used, stands halfway between the conventional process of ammoniation of superphosphoric acid and the direct reaction process between orthophosphoric acid and anhydrous ammonia. It combines most of the technological advantages by allowing to obtain a high physical and chemical quality product. It will mark an epoch in fertilizer production in general and liquid fertilizers in particular.

Now we have three question for Mr.WHITEHURST: the first one refers to the post-precipitation in the orthophosphoric acid produced. You state, Mr.WHITEHURST, that post-precipitation is not important in the case of orthophosphoric acid from North Carolina. However, we note that you operate with nearly no free sulphuric acid, which means that a relatively substantial amount of calcium oxide remains in solution and thus promotes post-precipitation. Could you clarify this point?

Second question: The magnesium oxide content of your superacid is about 0,4 %. We agree with you on the more specific sequestering effect on Mg and Ca of polymerized forms beyond the pyrophosphate. However, and this is my question, do these forms not revert too quickly, which would mean, taking account of the Mg content of the acid, accelerating the precipitation of magnesium phosphates within

the polyphosphate solution ?
Third question: What is the frequency and nature of maintenance operation on the Incomel 625 tubes of the second evaporation stage?

Mr. WHITEHURST

About the post-precipitation that occurs in our scid, I am not really able to explain some of the unusual things of mother-nature but she has done one thing : at the B % free sulphuric acid level, the calcium oxide content of our acid is somewhat less than 10 ppm. We have repeatedly been asked from customers for calcium analysis and what is the solubility , etc..., and ${f I}$ have answered zero. I have repeatedly been questioned, so I would rather give a number that is somewhat less than 18 ppm, rather than tell you it is 0. Certainly calcium is not a problem. The superphosphoric acid that we are producing does not have a postprecipitation problem because we are removing the cause of the postprecipitation, particularly in this case of the iron — magnesium pyrophosphate, and if you do not remove this or if you have some operating problems you might get some but this has not been the case. Another thing I would like to mention with the advent of the TVA pipe reactor system the temperatures that are reached in that pipe reactor, for whatever the reason might be, I would say are probably the main cause. Small emounts of the iron-magnesium pyrophosphate will be dissolved and so if the customer receives a tank car of acid in which the solid level is 0.2 - 0.3 % he really would not have any problems with it if he uses the pipe reactor and we don't produce any superphosphoric acid at the mament that is not intended for use with the pipe reactor. On the second question which has to do about the magnesium content of the acid and the polyphosphate level, as M. MELINE pointed out yesterday one of the things about the pipe reactor is that it does raise the poly level of the acid substantially to form further condensed series. In most of the superphosphoric acid, the first thing formed is the pyrophosphate. The second one is the tripolyphosphate. The tripolyphosphatehas its primary sequestering ability with the valence two level such as magnesium, iron 2, strontium, calcium and these particular things and the levels of tripolyphosphate run something in the order of 20 to 25 % tripolyphosphoric acid and there is really a very ample amount in this case to provide sequestration for periods in excess of a year's storage so we can market our acid in July and August and our customers can convert it to 10-34-0 and store it during the fall or winter, and early spring for use when they need it. On the third question, I can answer from a historical basis primarily because, as things stand now, we don't operate a two stage system any more. We only did this when we had to produce a 50 % poly level material. Now this second stage evaporator was, as said in the paper, constructed of Incomel 625, a material with about 65 % nickel and about 20 to 25 % chromium, the remainder is molybdenum. This is an excellent meterial, it is an extremely expensive material and you don't want infrequency with this material. Now our point is here, when we were operating the second stage, we were operating at something of the order

a year to fifteen months, between changes of this evaporator. Our first evaporator which concentrates to approximatively 35 % level has been in service for 7 years and the corrosion level then is still not bed and we are using Carpenter 20 for the tubes in this evaporator.

