PHOSPHORIC ACID, SLUDGES AND SOLID'S CHEMISTRY, PARTICLE SIZE AND HOW TO DEAL WITH THEM

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PHOSPHORIC ACID, SLUDGES AND SOLID'S CHEMISTRY PARTICLE SIZE AND HOW TO DEAL WITH THEM

This paper outlines ways to treat phosphoric sludges and solids during their manufacture, storage, shipment and use. It summarizes available information concerning the chemistry and physical particle size of these sludges and solids from phosphoric acid at different P_2O_5 concentration and origin of raw material source.

Solids and sludges produced in the manufacture of wet-process phosphoric acid are undersirable elements as one produces 29%, 41%, 53% phosphoric acids and super acid.

These solids and sludges are difficult to deal with under the best conditions. Their chemical and physical properties have been studied vigorously for the past 30 to 50 years. The selected history of these studies and results will be analyzied and evaluated for commercial applications.

If one plans to use 29, 41, 53 or Super acid that is; new acid, virgin acid or fresh acid that is the product of phosphate rock and the sulfuric acid reaction, we would design a system to deal with organic humics and calcium sulfate in the form of gypsum and a small amount of sodium fluosilicate.

As we concentrate the phosphoric acid to 41, 53 and Super Acid the types of chemical compounds change drastically.

It is common knowledge in the industry that the solids that precipitate as the P_2O_5 acid strength increases, result in smaller and smaller solids sludges, gels and semi-liquid gels.

The commercial solution to handling, removing and using these solids and sludges will be discussed and outlined by process application.

In the industry many of these solids and sludges are recycled backward in order to remove these solids and recapture the P_2O_5 values.

The effect of process operation can have unpredictable effect of acid quality and quantity.

The solid and sludges formation can be beneficial if their formation in controled and the type of compound formed are removed to enhance the quality of the acid.

Example of this concept is the removal of potassium fluosilicate by the addition of silica to prevent the formation of iron and aluminum phosphate in Merchant Acid.

Also the precipitation of magnesium by the addition of calcium carbonate to remove the solids before concentration to Super Acid.

A representative documentation of selected references will be included in this paper plus numerous commercial applications of how to deal with solids and sludges from Phosphoric Acid manufacturing.

Solids and sludges precipitate from phosphoric acid produced from the reaction of phosphate rock and sulfuric acid in a process called the "wet process method." The primary solid formed in this process in calcium sulfate as gypsum ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) or anhydrite ($CaSO_4$). These forms of $CaSO_4$ are formed depending on the temperature of the solution and the P_2O_5 content, i.e.

$CaSO_4 \cdot 2H_2O$ below 90°C and 30% P_2O_5.

$CaSO_4 \cdot \frac{1}{2}H_2O$ between 110°C and 120°C with P_2O_5 between 40 & 55%.

$CaSO_4$ above 130°C and the P_2O_5 between 40 & 55%

(A. W. Frazier, et.al. 1-17-83)

There are twelve (12) fluoride salts from filter grade wet process phosphoric acid. (TVA Bulletin Y-113, May 1977).

Solids and sludges are formed in solution of phosphoric acid, P_2O_5, as the strength, percent P_2O_5, of the acid is increased. (G. H. McClellan and J. R. Lehr, Round Table 1982.)

These compounds are calcium sulfate as gypsum and hemihydrate and florine compounds at the 28 to 32% P_2O_5 level.

Fluorphosphates at the 40 to 50% P_2O_5 and orthophosphates from the 40 to 54% P_2O_5 level. (J. R. Lehr Industrial Minerals, May 1984.)

The size of solids formed by the wet process phosphoric process and the concentration of the 29% P_2O_5 to 41% P_2O_5 by evaporation and the continued concentration to 53% P_2O_5 are quite varied. The size of the particles are as follows:

29% Solids

Gypsum: 400 to 10 micron

average 200 microns

(Masao, KUBO, Nisson Chemical Industries,

(ISMA Technical/Economic Conference, October 1978)

Hemihydrate:

100 to 10 micron

average 50 micron

(Masao KUBO, ISMA, October 1978)

41% Sludge, Solids

Gypsum: 400 to 10 micron

average 50 micron

Hemihydrate:

100 to 10 micron

average 50 micron

Fluorophosphates

10 to 1 micron

average 1-2 micron

(G. H. McClellan & J. P. Lehr, Round Table 1982)

Fluorine Compounds

100 to 10 micron

average 20 microns

(G. H. McClellan & J. P. Lehr, Round Table 1982)

Overall size about 20 micron.

