DECREASING IRON CONTENT IN WET-PROCESS PHOSPHORIC ACID

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FINAL REPORT

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PERSPECTIVE

The Florida phosphate industry has faced ever-increasing problems with the minor element--iron, aluminum, and magnesium--content of the phosphoric acid produced from the poorer-quality phosphate rock that is presently used, and the problem can be expected to grow even more critical as mining moves into the Southern Extension. Removal of magnesium from both the phosphate rock and the phosphoric acid has received the most attention but reduction and/or elimination of any one of the three elements would greatly benefit the industry by allowing the industry to produce on-grade DAP without having to utilize a supplemental nitrogen source.

Iron removal, if accomplished in the filter acid, would offer the additional advantage of reducing and/or eliminating some of the phosphate-containing solids formed as the acid is concentrated. Total iron removal would not be desirable since some iron is essential for good DAP granulation.

This project developed a method for removing a large portion of the iron from the phosphoric acid. The decision to adopt this acid treatment is an economic one that will be determined by the circumstances facing the individual phosphoric acid producer.

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ABSTRACT

A technique for the removal of iron from wet process phosphoric acid during manufacture utilizing chelating reagents was demonstrated. The process will benefit the phosphoric acid producer by reducing and/or eliminating the phosphate-containing solids formed as the phosphoric acid is concentrated and by allowing the production of DAP without the addition of supplemental nitrogen. Techniques for the recovery and recycling of the chelating agents were developed. Utilization of the process will be an economic decision by the individual phosphoric acid producer.

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EXECUTIVE SUMMARY

The major goal of this project is to decrease iron content in wet-process phosphoric acid using cost-effective reagents. Reducing the amount of post-precipitated sludge in the acid is another important objective in this study. In order to achieve these goals the following tasks have been conducted:

- Bench scale testing of four different chelating reagents [IR3, IR5, IR5-7H and IR5-3H] for the removal of iron from phosphoric acid produced from different Florida phosphoric acid plants. These chelating reagents are based on phosphonate chemistry as shown later. Effect of acid concentration is studied by adding the reagents to:
  Filter acid (25-27% P_2O_5), and
  Partially concentrated acid (42-45% P_2O_5), and
  Concentrated acid (52-56% P_2O_5).
- Regeneration and recycling of the precipitating reagent.
- In-plant testing using freshly produced concentrated acids for reducing the post-precipitated sludge,
- Recovery of P_2O_5 from post-precipitated sludge, and
- Cost-benefit analyses

The results are summarized in the following paragraphs.

TESTING IR3 REAGENT (AMINOTRI METHYLENE PHOSPHONIC ACID)

Testing a precipitating (chelating) reagent (IR3) to reduce iron content in phosphoric acid of various concentrations ranging from about 19% to 56% P_2O_5 was studied using different dosages of reagent. As shown in the following table, up to 63% Fe_2O_3 removal efficiency was achieved using filter acid at room temperature. The reaction time was one hour, followed by one day as clarification time.

Table 1. Iron Removal Efficiency from South Florida Filter Acid (25% P_2O_5).

Conditions	Chemical Analysis, %					Fe_2O_3 Removal Efficiency, %
	P_2O_5	Fe_2O_3	Al_2O_3	MgO	MER	
Filter Acid (Baseline), 23 ^{o}C	24.9	0.88	0.72	0.69	0.092	-
Acid + 0.1% R	25.0	0.88	0.72	0.70	0.092	-
Acid + 0.5% R	24.8	0.86	0.72	0.69	0.092	-
Acid + 1% R	24.7	0.73	0.71	0.70	0.087	17
Acid + 2% R	24.8	0.59	0.70	0.70	0.080	33
Acid + 4% R	24.8	0.33	0.70	0.69	0.069	63

MER: Σ Fe_2O_3 + Al_2O_3 + MgO / P_2O_5
X%R: is the weight % of precipitating reagent (IR3) as related to weight of phosphoric acid.

Regeneration and Recycling of IR3 Reagent

A regeneration scheme was developed to recover the precipitating reagent for reuse. Regeneration was carried out at different temperatures (room, 60°C, 80°C) for various reaction times (1 hr and 3 hrs). The optimum regeneration conditions were obtained. The results reveal that up to 69% of the reagent could be regenerated and recycled. Up to 60% Fe_2O_3 removal efficiency was achieved at room temperature for 1 hr reaction time while using a regenerated precipitating reagent. In this case however, the regenerated chemical was supplemented by a fresh IR3 reagent as a make-up. The amount of make-up was equivalent to 1.5% of phosphoric acid weight. The reagent was used and regenerated up to four times (stages) without loosing its efficiency as given below.

Table 2. Iron Removal Efficiency from Phosphoric Acid (26% P_2O_5) Using Regenerated IR3 Reagent with 1.5% Make-up.

Regeneration Conditions	Fe_2O_3 Removal Efficiency, %			
	First Stage	Second Stage	Third Stage	Fourth Stage
At Room Temp. for 1 hr	51.9	53.5	55.0	58.8
At 60 $^{\circ}$C for 1 hr	52.3	54.2	56.9	59.7
At 60 $^{\circ}$C for 3 hr	53.1	54.5	57.5	60.1
At 80 $^{\circ}$C for 1 hr	53.6	57.2	58.8	60.4

The chelating reaction using IR3 can be represented as:

$$C_3\,H_{12}\,O_9\,N\,P_3\ +\ Fe^{+3}\ \longrightarrow\ C_3\,H_9\,O_9\,N\,P_3\,Fe\ +\ 3H^+$$
$$\text{(Iron Phosphonate, one chelated ferric ion)}$$

or

$$C_3\,H_{12}\,O_9\,N\,P_3\ +2\,Fe^{+3}\ \longrightarrow\ C_3\,H_9\,O_9\,N\,P_3\,Fe_2\ +\ 6H^+$$
$$\text{(Iron Phosphonate, two chelated ferric ions)}$$
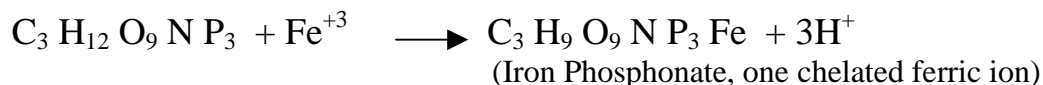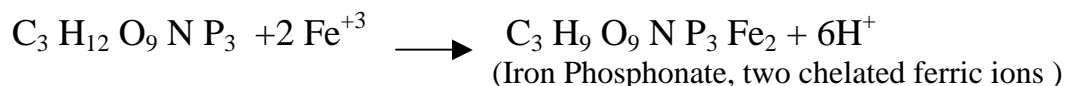
The ferric phosphonate chelate can stay soluble in acid or precipitate out depending on many factors including phosphoric acid strength, concentration of IR3, and temperature.

The precipitated iron phosphonate chelate dissolves as pH is raised to pH 5.0, then a precipitate is formed as the pH is raised to 8.0 using ammonium hydroxide. Ammonium hydroxide reacts with free phosphoric acid to form diammonium phosphate and three molecules of Fe-IR3 complexes react together to form one containing Fe3-IR3 complex (insoluble) and two molecules of IR3 complexes in ammonium form (ammonium phosphonate complex). IR3 ammonium form is completely soluble in the

medium and precipitates with iron at low pH. Therefore, it is believed that this process can lead to partial regeneration of IR3. Thus, regeneration process involves raising the pH to 8.0 then separating the liquor that is used with a make up IR3 for subsequent stages of iron precipitation.

The Use and Regeneration of Other Precipitating Reagents (IR5, IR5-7H and IR5-3H)

Other chelating reagents (IR5, IR5-7H and IR5-3H), containing different number of phosphonate groups, were tested for technical and economic comparison with IR3 reagent. The results of decreasing iron content using these additives are given in the following table. In this case also, it was found that, addition of 1.5% make-up precipitating reagent would be needed. However, removal efficiency was found to be lower (as low as 50%) depending on the type of the reagent.

Table 3. Iron Removal Efficiency from Phosphoric Acid (26% P_2O_5) Using Regeneration of The Reagents With 1.5% Make-up Reagent Related to Phosphoric Acid Weight.

Precipitating Reagent	Fe_2O_3 Removal Efficiency, %			
	First Stage	Second Stage	Third Stage	Fourth Stage
IR3	51.9	53.5	55.0	58.8
IR5	28.2	46.8	50.1	51.0
IR5-7H	27.4	46.8	47.5	47.9
IR5-3H	18.1	23.1	25.4	26.2

In-Plant Testing: Decreasing the Post-Precipitated Sludge in Phosphoric Acid

Addition of 0.5% IR3 precipitating reagent to freshly concentrated phosphoric acid leads to about 84% decrease in sludge volume (as compared to that obtained in absence of IR3) depending on acid type and clarification conditions. Decreasing the sludge volume facilitates acid handling as well as decreases the adherent water-soluble P_2O_5 with the sludge. Also, with 0.5% IR3 reagent, the total P_2O_5 losses decrease (or P_2O_5 recovery increases) by about 1.6% - 6.1% depending on acid type and clarification conditions. The data given in the table below, show that volume of sludge and P_2O_5 losses decrease in presence of IR3. It should be mentioned that the increase in recovery can also attributed to the type of sludge precipitated in presence of chelating reagent. In this case, less iron phosphate is precipitated. In other words, less P_2O_5 losses are produced in presence of IR3.

Table 4. P_2O_5 Losses With and Without IR3 Additive after 10 Days Clarification Time.

Item	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5 Losses, %	8.67	6.38	2.58	0.29
Water-insoluble P_2O_5 Losses, %	3.41	1.99	0.81	0.03
Sludge Volume %	31.2	28.80	8.80	1.60
Dry Sludge, wt. %	9.36	6.94	2.92	0.43

Recovery of P_2O_5 from Post Precipitated Sludge

In an attempt to recover P_2O_5 from 52% acid post precipitated sludge, IR3 reagent at 2.0% by weight of sludge was found to help in recovering over 92% of the P_2O_5 as compared to only 70% recovered without IR3 addition. The recovered acid contains 25% P_2O_5 and very low iron content (0.055% Fe_2O_3).