Mr. ROGERS (New Zealand Fertilizer Association, New Zealand)

I have three questions. It would be interesting if Mr.WHITEHURST could tell us something of the distances that his company covers with his product, and secondly, as somebody who comes from a country which is very conscious of the need for sulphur in its crops, could Mr.WHITEHURST indicate whether the people that are marketing this material to the farmers either in the liquids or in a suspension formulation include sulphur and thirdly, also on the question of sulphur, how does his company deal with the problem of the disposal of the calcium sulphate which is produced in making the phosphoric acid. In my travels in the last four months around the world, it would appear that the mountains of calcium sulphate which this industry is producing is one of the major problems for disposal in front of technologists.

M = WHITEHURST

Let me start backwards in this particular case, the disposal of calcium sulphate is accomplished with difficulty; when we have our fourth train operating we will be producing calcium sulphate at a level of 11 000 t/day. Now, this obviously is a disposal problem, our waste gypsum piles are the highest point in Eastern North Carolina... and I had jokes with one of my Japanese friends, indicating that it was our entry to Mount Fuji, but what we really plan to do with this material is to put it back into the mined out area as a filling material and this is one of the very interesting things that happened there: in the mining of phosphate, as all of you know, you get along with the phosphate rock a certain material which is referred to as slimes. The slimes in North Carolina are a little different than they are in Florida, not all that much. We have found that if you take these slimes and mix them with waste send and mix to the calcium sulphate, you can make a synthetic soil, which is quite good for the raising of grass, trees and the like, and so actually the disposal of this calcium sulphate will become part of our land reclamation programme. Now that is a partial answer, now the other part of the answer is this.

In North Carolina and Southern Virginia, they grow quite a lot of peanuts, there are 200 000 acres of peanut that are grown in the two States and we sell about 100 000 t a year of this calcium sulphate to the peanut farmers. They need this as a source of calcium. Now, secondly, the crops that we have there, soybeans are common, and we are now testing the use of calcium sulphate on soybeans and on some of the grasses, so that we hope to use some of this material in agricultural uses. We are also working with a wallboard manufacturer to convert this material into wallboards and this looks quite promising at the moment.

In terms of sulphur deficiency from the use of liquid fertilizers,

I think this brings up another point. Yes, you can add elemental sulphur in a suspension and this is done. Certainly it is a high analysis material. As far as we can say, liquid fertilizer is a material which has a special use. But certainly it does not appear to us that liquid fertilizers can contain certain agronomic things that the liquid may not handle. Now suspensions are being developed rather rapidly in the United States and certainly if we are going into no-till farming, which is becoming quite popular in areas of the United States, you can include pesticides, herbicides, many of the trace-elements, sulphur all along with the NPK liquid and f I know some areas in the State of Virginia where they are doing just this. So they need a total liquid programme. I want to comment on one of the points of yesterday : someone mentioned about the energy with regards to superphosphoric acid. The acid does take more energy. This gets into the next part of the question. Dur market for superphosphoric acid is in the Corn Belt of our country which is of the order of 1 880 to 1 580 miles from our plant. We ship halfway across the United States to our customers and at a point somewhere in the order of 800 miles from our plant it actually delivers P 0, to the customer cheaper at 69 % level, as compared to the 54 % level. In terms of energy saving, we are actually saving energy by this instead of shipping water. Also no-till farming requires about 30 % of the fuel that normal tillage and normal ploughing would require and so we suspect that there is going to be a bit of no-till farming in the future.

Mrs. SKUDLARSKA (Technical University Wroclaw . Poland)

I am interested in the amount of P₂O₅ and fluorine in phospho-gypsum cake. Is it possible to get the number?

Mr. WHITEHURST

The amount of P_2O_5 in our gypsum cake is of the order of 1 % total and of that there is about .3 % as water soluble P_2O_5 . Now I might add that in the system that we have at the plant, the P_2O_5 that is lost in the filter cake, is not really lost. We have a special water recycle system so that in the gypsum pile that is water soluble P_2O_5 and a portion of the other which becomes slightly soluble, is returned to us so that our actual net loss is a little less than what you might calculate if you took the overall data from our plant. This is a very very important consideration from an environmental point of view.

Mrs. SKUDLARSKA

What about the fluorine amount in the phospho-gypsum?

Mr. WHITEHURST

The concentration of fluorine is 3/4 to 1 % and that will be as the silicofluorides of solid potassium and calcium.