53% Sludge, Solids

Orthophosphates: 50 to $<$ 1 gels micron

average 10 micron

Fluorphosphates

Fluorine Compounds

Gypsum

Hemihydrate

Average size 10 micron, plus gels

(G. H. McClellan & J. R. Lehr, Round Table, 1982)

The previous identification of solid forms and sizes are from a once through system where wet process phos acid, raw acid, is formed at 29% P_2O_5 and concentrated first to 41% P_2O_5 and then to 53% P_2O_5.

If however, sludges are recycled backward 41% to 29% or 53% to 29% the chemistry is totally changed. Where acid sludge from high strength to lower strength, the sludges may dissolve and cause smaller solids to form, gels to form and new sludges to form because of a change in chemical composition and solution concentration. This will generate colloidal particles.

The complexity of the chemical compound the precipitate and best described by G. H. McClellan in his paper, to the Round Table in 1982.

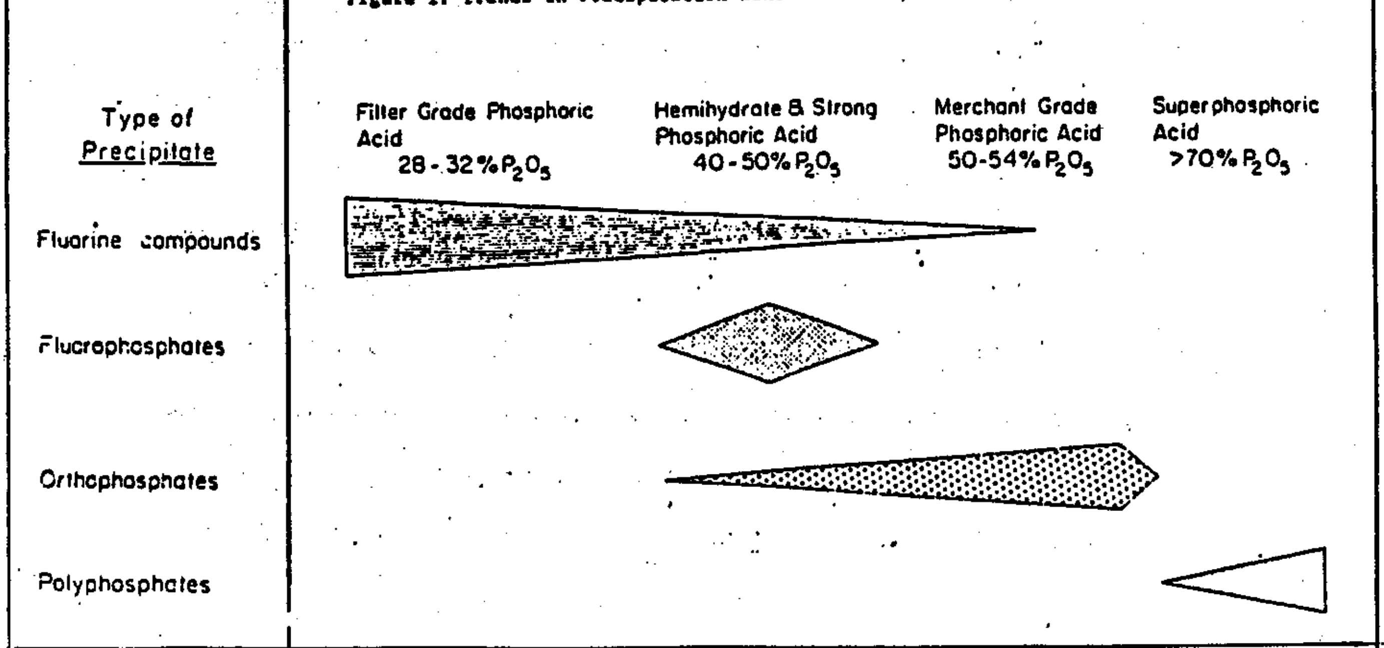
These complex precipitate are pictorally described in the attached Figure 1 from that paper.