Quality of DAP Prepared from Treated Phosphoric Acid

Quality of diammonium phosphate fertilizers prepared from phosphoric acid mixed with different proportions of IR3 reagent needs to be investigated further since the bench scale ammoniation results are inconclusive.

COST BENEFIT ANALYSIS

Recovery of P_2O_5 from Post-Precipitated Sludge

Treating post-precipitated sludge by the chelating reagent IR3 indicate that 92% of P_2O_5 can be recovered which represents a gain of 22% in P_2O_5 recovery as compared to washing the sludge with water alone. Also, the recovered acid is low in iron content as compared to that obtained in water alone. However, quantification of the value of such gain depends on many factors such as: a) Price of recovered P_2O_5 as dilute (25% P_2O_5) phosphoric acid, and b) value of P_2O_5 if used as sludge for one purpose or another. Thus the cost benefit analysis is left to the reader in this case.

Prevention of Formation of Post-Precipitated Sludge

A cost of about \$4.7/ton P_2O_5 could be incurred for prevention of sludge formation in concentrated phosphoric acid. Such costs could be acceptable to phosphoric acid producers who ship the concentrated acid for a long distance.

Reduction of Iron in Dilute Phosphoric Acid

The use of these chelating reagents to decrease iron content in dilute acids may not be economical since the minimum required amount is about 15.0 Kg/ ton of acid. However, addition of a smaller quantity (2.5 kg/ton acid) may be beneficial in: a) preventing sludge formation during evaporation, b) preventing sludge formation during clarification since the concentration of chelating reagent will also increase during evaporation, and c) increase in P_2O_5 recovery by at least 2.0%. This may lead to an economic gain since the IR3 consumption may be not exceed 5 Kg /ton P_2O_5.

INTRODUCTION

Phosphoric acid is an important intermediate for production of fertilizers. It is mainly produced by the wet process in which phosphate rock leached with sulfuric and weak phosphoric acids to produce phosphoric acid (Fig. 1) and calcium sulfate dihydrate (phosphogypsum) as a by-product. According to the type of process, calcium sulfate dihydrate (gypsum) ($CaSO_4.2H_2O$) or calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) is crystallized. The primary reaction for the dihydrate process is as follows (Becker 1989):

$$Ca_{10}F_2(PO_4)_6 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$$

$$Ca(H_2PO_4)_2 + H_2SO_4 + 2H_2O \rightarrow 2H_3PO_4 + CaSO_4 \cdot 2H_2O$$

_____

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$$
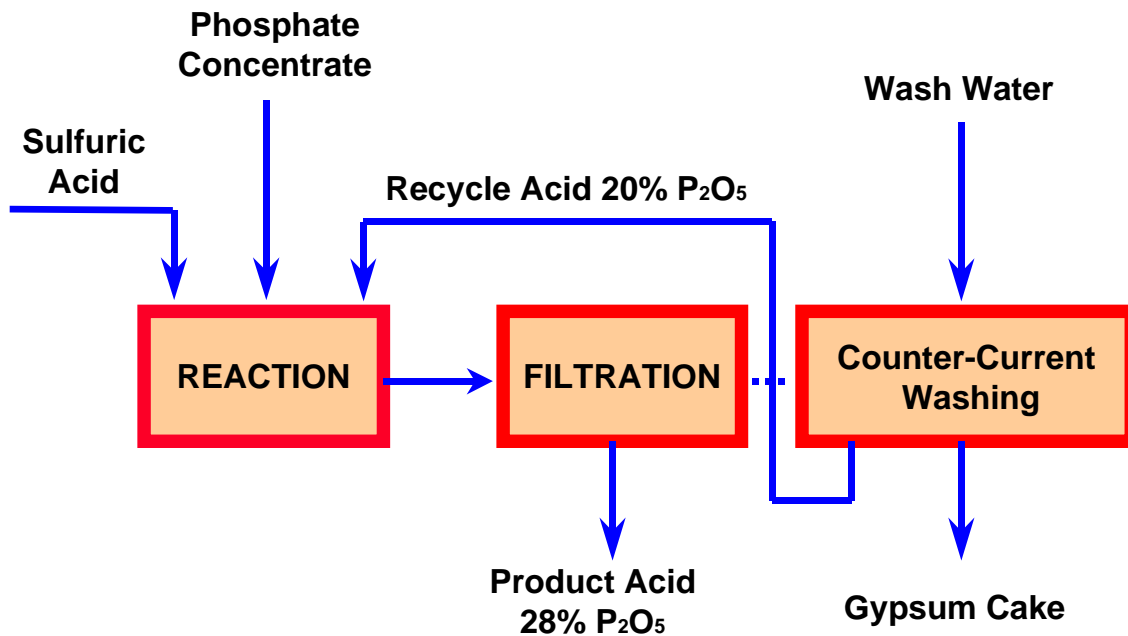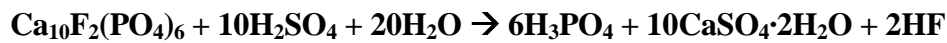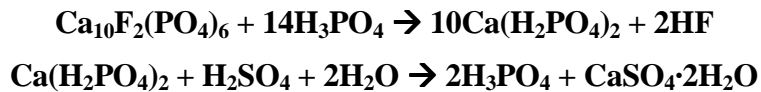
Figure 1. Simple Dihydrate Process Flow Sheet.

After filtration and separation of phosphogypsum, the filter acid (28% P_2O_5) contains many kinds of anionic impurities, such as sulfate and fluorine compounds and cationic impurities, the most important of which are iron, aluminum and magnesium as well as organic impurities. The quantity and type of the impurities are dependent primarily on the nature and composition of phosphate rock used as the raw material. The filter acid is concentrated by evaporation under vacuum to a concentration of as high as 70% P_2O_5 either through a single or a double stages of evaporation. During concentration, the volatile impurities such as fluorine compounds are partially removed along with the evaporating water vapor, but the concentrations of other impurities increase. Presence of impurities in phosphoric acid adversely affects process performance as well as quality of produced fertilizers.

Iron is present in most commercial phosphate rocks in variable percentages ranging from as low as 0.1%-0.4% as Fe_2O_3 in Morocco phosphate (Becker 1989) up to 3%-4% in Egyptian phosphate (Ismail and others 1988; Abdel-Aal 1984, 1989; Abdel-Aal and others 1991, 1999). During the reaction, most of iron impurities present in the phosphate rock (50-95%) react and end in the phosphoric acid. Distribution of iron between phosphoric acid and gypsum cake depends essentially on the nature of contaminating iron-bearing minerals and process conditions. Dissolved iron has a strong effect on increasing the viscosity and consequently decreases the filtration rate. In addition, it forms precipitates during concentration, clarification and storage causing sludge problems accompanied by P_2O_5 losses. Also, the P_2O_5 water-solubility of the fertilizers produced from high iron acids will be inferior due to presence of iron phosphates.

In the following paragraphs, different techniques to remove the impurities from wet-process phosphoric acid by addition of chemicals are reviewed. Various precipitants or flocculating agents are employed. These additives should be capable of forming insoluble compounds, which are removed further by filtration, decantation, centrifugation or any other known method.

Precipitation of iron from phosphoric acid can be achieved by addition of potassium salt to the acid during concentration. The formed complex (x-compound or Lehr's salt) can be post-precipitated according to the following equation (El-Barbary 1992, Abdel-Aal and others 1999):

$$K^+ + 3Fe^{3+} + 8H_3PO_4 + 4 H_2O \ ---------> Fe_3KH_{14}(PO_4)_8 .4H_2O + 10H^+$$
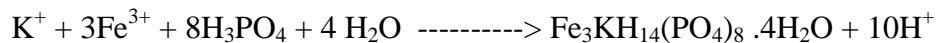
The disadvantage of this process is the high P_2O_5 losses. For decreasing Fe_2O_3 content in phosphoric acid by 1%, the corresponding P_2O_5 losses will be about 2.4%. Also, ammonium salts can form analogous compounds.

On lab-scale, McCullough and Fredrich (1973) precipitated the impurities from slightly ammoniated acid by addition of methanol. The produced acid was suitable for liquid fertilizer production. 90% of the iron, aluminum and fluorine and 50-70% of the

magnesium were removed from the raw acid. Also, Thompson and Worthington (1970) reported that pure phosphoric acid suitable for use in detergents; food and water treatment was produced from concentrated crude phosphoric acid by precipitation of impurities with methanol in presence of KH_2PO_4.

Kenneth and Donald (1967) found that a precipitate containing both iron and aluminum was formed upon addition of ammonium salt to wet-process phosphoric acid. Either ammonium carbonate or ammonium hydroxide could be used as base ammonium neutralizer. Usually, acid of lower iron and aluminum contents with minimal post-precipitation sludge will be produced after removal of this precipitate. The applied and suitable conditions are given below:

Amount of ammonium salt	: 0.3-2%
Clarification time	: 4-8 day
Clarification temperature	: Ambient - 82 ^{o}C

Frankenfeld and Goetzmann (1970) reported that Fe, Al, Ca and Ti were removed from crude phosphoric acid by adding isopropanol and 0.06-0.12 mole NH_3/mole P_2O_5. Fe content was decreased from 0.48% to 0.005%.

Weston and others (1982) treated the phosphoric acid with soluble compounds of Na and F to remove Al as Na_3AlF_6. The iron content was decreased to acceptable level by addition of ammonia and iron was precipitated as crystalline salt, principally in the form of $NH_4Fe_3H_8(PO_4)_6.4H_2O$.

McDonald and Wade (1983) found that the metallic impurities (mainly Fe, Al and Mg) were removed from technical-grade phosphoric acid by precipitation with ammonia at 52-108 ^{o}C for 2-16 hr and at N/P_2O_5 wt. ratio of 0.016-0.15. Fe content was decreased from 0.82% to 0.04%.