It is common knowledge in the industry that solids that precipitate as the P_2O_5 acid strength increases, result in smaller and smaller solids, sludges, gels and simi-liquid gels. This was confirmed in all our discussions with Lehr, Frazier and McClellan.

It was also confirmed that if one recycles, smaller particles, gels, semi-gels, and super saturation will result.

Also due to the introduction of recycled impurities, post precipitation will occur and new and differ compounds are formed.

Figure 1. Trends in Precipitation Behavior of Impurities in WPA.



Size of Solids and Sludges

The size of solids formed by the wet-process phosphoric process and the concentration of the 29% P_2O_5 to 41% P_2O_5 by evaporation and the continued concentration by evaporation to 53% P_2O_5 are quite varied.

The three phosphoric acid concentrations of interest to us are 29%, 41% and 53% P_2O_5. As we know, these are only names and the phosphoric acid strength will vary from hour to hour, day to day and week to week. However, within the variation, we are interested in the size of the solid, sludges are relative.

The individual size of the particles are primarily controlled by the chemical composition and the environment in which they were formed.

29% Phosphoric Acid, Solids

"A previous report (Frazier, Lehr, and Dillard, TVA Bulletin Y113, NFDC, Muscle Shoals, Alabama) shows that 30 percent P_2O_5 acid is a sufficient solvent for the associated impurities, so that only $CaSO_4 2H_2O$ is a byproduct. The results show that $(Na,K)_2SiF_6$ is precipitated with the gypsum but is redissolved during the wash cycle and returned to the acid product. Also, the report shows that the other possible, stable precipitates at 30 percent P_2O_5, will require significant compositional increases in impurity levels to effect their crystallization as solid phases. The primary reason for this lack of impurity precipitation is the high quantity of free water available for ionization of the acid hydrogen which acts as an effective solvent." (Frazier, U.S. Patent No. 4,435,372)

29% Raw Acid, Gypsum Solids

100 m, microns, average

1. 150-30 microns
   (O. B. Bower, Badger, British Sulfur, 1979)
2. 200-70 microns
   (N. Popovici, IPROCHIM, British Fulfur, 1979)
3. 250-100 microns
   (A. Varsanyl, IFDC, TVA, British Sulfur, 1970)

4. 120-50 microns
(A. Varsanyl, IFDC, 1979)

5. 200-50 microns
(A. Varsanyl, IFDC, 1979)

6. 150-100 microns
(A. Varsanyl, IFDC, 1979)

Particle Size

Tyler Seive	Microns
#65	208
#100	147
#200	74
#325	43
#-325	-43

41% Phosphoric Acid, Solids

20 Micron, Average

Gypsum, average 30 micron

Hemihydrate, average 30 micron

(Slack, Chpt.4, Page 371, <75 microns)

Anhydrite, small particles

(Slack, Chpt. 4, page 337)

(Lehr, Frazier, Myrick, Worthington, TVA, 1985)

(Calcium sulfate, all three forms)

(Crystals are likely to be small in size)

Fluorine Compounds, average 20 microns

100 to 10 microns

(McClellan & Lehr, Round Table 1982)

Small particle size

(Slack, Chpt. 7, Page 610) "The small particle size of the salts has become quite a problem because of the difficulty in removing them from the acid.)

10 to 5 microns

(Slack, Chpt. 7, Page 629)

Fluorophosphates, average 1-2 microns

1-2 microns

(McClellan & Lehr, Round Table 1982)

100-10 gel microns

(McClellan & Lehr, Round Table 1982)

10-5 microns

(Slack, Chpt. 7, Page 629)

53% Sludge, average 10 microns, plus gel

Orthophosphates - 10 to 1 micron, gel

(McClellan, Lehr, Round Table 1982)

Less than 5 microns

(Lehr, Myrick, Worthington, TVA, 1985)

10-5 Microns

(Slack, Chpt. 7, Page 629)

Fluorophosphates

Fluorine Compounds

Calcium Sulfate

Anhydrite, Hemihydrate

(Slack, Chpt. 4, Page 337)

Mainly phosphate, some gyp and fluosilicate, relative reluctant to settle. (N. Popovici, British Sulfur, 1979)