Theodor and Donald (1964) adjusted concentrations of CaO and F in weak phosphoric acid (20% P_2O_5) to about 3% and 5%, respectively. Calcium fluoride was precipitated with co-precipitating of magnesium, iron and aluminum insoluble impurities. The percentage removal of iron and aluminum was found as high as 89%.

Goldstein (1971) precipitated magnesium as $MgSiF_6.6H_2O$ by addition of fluosilicic acid. He found that iron and aluminum were removed by about 25% and 10%, respectively. Also, Moore and others (1969) precipitated magnesium from phosphoric acid containing 25-35% P_2O_5 and $MgO-Al_2O_3-F$ in the ratio of 1: 1.4 : 2, by addition of additional Al and free HF.

Shimazaki and Nagahama (1975) reported that ethanol and aqueous ammonia could be used for purification of phosphoric acid. The raw acid containing 28.3% P_2O_5 and 1.9% R_2O_3 was purified to pure acid containing 54.5% P_2O_5 and 0.06% R_2O_3. However, the P_2O_5 recovery was very low (66.1%).

Waggaman (1952) stated that both lead and arsenic could be precipitated either by passing hydrogen sulfide gas or adding a soluble sulfide directly into the acid. Also, lead might be removed by adding a soluble lead or barium salt to a solution of acid having a small amount of free sulfuric acid (Noyes 1967).

Iron, aluminum and lead were precipitated by the use of glacial acetic acid (Noyes 1967, El-Barbary 1992). Acetic acid was then recovered by distillation.

In most of the above studies, high losses of P_2O_5 could be incurred. Thus, the major goal of this project is to conduct a study to reduce iron content in phosphoric acid by as much as 30%-50%, with minimum losses of phosphate values. In addition, decreasing the amount of post-precipitated sludge from concentrated phosphoric acid, in a cost effective way, is another goal of this study.

METHODOLOGY

MATERIALS

Various types of phosphoric acids (recycle acid, 26% P_2O_5 filter acid, 40% P_2O_5 acid and 54% P_2O_5 acid) as well as two types of phosphoric acid sludge (40% sludge and 50% sludge) from Central Florida phosphate plants are used for this study. Phosphoric acids of different concentrations prepared in our laboratory from South Florida phosphate rock are also studied. Iron precipitating reagents (patent pending) are purchased from conventional chemicals companies. All the other needed chemicals are acquired from Fisher Scientific Co.

APPARATUS

The precipitation of iron is carried out in a cylindrical 1.0-liter reactor of 10 cm diameter, fitted with Teflon-coated stirrer of 3.5 cm and placed in a water bath adjusted to the required temperature. The impeller tip speed is adjusted at 1.44 m/s (550 rpm). Phosphoric acid and additive are added batch wise. Filtration is performed using Buchner type filter of 4.6 inch diameter. Polypropylene filter cloth of 200 mesh aperture size is used with filter paper No. 40. A vacuum pump is used for filtration.

PROCEDURES

Addition of Precipitating Reagents:

During Clarification:
1. Take known amount of filter acid.
2. Evaporate until P_2O_5 content reaches about 52-54%.
3. After evaporation and directly before start-up of the clarification stage, add the calculated amount of additive.
4. Clarify the concentrated acid at industrially applied conditions (ambient temperature and 5-10 days).
5. Separate the sludge, wash with methanol, dry at 60 ^{o}C for 24 hr and characterize.
6. Determine P_2O_5 and Fe_2O_3 in both acid and sludge using ICP Perkin Elmer Model OPTIMA 3200 RL.

To Phosphoric Acids of Different P_2O_5 Concentrations:
1. Take known amount of phosphoric acid (recycle acid, 26% P_2O_5 filter acid, 40% P_2O_5 acid and 54% P_2O_5 acid).
2. Heat to the required temperature.
3. Add the calculated amount of precipitating reagent and stir for the required time.

4. After the precipitation time, filter to separate the acid.
5. Wash the sludge with water.
6. Determine P_2O_5 and Fe_2O_3 in the produced phosphoric acid and sludge as well as the wash liquor.

To Sludge:
1. Take known amount of concentrated phosphoric acid sludge (e.g. 100 g)
2. Add equal amount of water (e.g. 100 g) and mix
3. Add the calculated amount of precipitating reagent and stir for the required time.
4. Separate the formed sludge, regenerate the precipitating reagent and separate the precipitated solids as in the following procedures.
5. Analyze both liquor and formed sludge for P_2O_5 and Fe_2O_3 contents.
6. Calculate % recovery of P_2O_5 and % Fe_2O_3 removed.

Separation of Sludge

1. Pour the slurry (phosphoric acid containing sludge) into Buchner-type funnel containing 200 mesh polypropylene filter cloth pore size.
2. Apply the required vacuum (22" Hg)
3. After complete filtration, wash the sludge with the required amount of wash water one time.
4. Determine P_2O_5 and Fe_2O_3 in the acid, wash liquor and sludge.
5. Collect the sludge for further treatment (regeneration of the precipitating reagent).

Regeneration of Precipitating (Chelating) Reagents

1. Take the precipitated amount of sludge.
2. Add the required amount of water to decrease the solid content to about 30%.
3. Then add the required amount of ammonium hydroxide to increase the pH of the medium to the required level (about pH 8.0 in case of IR3).
4. Stir the slurry mixture for the required reaction time (1.0 – 3 hrs).
5. Heat the slurry mixture if necessary to required reaction temperature (23° C– 80° C).
6. After the regeneration time, centrifuge to separate the regenerated reagent (as explained below).
7. Wash the precipitated solids with water and centrifuge again.
8. Determine P_2O_5 and Fe_2O_3 in the regenerated reagent and precipitated solids as well as the wash liquor.
9. Calculate Fe_2O_3 removal efficiency and P_2O_5 recovery.

Separation of Precipitating Solids After Regeneration

1. Take the slurry after regeneration and put in the centrifuge vials.
2. Centrifuge for 15 minutes at 10,000 rpm.
3. Collect the clear solution.
4. Add the required amount of wash water and mix with solids.
5. Centrifuge again for 15 minutes, at 10,000 rpm.
6. Collect the wash liquor and the wet precipitated solids.
7. Determine P_2O_5 and Fe_2O_3 in the regenerated solution, wash liquor and precipitated solids.

The proposed flow sheet for iron precipitation process is given in Fig. 2.
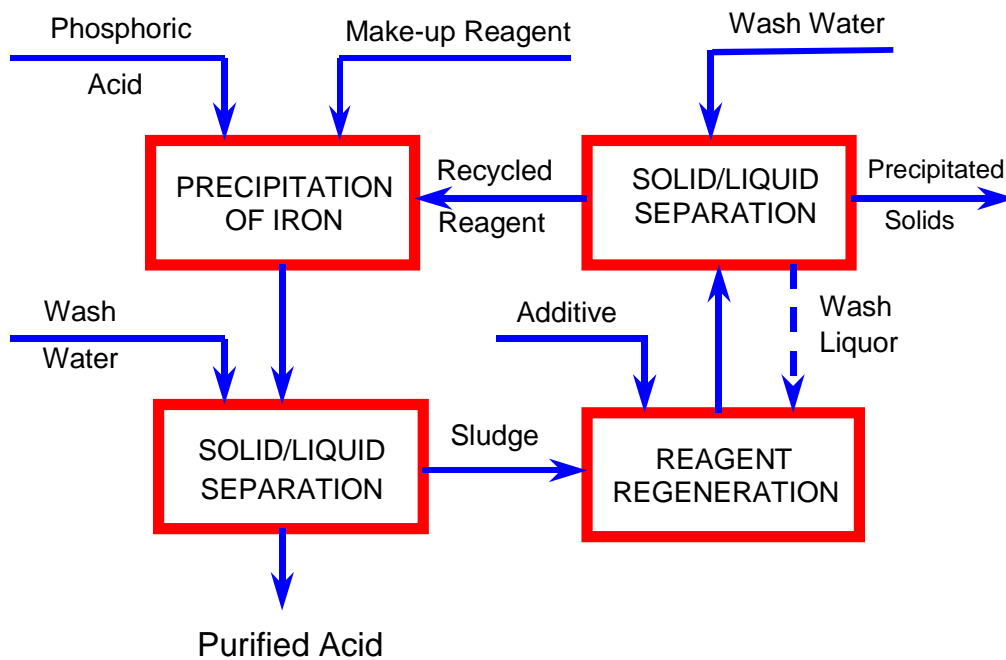
Figure 2. Proposed Flow Sheet for Iron Precipitation Process.

Preparation of Diammonium Phosphate With and Without IR3 Reagent

1. Take known amount of concentrated phosphoric acid (about 55% P_2O_5) with and without different amounts from IR3 reagent (0.02% to 0.5% related to the weight of acid).
2. Mix with the stoichiometric amount of ammonium hydroxide to form diammonium phosphate.
3. Dry the formed paste at 60° C for 24 hr.
4. Determine Total, citrate-soluble and water-soluble P_2O_5.

RESULTS AND DISCUSSION

MATERIALS CHARACTERIZATION

Chemical analyses of phosphoric acids and 40% P_2O_5 sludge samples used in this study are given in Tables 5-8.

Table 5. Chemical Analyses of Phosphoric Acids and Sludge Samples From Florida Phosphoric Acid Plants.

Constituent	% in		
	26% P_2O_5 Filter Acid	40% P_2O_5 Acid	40% P_2O_5 Sludge
P_2O_5	25.43	45.26	36.21
Fe_2O_3	1.22	2.06	2.31
SO_4	2.27	3.76	7.22
CaO	0.47	0.87	3.25
MgO	0.56	0.92	0.97
Al_2O_3	0.95	1.52	1.44
Na_2O	0.23	0.38	1.51
K_2O	0.12	0.19	0.52
SiO_2	1.26	0.49	1.86
F	2.45	2.02	4.51
MER	0.107	0.099	0.130

MER: $\sum Fe_2O_3 + Al_2O_3 + MgO / P_2O_5$

Table 6. Chemical Analyses of Concentrated Phosphoric Acid Samples From Florida Phosphoric Acid Plants.

Constituent	% in Concentrated Phosphoric Acid From		
	Plant A	Plant B	Plant C
P_2O_5	55.91	54.83	55.64
Fe_2O_3	2.41	1.79	1.84
SO_4	3.56	3.26	3.58
CaO	0.21	0.27	0.24
MgO	1.20	0.74	0.38
Al_2O_3	1.64	2.16	1.27
Na_2O	0.11	N.D.	0.12
K_2O	0.110	N.D.	0.077
SiO_2	0.040	N.D.	0.039
F	1.04	N.D.	0.62
MER	0.094	0.086	0.063

MER: $\sum Fe_2O_3 + Al_2O_3 + MgO / P_2O_5$ ND.: Not determined

Table 7. Chemical Analyses of Phosphoric Acids from South Florida Phosphate (Prepared in Lab.).

Constituent	% in	
	Recycle Acid	Filter Acid
P_2O_5	18.9	24.9
Fe_2O_3	0.70	0.88
SO_4	1.73	2.31
CaO	N.D.	0.12
MgO	0.54	0.69
Al_2O_3	0.67	0.72
SiO_2	N.D.	1.00
MER	0.101	0.092

MER: $\sum Fe_2O_3 + Al_2O_3 + MgO / P_2O_5$ N.D.: Not determined

Table 8. Chemical Analyses of Partially Concentrated Phosphoric Acids (Prepared in Lab.).

Constituent	% in	
	35% P_2O_5 Acid	40% P_2O_5 Acid
P_2O_5	35.3	41.0
Fe_2O_3	0.73	0.85
MgO	0.67	0.78
Al_2O_3	1.54	1.79
MER	0.083	0.083

MER: $\sum Fe_2O_3 + Al_2O_3 + MgO / P_2O_5$

ADDITION OF IR3 PRECIPITATING REAGENT TO PHOSPHORIC ACID

Effect of Reagent Dosage

A series of experiments is carried out using various amounts of IR3 additive (precipitating reagent) ranging from 0.1% to 5.0% by weight of the phosphoric acid samples. The applied conditions for these tests are given below:

Reaction temperature:	room temperature (23°C)
Reaction time:	1 hr
Weight of acid used:	500 g
Clarification time:	1 day

The obtained results (for 25% acid and 40% acids) are given in Tables 9 & 10, respectively. The results indicate that the removal efficiency of iron is increased with increasing the amount of precipitating reagent. However, the efficiency decreases as the

P_2O_5 content increases. For example, using precipitating reagent equivalent to 4% of the weight of the acid gives iron removal efficiency of 63% with 25 % P_2O_5 filter acid and only 30% with 40% P_2O_5 acid under the studied conditions. The difference in iron removal efficiency may be due to the change of precipitate solubility with P_2O_5 concentration. In addition, a longer precipitation time may be needed in the case of high viscosity 40 % acid. Consequently, effect of precipitation time is studied next as discussed below.

Table 9. Iron Removal Efficiency from South Florida Filter Acid (25% P_2O_5).

Conditions	Chemical Analysis, %					Fe_2O_3 Removal Efficiency, %
	P_2O_5	Fe_2O_3	Al_2O_3	MgO	MER	
Filter Acid (Baseline), 23 ^{o}C	24.9	0.88	0.72	0.69	0.092	-
Acid + 0.1% R	25.0	0.88	0.72	0.70	0.092	-
Acid + 0.5% R	24.8	0.86	0.72	0.69	0.092	2
Acid + 1% R	24.7	0.73	0.71	0.70	0.087	17
Acid + 2% R	24.8	0.59	0.70	0.70	0.080	33
Acid + 4% R	24.8	0.33	0.70	0.69	0.069	63

MER: $\sum Fe_2O_3 + Al_2O_3 + MgO / P_2O_5$
R: Precipitating Reagent

Table 10. Iron Removal Efficiency from Concentrated Acid (40% P_2O_5).

Conditions	Fe_2O_3 Removal Efficiency, %	P_2O_5 Content in Acid, %	Fe_2O_3 Content in Acid, %
Baseline, 40% Acid, 23°C	-	40.2	0.832
Acid + 1% R	2	38.3	0.774
Acid + 2% R	4	38.0	0.758
Acid + 3% R	19	39.2	0.657
Acid + 4% R	30	39.2	0.570
Acid + 5% R	42	38.9	0.464

R: Precipitating Reagent

Effect of Clarification Time on Iron Removal Efficiency from 40% Acid

Experiments are conducted using various amounts of additive (precipitating reagent) ranging from 1% to 5.0%. Precipitation time is varied between 1.0 hour and 120 hours (5 days). The applied conditions for these tests are given below:

Reaction temperature:	room temperature (23°C)
Reaction time:	1 hr
Weight of acid used:	500 g
Clarification time:	1 hr, 1 day, and 5 days

The obtained results are given in Table 11 and Fig. 3. The data suggest that with increasing the clarification time, the iron removal efficiency can be increased. However, the removal is still lower than in dilute (filter) acid as given in Table 5 above. The optimum clarification time depends on acid concentration, amount of precipitating reagent, and reaction temperature as discussed in the following paragraphs.

Table 11. Iron Removal Efficiency from Concentrated Acid (40% P_2O_5).

Conditions	Fe_2O_3 Removal Efficiency, %			P_2O_5 Content in Acid, %			Fe_2O_3 Content in Acid, %		
	1 hr	1 day	5 day	1 hr	1 day	5 day	1 hr	1 day	5 day
Baseline, 40% Acid, 23°C	-	-	-	41.0	40.2	38.7	0.853	0.832	0.795
Acid + 1% R	2	2	2	40.1	38.3	39.1	0.815	0.774	0.789
Acid + 2% R	5	5	14	39.8	38.0	39.1	0.783	0.758	0.690
Acid + 3% R	9	19	27	40.5	39.2	38.3	0.768	0.657	0.574
Acid + 4% R	10	30	37	38.8	39.2	39.0	0.726	0.570	0.505
Acid + 5% R	16	42	42	37.1	38.9	38.5	0.647	0.464	0.457

R: Precipitating Reagent

Effect of Temperature on Iron Removal Efficiency
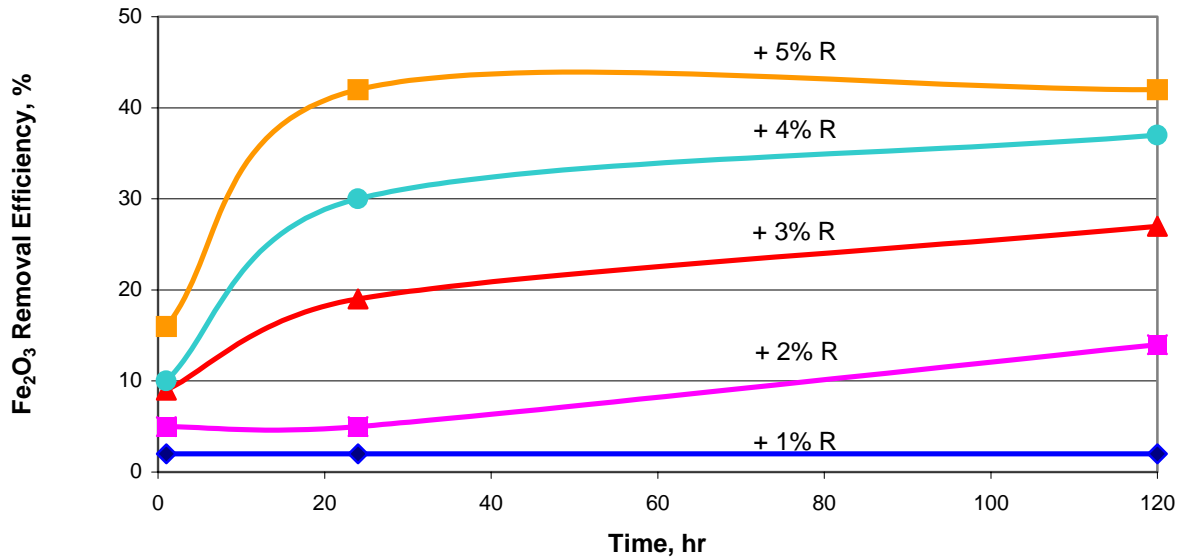
Figure 3.   Effect of Clarification Time on Fe_2O_3 Removal Efficiency (40% P_2O_5 Acid at 23 ^oC).

Tests are performed to study effect of temperature on iron removal efficiency using various amounts of additive (precipitating reagent ranging from 1% to 5%. The study is done at different clarification times ranging from 1 hr. to 24 hrs. The applied condition for these tests are given below:

Reaction temperature: 23-60 ^{o}C
Reaction time: 1 hr
Weight of acid used: 500 g
Clarification time: 1 hr, 3 hr, and 1 day

The obtained data are given in Tables 12 and 13. It is clear from the results shown in Table 13 that higher removal can be obtained at the low temperature range. This may be attributed to increase in solubility of iron complex at higher temperature.

Table 12. Iron Removal Efficiency from Concentrated Acid (40% P_2O_5) at 60°C.

Conditions	Fe_2O_3 Removal Efficiency, %			P_2O_5 Content in Acid, %			Fe_2O_3 Content in Acid, %		
	1 hr	3 hr	1 day	1 hr	3 hr	1 day	1 hr	3 hr	1 day
Baseline, 40% Acid, 60°C	-	-	-	40.3	41.9	41.7	0.826	0.873	0.862
Acid + 1% R	6	5	10	38.2	44.7	44.7	0.740	0.883	0.833
Acid + 2% R	6	4	12	38.2	41.8	42.3	0.740	0.836	0.773
Acid + 3% R	12	10	13	40.2	41.3	41.2	0.729	0.779	0.742
Acid + 4% R	15	14	18	40.6	42.5	42.0	0.709	0.763	0.714
Acid + 5% R	30	29	28	36.2	40.7	40.4	0.522	0.606	0.603

R: Precipitating Reagent

Table 13. Comparison of Iron Removal Efficiency from Concentrated Acid (40% P_2O_5) at Different Temperatures (Clarification Time 1 day).