"The viscosity of 50-54% P_2O_5 acid at ambient temperature can be as high as 80 cP in certain cases and most of the solid particles to be removed are small, often with an order of magnitude of 10 μm. This explains why the use of chemical additives (flocculants) has become common practice. Generally, they are polyacrylamides added to the acid as a dilute solution (1 g/liter) at a rate of some 5-15 ppm." (Becker, P. Chapter 8, Page 445)

"Taking as an example a solid particle of 50 um diameter and specific gravity 2.3, and a phosphoric acid with a viscosity of 20 cP and a specific gravity of 1.65, the settling speed will be 0.159 m/hr. and for a 10-μm particle only 0.006 m/hr, which is very low. These figures illustrate well why settling has taken such advantage of flocculation technology, where the buildup of flocs permits acceleration of the settling speed." (Becker, Chpt. 8, Page 446, 1983)

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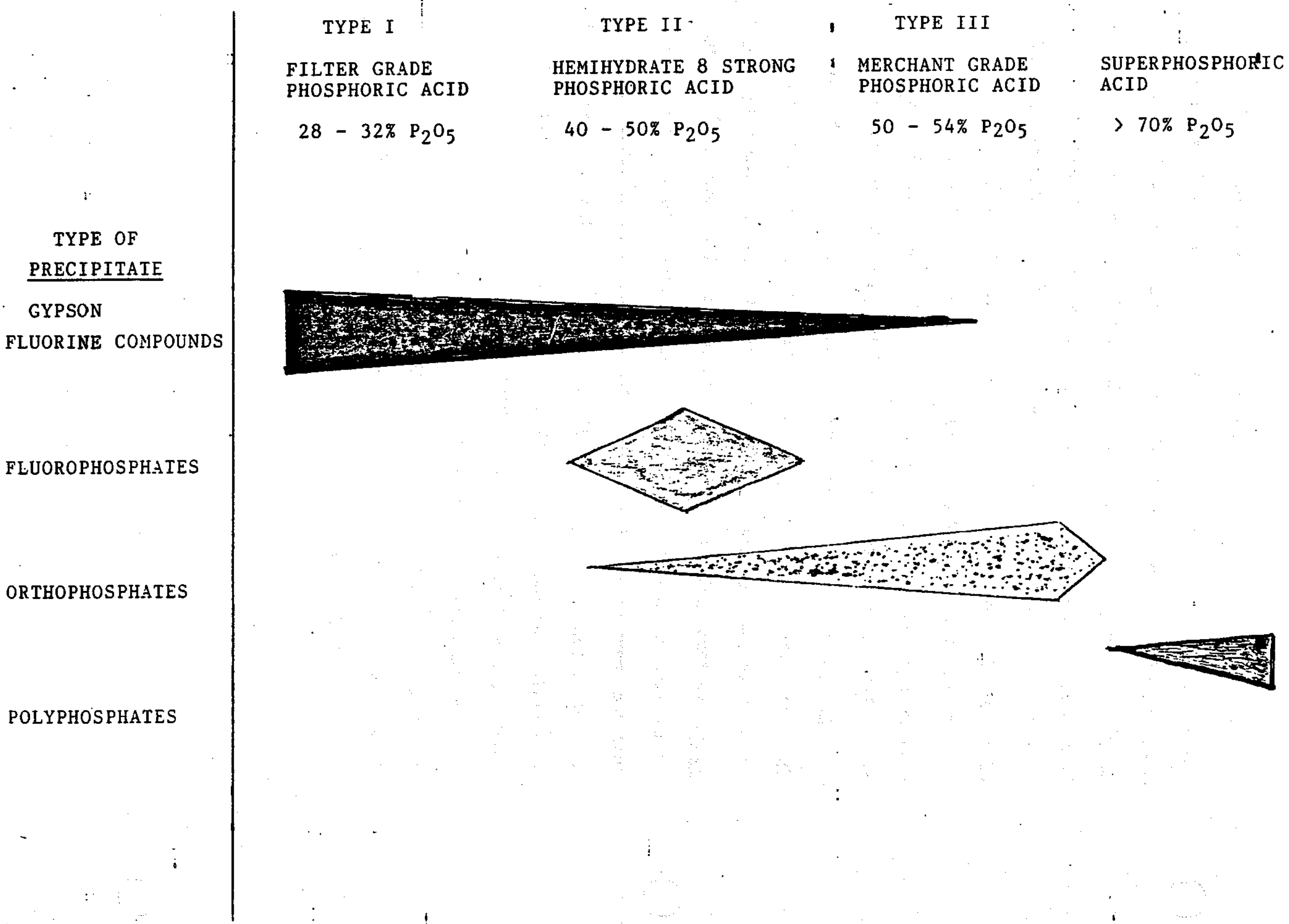
If, however, sludges are recycled backward 41% to 29% or 52% to 29%, the chemistry is totally changed. Where acid sludge from high strength to lower strength, the sludges may dissolve and cause smaller solids to form, gels to form and new sludges to form because of a change in chemical composition and solution concentration. This will generate colloidal particles. (Discussion between J. R. Lehr, W. Frazier, R. Worthington and J. Myrick, NFDC, Muscle Shoals, Alabama, February 1985) (Discussion between G. H. McClellan, A. F. Little and J. Myrick, IFDC, Muscle Shoals, Alabama, February 1985)