Conditions	Fe_2O_3 Removal Efficiency, %		P_2O_5 Content in Acid, %		Fe_2O_3 Content in Acid, %	
	1 day		1 day		1 day	
	23 ^{o}C	60°C	23 ^{o}C	60°C	23 ^{o}C	60°C
Baseline, 40% Acid	-	-	40.2	41.7	0.832	0.862
Acid + 1% R	2	10	38.3	44.7	0.774	0.833
Acid + 2% R	5	12	38.0	42.3	0.758	0.773
Acid + 3% R	19	13	39.2	41.2	0.657	0.742
Acid + 4% R	30	18	39.2	42.0	0.570	0.714
Acid + 5% R	42	28	38.9	40.4	0.464	0.603

R: Precipitating Reagent

Effect of Acid Concentration on Iron Removal Efficiency

A series of experiments is carried out using amount of additive (precipitating reagent) equivalent to (4% by weight) of phosphoric acid samples of different concentrations (P_2O_5 contents). The applied conditions for these tests are given below:

Reaction temperature:	23 ^{o}C
Reaction time:	1 hr
Weight of acid used:	500 g
Clarification time:	1 day
Amount of precipitating reagent:	4%

The results given in Table 14 and Fig. 4 indicate that after one day clarification time, the iron removal efficiency at 23 ^{o}C is increased with decreasing P_2O_5 content in the acid. Mainly, this is related to increase in the solubility of the precipitated sludge as acid concentration is increased.

Table 14. Effect of Phosphoric Acid Concentration on Fe$_2$O$_3$ Removal Efficiency.

Acid Concentration, % P_2O_5	Fe$_2$O$_3$ Removal Efficiency, %
Recycle Acid, 18.9%	72.9
Filter Acid, 24.9%	63.0
Concentrated Acid, 40.2%	30.0
Concentrated Acid, 55.9%	0.0
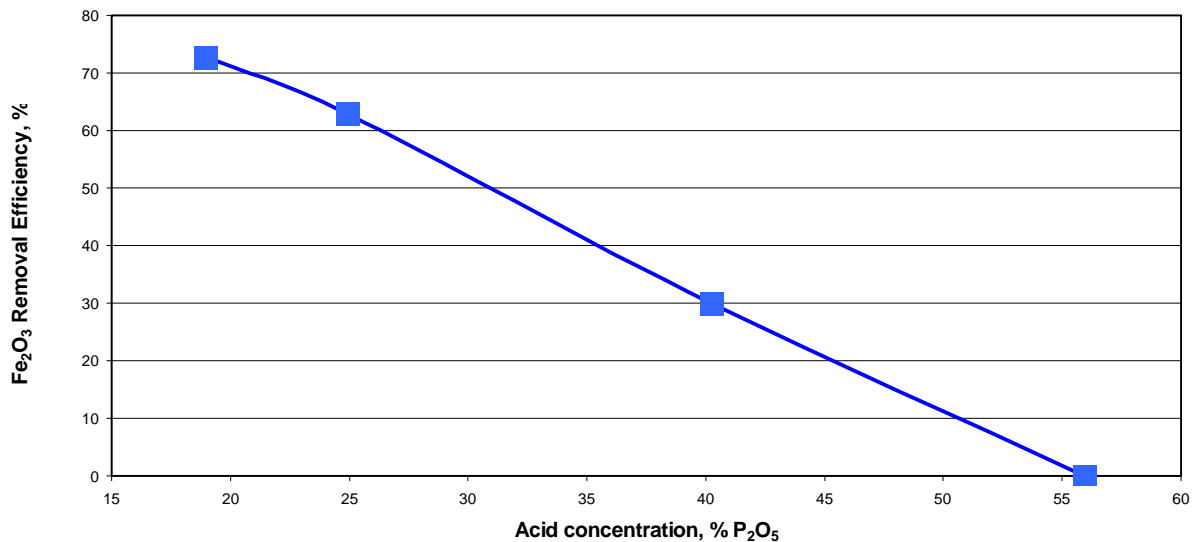
Figure 4. Effect of Phosphoric Acid Concentration on Fe$_2$O Removal Efficiency at 23°C.

REGENERATION OF PRECIPITATING REAGENT

Reduction of reagent consumption is very important to the process economics. Thus, regeneration and recycling of the precipitating reagent can be helpful in reducing process costs. To explore the possibility of regenerating this reagent, a series of exploratory experiments is carried out under the following conditions:

Precipitation:

Reaction temperature:	23 $^{\circ}$C
Reaction time:	1 hr
Weight of acid used:	500 g
Clarification time:	1 day
Amount of precipitating reagent:	4%

Regeneration:

Reaction temperature:	23 $^{\circ}$C
Reaction time:	1 hr

The results shown in Table 15 suggest that after 1 day clarification time, the iron removal efficiency is about 51% and 23% in the first and second regeneration stages, respectively. Addition of make-up precipitating regent is necessary to maintain the same removal efficiency level. In general, it may be concluded that, on the average, about 50% of iron can be removed using 1.3% by weight of treated acid as the amount of precipitating reagent.

Table 15. Effect of Recycling the Regenerated Reagent on Fe_2O_3 Removal Efficiency (20% P_2O_5 Acid).

Conditions	Fe_2O_3 Removal Efficiency, %	P_2O_5 Content in Acid, %	Fe_2O_3 Content in Acid, %
Baseline, Acid + 4% water, 23°C	-	19.6	0.620
Acid + 4% R	74.0	19.7	0.162
Acid + Regenerated reagent from previous test	50.8	19.6	0.305
Acid + Regenerated reagent from previous test	22.8	18.1	0.442
Average: Acid + 1.33% R	49.2	19.1	0.303

R: Precipitating Reagent

In order to optimize the regeneration process, a series of experiments is carried out to regenerate the reagent. The applied conditions for these tests are given below:

Precipitation:

      Reaction temperature: Room temperature (23 ^{o}C)
      Reaction time: 1 hr
      Weight of acid used: 500 g
      Clarification time: 1 day
      Amount of make-up precipitating reagent: 1.5%

Regeneration:

      Reaction temperature: Room temperature, 60 ^{o}C and 80 ^{o}C
      Reaction time: 1 and 3 hr

Moreover, four regeneration stages are performed using 1.5% make-up IR3 precipitating reagent. The obtained results are given in Table 16 and Fig. 5. These results indicate that after 1 day clarification time, the iron removal efficiencies range from 51.9-53.6% in the first regeneration stage depending on the applied conditions. The iron removal efficiency is increased with progressing in regeneration stages. This may suggest that 1.5% make-up precipitating reagent is sufficient or even more than sufficient to maintain the same removal efficiency level. The average results indicate that, about 56.1% of iron can be removed using 1.5% precipitating reagent.

Table 16. Iron Removal Efficiency from Phosphoric Acid (26% P_2O_5) Using Regeneration of IR3 Reagent with 1.5% Make-up.

Regeneration Conditions	Fe_2O_3 Removal Efficiency, %			
	First Stage	Second Stage	Third Stage	Fourth Stage
At Room Temp. for 1 hr	51.9	53.5	55.0	58.8
At 60 ^{o}C for 1 hr	52.3	54.2	56.9	59.7
At 60 ^{o}C for 3 hr	53.1	54.5	57.5	60.1
At 80 ^{o}C for 1 hr	53.6	57.2	58.8	60.4

Figure 5. Iron Removal Efficiency from Phosphoric Acid (26% P_2O_5) Using Regeneration of IR3 Reagent With 1.5% Make-up.

SOLUBILITY OF IR3 SLUDGE IN PHOSPHORIC ACID

Effect of Acid Concentration

The solubility of IR3 sludge in phosphoric acid was determined at different P_2O_5 concentrations ranging from 17% to 56% and at room temperature. The results are given in Fig. (6). These results show that, the solubility of IR3 sludge increases with increase P_2O_5 concentration. Consequently, to reduce IR3 consumption it is preferable to precipitate iron at low P_2O_5 concentrations e.g. filter acid of 25-28% P_2O_5.
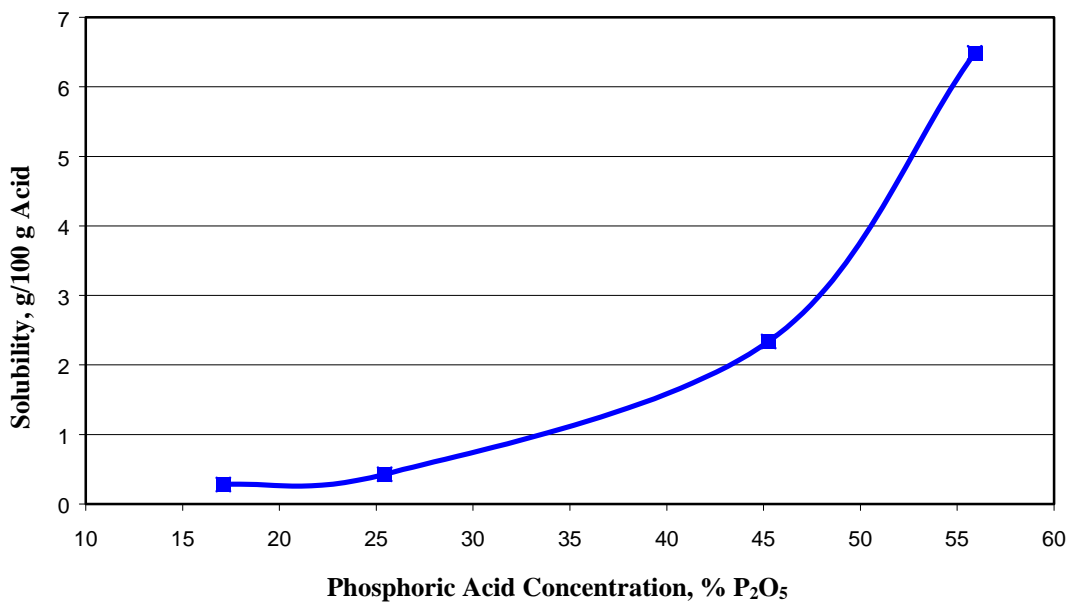
Figure 6. Solubility of IR3 Sludge in Phosphoric Acids of Different P_2O_5 Concentrations.

Effect of Temperature

The solubility of IR3 sludge in 26% P_2O_5 phosphoric acid was measured at different temperatures ranging from 20 to 100 ^{o}C. The results given in Fig. 7 indicate that, relatively low solubility at lower temperatures (20-40°C), then as the temperature increases the solubility increases. Consequently, it is preferable to separate the IR3 sludge at low temperatures.
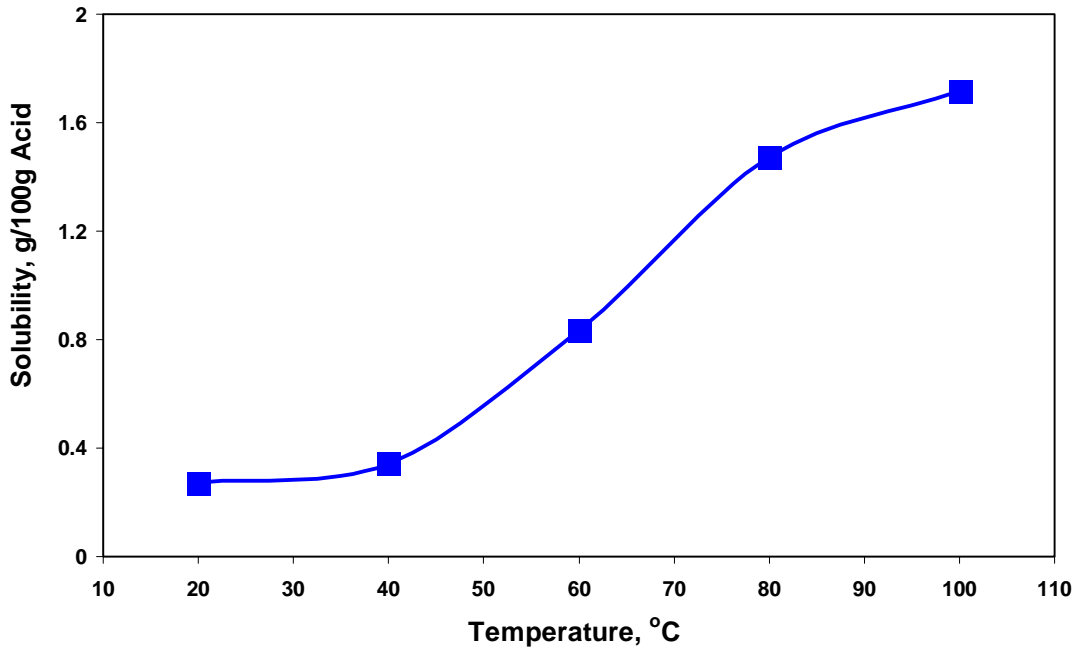
Figure 7. Solubility of IR3 Sludge in 26% P_2O_5 Phosphoric Acid at Different Temperatures.

MASS BALANCE USING IR3 PRECIPITATING REAGENT

The mass balance of the whole process including material balance, P_2O_5 and Fe_2O_3 component mass balance are calculated. These calculations are based on chemical analysis of filter acid, purified acid, wash liquor, precipitated solids, regenerated pregnant liquor and recycled liquor, given in Table 17. Mass balance results are reported in Tables 18-20 and Figs. 8-10. These data show that 90 kg of ammonium hydroxide (additive) is used per 1 ton phosphoric acid during regeneration stage. This amount is recycled almost completely. In addition, 400 kg wash water is used for 1 ton phosphoric acid. This is a large amount of water / ton of phosphoric acid. However, it is expected that if counter-current washing is used, this amount could be reduced. Further testing is needed to prove this point.

Table 17. Chemical Analysis of Different Streams of Phosphoric Acid Precipitation Process.

Stream	% P_2O_5	% Fe_2O_3	P_2O_5/Fe_2O_3 Ratio
Filter acid	25.43	0.994	25.58
Purified acid	22.00	0.345	63.77
Wash liquor	17.816	0.189	94.26
Precipitated solids*	0.808	1.879	0.43
Regenerated pregnant liquor	10.333	0.494	20.92
Recycled liquor	3.991	0.108	36.95

* Based on wet basis

Table 18. Material Balance of Iron Precipitation Process (Using IR3 Reagent).

Input	Amount of Materials, g	Output	Amount of Materials, g
Reaction Phosphoric acid Make-up precipitating reagent Regenerated pregnant solution	1000 15 360	Reaction Slurry	1375
Total	1375	Total	1375
Solid/liquid separation Slurry Wash water	 1375 200*	Solid/liquid separation Purified acid Wash liquor Sludge Losses	 974 206 380 15
Total	1575	Total	1575
Reagent regeneration Sludge Additive Recycled liquor	 380 90 223	Reagent regeneration Precipitated solids slurry	693
Total	693	Total	693
Solid/liquid separation Precipitated solids slurry Wash water	 693 200*	Solid/liquid separation Precipitated solids Regenerated pregnant solution Recycled liquor Losses	 297 360 223 13
Total	893	Total	893

* Wash water is expected to be less if counter current washing is used

Table 19. P$_2$O$_5$ Component Mass Balance of Iron Precipitation Process (Using IR3 Reagent).

Input	Amount of P$_2$O$_5$, g	Output	Amount of P$_2$O$_5$, g
Reaction Phosphoric acid Make-up precipitating reagent Regenerated pregnant solution	254.3 0.0 37.2	Reaction Slurry	291.5
Total	291.5	Total	291.5
Solid/liquid separation Slurry Wash water	291.5 0.0	Solid/liquid separation Purified acid Wash liquor Sludge Losses	214.3 36.7 40.0 0.5
Total	291.5	Total	291.5
Reagent regeneration Sludge Additive Recycled liquor	40.0 0.0 8.9	Reagent regeneration Precipitated solids slurry	48.9
Total	48.9	Total	48.9
Solid/liquid separation Precipitated solids slurry Wash water	 48.9 0.0	Solid/liquid separation Precipitated solids Regenerated pregnant solution Recycled liquor Losses	2.4 37.2 8.9 0.4
Total	48.9	Total	48.9

Table 20. Fe_2O_3 Component Mass Balance of Iron Precipitation Process (Using IR3 Reagent).

Input	Amount of Fe_2O_3, g	Output	Amount of Fe_2O_3, g
Reaction Phosphoric acid Make-up precipitating reagent Regenerated pregnant solution	9.94 0.00 1.78	Reaction Slurry	11.72
Total	11.72	Total	11.72
Solid/liquid separation Slurry Wash water	11.72 0.00	Solid/liquid separation Purified acid Wash liquor Sludge Losses	3.36 0.39 7.67 0.30
Total	11.72	Total	11.72
Reagent regeneration Sludge Additive Recycled liquor	7.67 0.00 0.24	Reagent regeneration Precipitated solids slurry	7.91
Total	7.91	Total	7.91
Solid/liquid separation Precipitated solids slurry Wash water	7.91 0.00	Solid/liquid separation Precipitated solids Regenerated pregnant solution Recycled liquor Losses	5.58 1.78 0.24 0.31
Total	7.91	Total	7.91