The complexity of the chemical compound the precipitate and best, described by G. H. McClellan in his paper to the Round Table in 1982. These complex precipitate are pictorally described in the attached Figure 1 from that paper.

FIGURE 1. TRENDS IN PRECIPITATION BEHAVIOUR OF IMPURITIES IN WPA.



SLUDGE RECYCLE

The solids and sludges formed from 29% acid that the percipitates are mainly calcium sulphate and crystalline sodium and ptassium fluosilicate. From 41% acid, the precipitates are again calcium suplahte and sodium and potassium fluosilicates plus a major amount of (mgCa). $AI_2F_8.2H_2O$ is produced in very small crystals <5mm and does not redissolve in 30% acid and some (MgNa) AI $F_6.2H_2O$ ralstanite.

53% acid gives a completely different group of solids in which TVA salt, $Fe_3KH_{14}(PO_4)_8$, is the most important. However, many other salts can crystallize depending on condition and on the quantity of other ions such as F, Mg, Al, etc. being present. These materials will dissolve incongruently in 30% acid to generate a colloidal ferric phosphate, $FePO_4.2H_2O$ or $FePO.H_3PO_4.2H_2O$, which will metamorphose inot other ferric acid phosphates depending upon the acid strength.

Such colloidal materials would be extremely active emulsion stablilizers as sould the small fluosilicate crystals produced in post precipitation. Any K recycled from 53% as TVA salt will precipitate more K_2SiF_6 in 30% acid and these will give considerable post precipitation problems and the Na:K ratio change can have profound effects downstream.

The calcium sulphate produced in high strength (40-55%) acid could be in any one or even all of the three forms, $CaSO_4$, $CaSO_4\frac{1}{2}H_2O$ or $CaSO_4.2H_2O$. The solutions are not at thermodynamic equilibrium even with 30% P_1O_2 dehydrate processes, anhydrite should be the stable phase not gypsum. The form will be governed by the conditions of temperature, viscosity, presence of seeds and presence of other ions which affect the crystallizations kinetics of the species. Such crystals are, however, likely to be small in size.

The following graphs are the result of studying the effect of solid, sludge recycled backwards from the 41% to 30% and 53% to 30%, all at the same time at changing production rates and varying % of solids.

This data is from three (3) phosphoric acid plants combined through one clarification system. The data was summarizied by computers and represents over one millin data points, collected for the years 1984 and 1985, divided into quarters of a year.

Graph A shows how 30% phosphoric acid production to evaporation increased over 30% produced as filter product from the reactor. This increase is due to 41% and 53% recycle.

The percent solids in 30% phos acid increase due to the recycle of 41% and 53% sludges into the 30% phos acid the lower line shows how low the % solids would have been without recycle of 41% and 53% sludges.

This data shows that sludges are determined to the quality of 30% phosphoric acid.