Figure 8. Material Balance of Iron Precipitation Process (all Values in Grams).
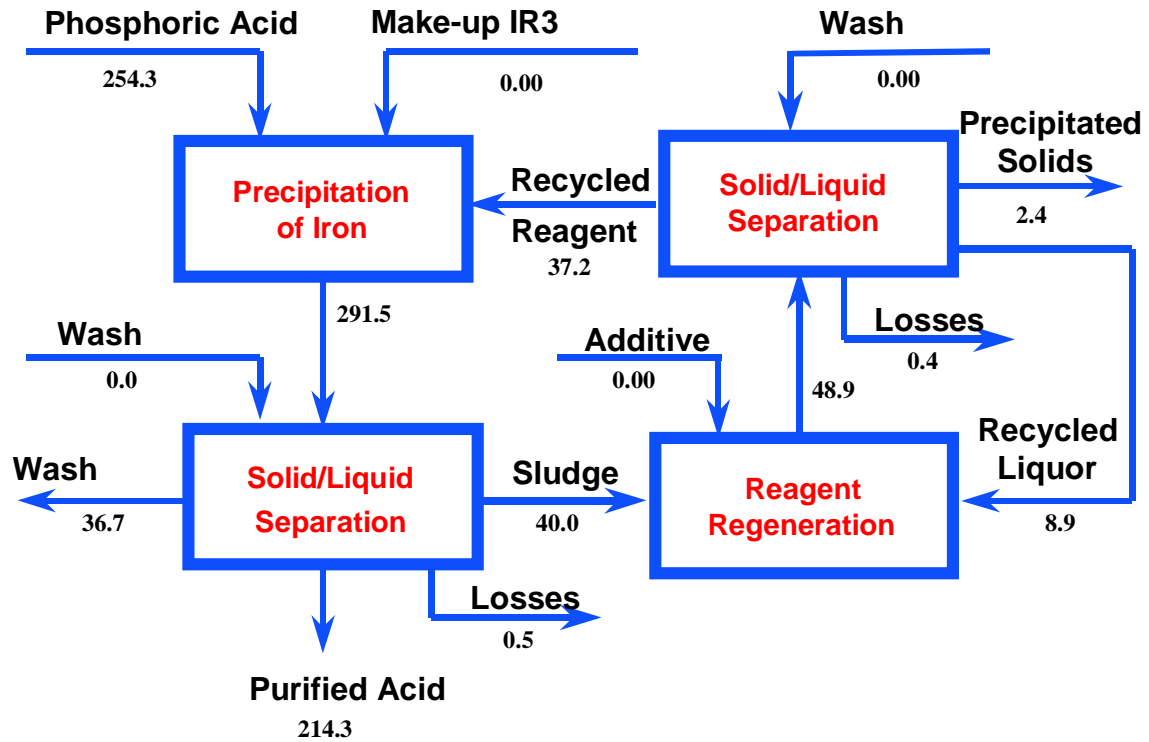
Figure 9. P$_2$ O$_5$ Component Mass Balance of Iron Precipitation Process (All Values in Grams).
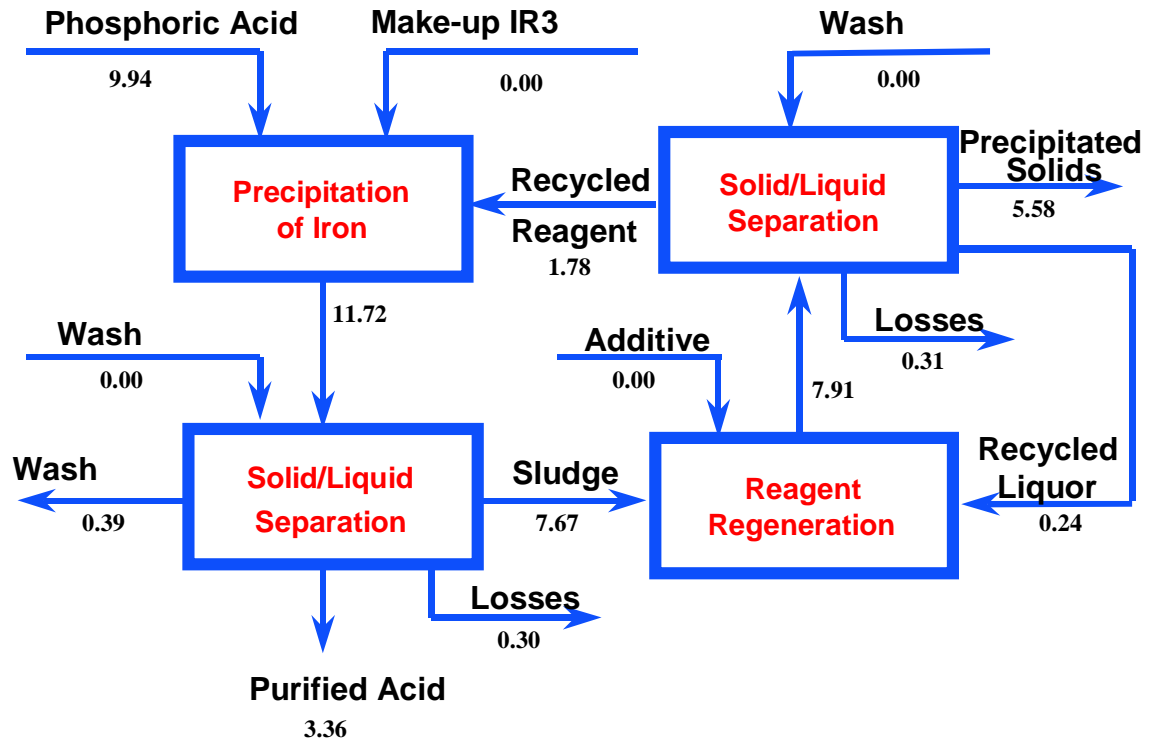
Figure 10. Fe$_2$O$_3$ Component Mass Balance of Iron Precipitation Process (All Values in Grams).

TESTING DIFFERENT PRECIPITATING REAGENTS

Three more precipitating (chelating) reagents namely IR5, IR5-7H and IR5-3H were tested for precipitation of iron from phosphoric acid. Once again, these reagents are based on phosphonate chemistry. The results of testing these reagents in comparison with IR3 reagent are given in the following paragraphs.

Effect of Precipitating Reagent Amount on Iron Removal Efficiency

Three series of experiments were carried out using various amounts of additives (precipitating reagents) ranging from 1% to 4% with the phosphoric acid samples. The applied conditions for these tests are given below:

Reaction temperature:	room temperature (23°C)
Reaction time:	1 hr
Weight of acid used:	500 g
Clarification time:	1 day

The obtained results are given in Table 21 and Fig. 11. The data show that with increasing the amount of precipitating reagent added to phosphoric acid samples, the removal efficiency of iron is increased. Using precipitating reagent equivalent to 4% of the weight of the acid gives iron removal efficiency of about 28%, 27% and 18% with IR5, IR5-7H and IR5-3H, respectively. The iron removal efficiencies with IR5 and IR5-7H are more or less the same while it is lower with IR5-3H. However, it should be noted that these reagents are not as efficient in reducing iron content as the chelating reagent IR3.

Table 21. Iron Removal Efficiency From Filter Acid (26% P_2O_5).

Conditions	Fe_2O_3 Removal Efficiency, %			
	IR3	IR5	IR5-7H	IR5-3H
Acid + 1% R	17.0	10.0	8.7	3.4
Acid + 2% R	33.0	20.2	18.9	8.5
Acid + 3% R	42.7	24.1	23.3	14.4
Acid + 4% R	63.0	28.2	27.4	18.1

R: Precipitating Reagent
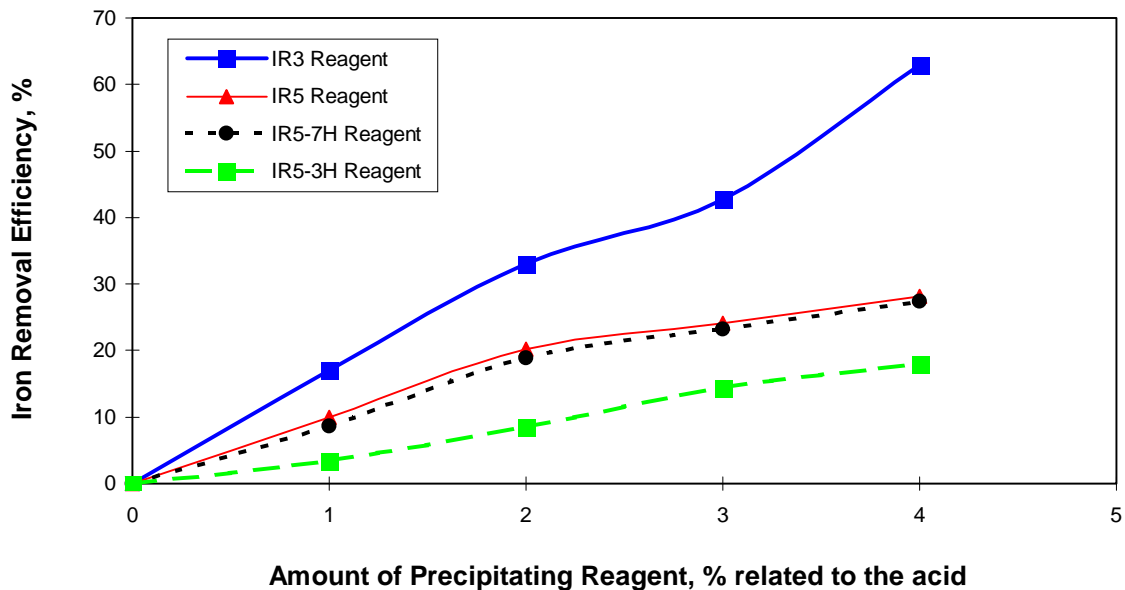
**Figure 11. Iron Removal Efficiency From Filter Acid (26% P_2O_5)
Using Different Precipitating Reagents.**

Regeneration of Precipitating Reagent

Experiments were conducted to explore the possibility of regenerating these chelating reagents. The applied conditions for these tests are given below:

Precipitation:

Reaction temperature:	23 ^{o}C
Reaction time:	1 hr
Weight of acid used:	500 g
Clarification time:	1 day
Amount of make-up precipitating reagent:	1.5% of phosphoric acid weight

Regeneration:

Reaction temperature:	23 ^{o}C
Reaction time:	1 hr

The obtained results are given in Table 22 and Figures 12 and 13. As in the case of IR# discussed earlier, regeneration results suggest that the iron removal efficiency is increased as the regeneration stage increased. To keep the same level of removal efficiency, make-up IR3 reagent equivalent to 1.5% of phosphoric acid weight is required.

Table 22. Iron Removal Efficiency from Phosphoric Acid (26% P_2O_5) Using Regenerated Reagent With 1.5% Make-up Related to Phosphoric Acid Weight.

Precipitating Reagent	Fe_2O_3 Removal Efficiency, %			
	First Stage	Second Stage	Third Stage	Fourth Stage
IR3	51.9	53.5	55.0	58.8
IR5	28.2	46.8	50.1	51.0
IR5-7H	27.4	46.8	47.5	47.9
IR5-3H	18.1	23.1	25.4	26.2

Figure 12. Iron Removal Efficiency From Filter Acid (26% P_2O_5) Using Regenerated Reagent With 1.5% Make-up.