Conclusion

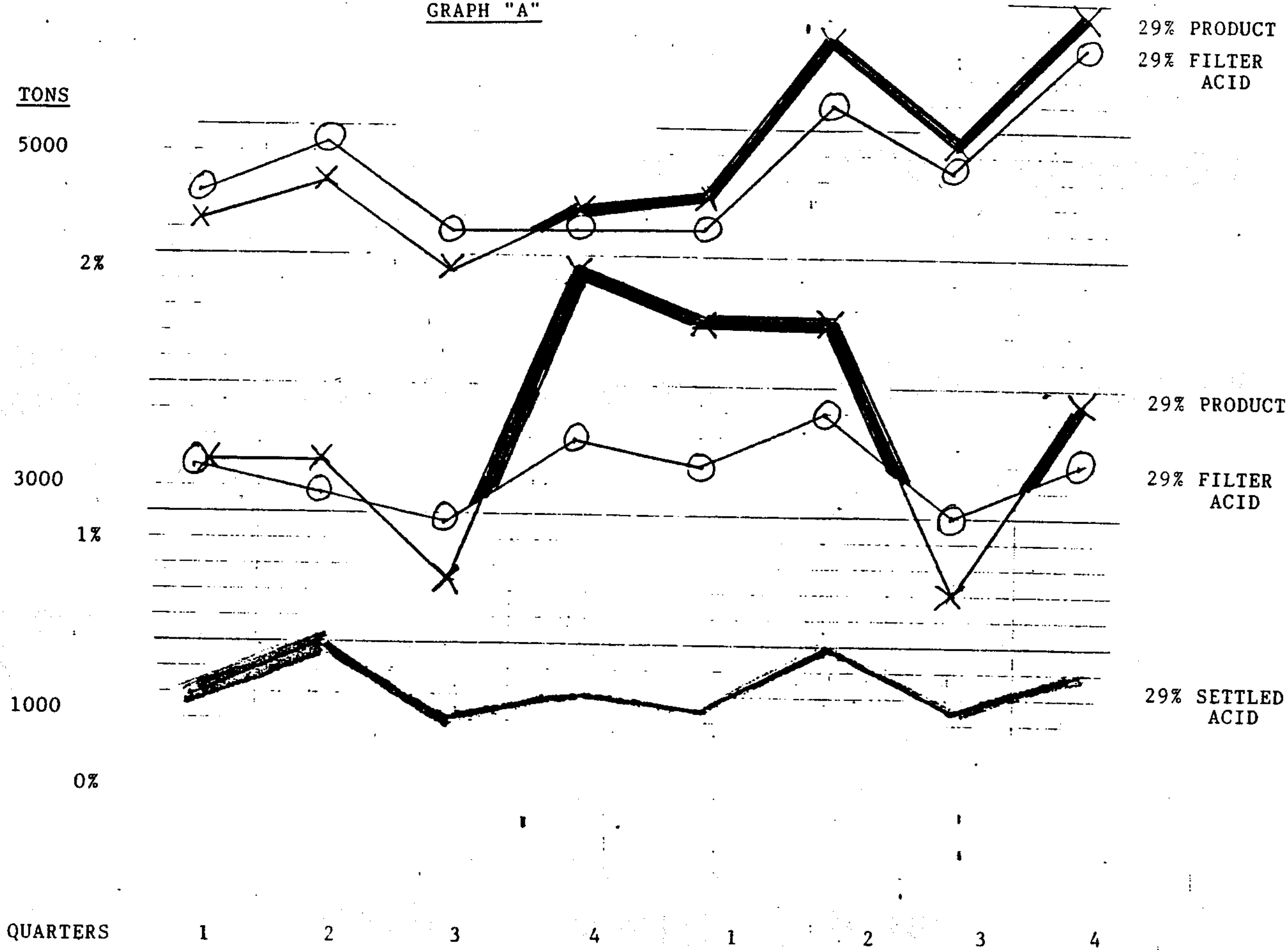
If you recycle sludge in a phosphoric acid plant the quality of 30% phos acid will deteriorate.

Phosphoric acid sludges should be treated by some other means besides recycling.

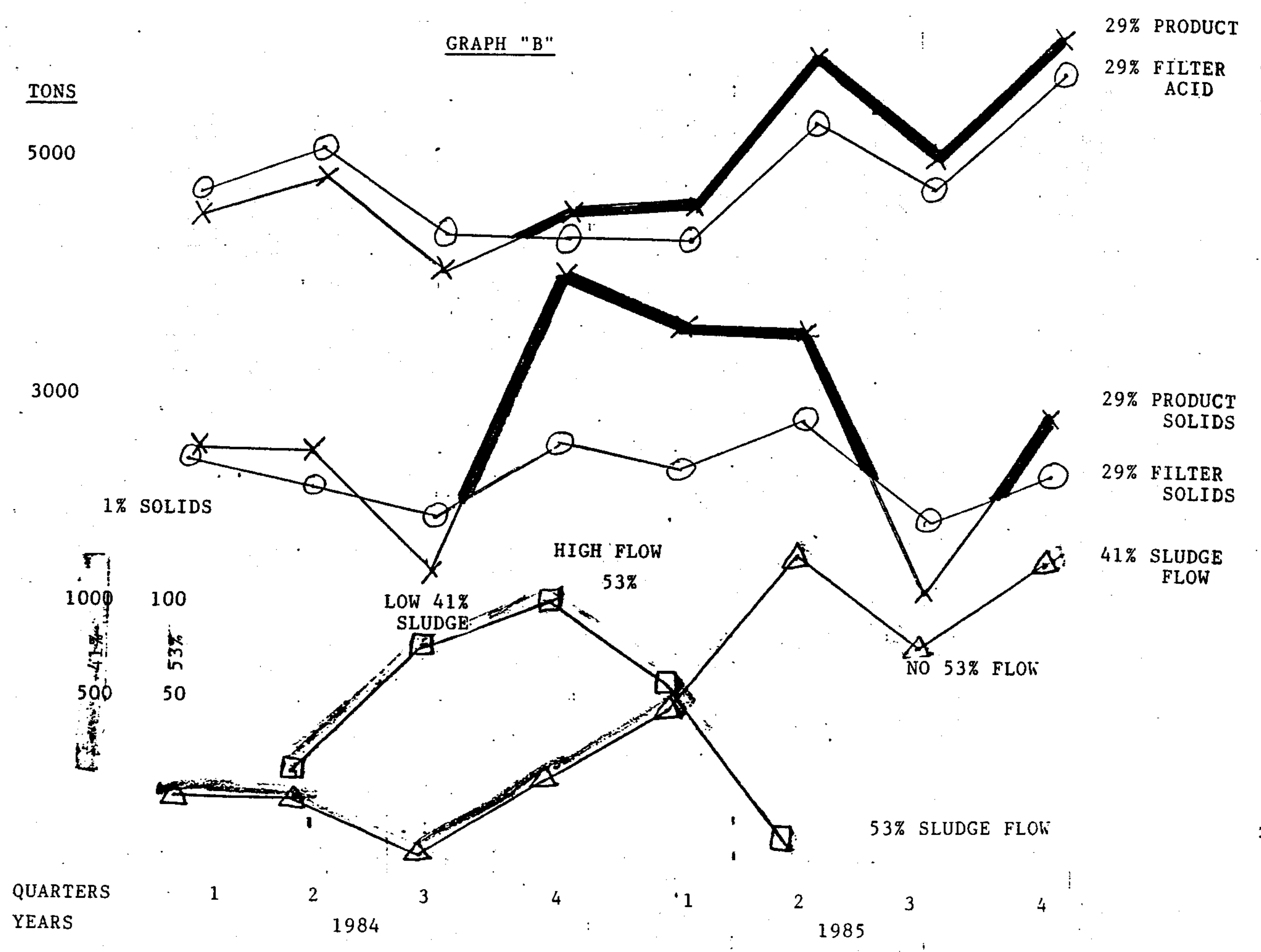
The preferred method is secondary filtration of the 41% or 53% sludge weight one (1) gram

size micron	100	50	10	1
number particles	500,000	4,000,000	500,000,000	500,000,000,000
	1	8	1,000	1,000,000

GRAPH "A"


TONS
5000
2%
3000
1%
1000
0%
QUARTERS
1
2
3
4
1
2
3
4
29% PRODUCT
29% FILTER ACID
29% PRODUCT
29% FILTER ACID
29% SETTLED ACID

GRAPH "B"



TONS
5000
3000
1% SOLIDS
1000
500
41%
100
50
53%
29% PRODUCT
29% FILTER ACID
29% PRODUCT SOLIDS
29% FILTER SOLIDS
41% SLUDGE FLOW
HIGH FLOW 53%
LOW 41% SLUDGE
NO 53% FLOW
53% SLUDGE FLOW
QUARTERS
1
2
3
4
1
2
3
4
YEARS
1984
1985

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