34
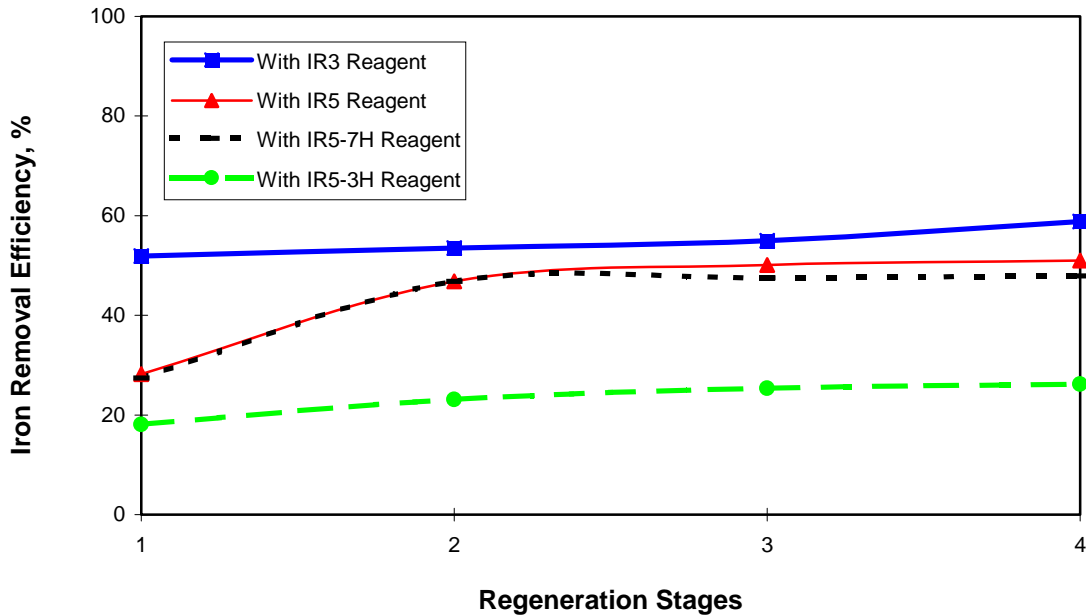
Figure 13. Iron Removal Efficiency From Filter Acid (26%
P_2O_5) Using Regenerated Reagent With 1.5% Make-up.

IN-PLANT TESTING - ADDITION OF REAGENTS DURING CLARIFICATION TO MINIMIZE SLUDGE FORMATION

The four precipitating reagents were tested using samples collected from one of Central Florida phosphoric acid plants. Bench scale samples from 42% P_2O_5 and 52% P_2O_5 ex-evaporator phosphoric acids were mixed with the calculated amount of the reagent and the sludge volume percentage as related to total volume of the original acid were determined as a function of time. Acid samples were analyzed for P_2O_5 and Fe_2O_3 contents. In addition, ex-evaporated phosphoric acid samples from another two phosphoric acid plants in Florida were also tested for sludge decreasing with and without IR3 reagent for different clarification times.

Using 42% P_2O_5 Ex-Evaporator Phosphoric Acid (Plant A)

The results of testing of the additives with 42% P_2O_5 acid are summarized in Tables 23 & 24. The data show that with increasing the amount of IR3 and IR5 additives, the sludge volume percentage is decreased. The best results are achieved upon using 1.5% IR3 after 6 days clarification time. The decrease in volume of sludge is 25%. In addition, the iron removal efficiency from the acid is about 52%. It is noticed that both IR5-3H and IR5-7H has no effect on decreasing volume sludge percentage.

Table 23. Sludge Volume Percentage in Phosphoric Acid (42% P_2O_5 from Plant A) With and Without Additives.

Additive	Amount, %	Volume % After Clarification Time of			
		18 hr	1 d	6 d	8 d
Without Additive (Control Test)	-	11	10	12	12
IR3	0.3	16	14	12	13
IR3	0.5	12	10	10	9
IR3	1.5	11	10	9	9
IR5	0.5	13	11	12	12
IR5	1.5	10	10	10	10
IR5-3H	0.5	18	16	16	16
IR5-7H	0.5	14	12	12	12

Table 24. Chemical Analysis of the Clarified Phosphoric Acid (42% P_2O_5 from Plant A) (After 6 d with 1.5% IR3).

Constituent	% in	
	Without Additive	With 1.5 % IR3
P_2O_5	43.0	42.6
Fe_2O_3	1.17	0.56

Using 52% P_2O_5 Ex-Evaporator Phosphoric Acid (Plant A)

The results of testing the additives with 52% P_2O_5 acid are summarized in Tables 25 & 26 and Figs 14-16. These results show that with increasing the amount of IR3 and IR5 additives, the sludge volume percentage is decreased. The best results were achieved upon using 1% IR3 after 6 days clarification time. The decrease in volume of sludge was about 64%. In addition, the iron removal efficiency from the acid was about 40%. Using 1% from the additive and after 6 days, the decrease in volume percentage of sludge compared to the control test are 64% with IR3, 51% with IR5-7H, 47% with IR5 and 43% with IR5-3H.

For comparison between these additives, results of addition 1% dosage of these reagents are summarized in Table 27 and plotted in Fig. 17. It is clear that IR3 reagent gives the lowest sludge volume.

Table 25. Sludge Volume Percentage in Phosphoric Acid (52% P$_2$O$_5$ from Plant A) With and Without Additives.

Additive	Amount, %	Volume % After Clarification Time of			
		18 hr	1 d	6 d	8 d
Without Additive (Control Test)	-	48	48	72	72
IR3	0.5	29	28	27	27
IR3	1.0	26	26	26	27
IR5	1.0	52	52	53	53
IR5	1.5	35	36	38	38
IR5-3H	1.0	40	40	41	41
IR5-7H	1.0	35	35	35	35

Table 26. Chemical Analysis of the Clarified Phosphoric Acid (52% P$_2$O$_5$ from Plant A) (After 6 d With 1% IR3).

Constituent	% in	
	Without Additive	With 1% IR3
P$_2$O$_5$	53.3	53.2
Fe$_2$O$_3$	1.17	0.70

Table 27. Sludge Volume Percentage in Phosphoric Acid (52% P$_2$O$_5$ from Plant A) without Additives and with 1.0% Dosage of Additives.

Additive	Amount, %	Volume % After Clarification Time of			
		18 hr	1 d	6 d	8 d
Without Additive (Control Test)	-	48	48	72	72
IR3	1.0	26	26	26	27
IR5	1.0	52	52	53	53
IR5-3H	1.0	40	40	41	41
IR5-7H	1.0	35	35	35	35
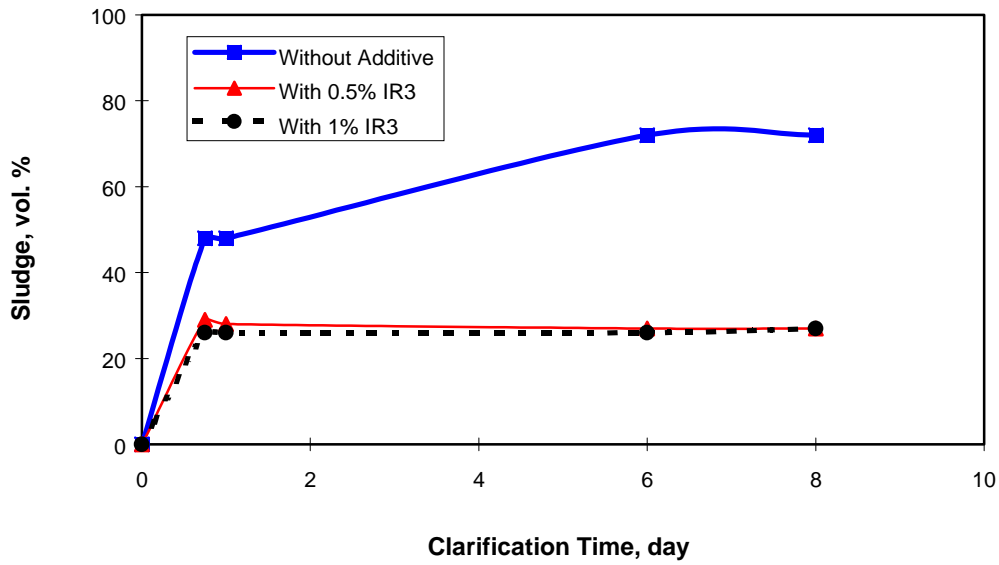
Figure 14. Effect Of IR3 Additive on Sludge Volume Percentage from 52% P_2O_5 Plant (A) Acid at Different Clarification Times.
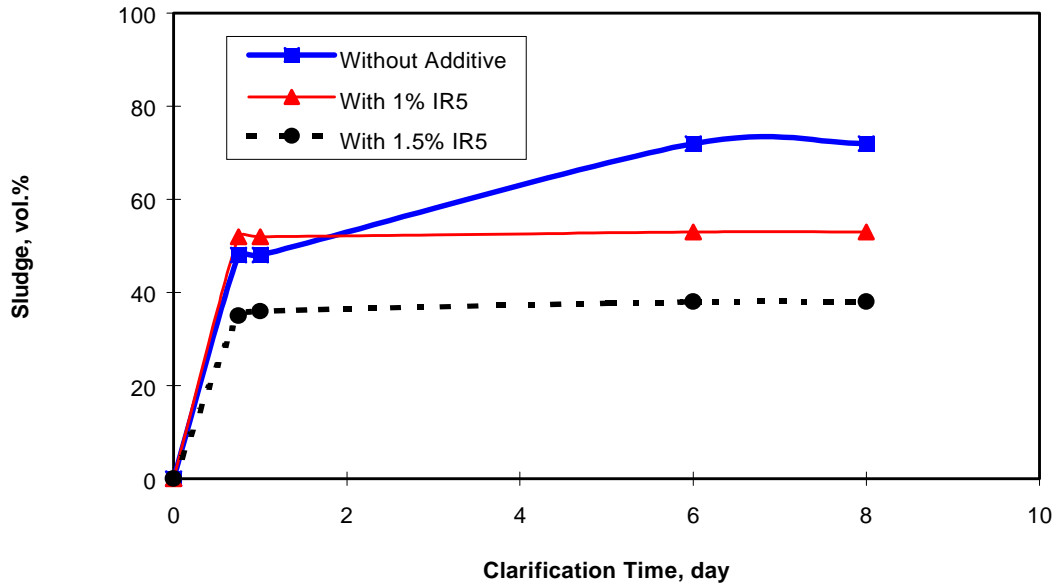
Figure 15. Effect of IR5 Additive on Sludge Volume Percentage from 52% P_2O_5 Plant (A) Acid at Different Clarification Times.
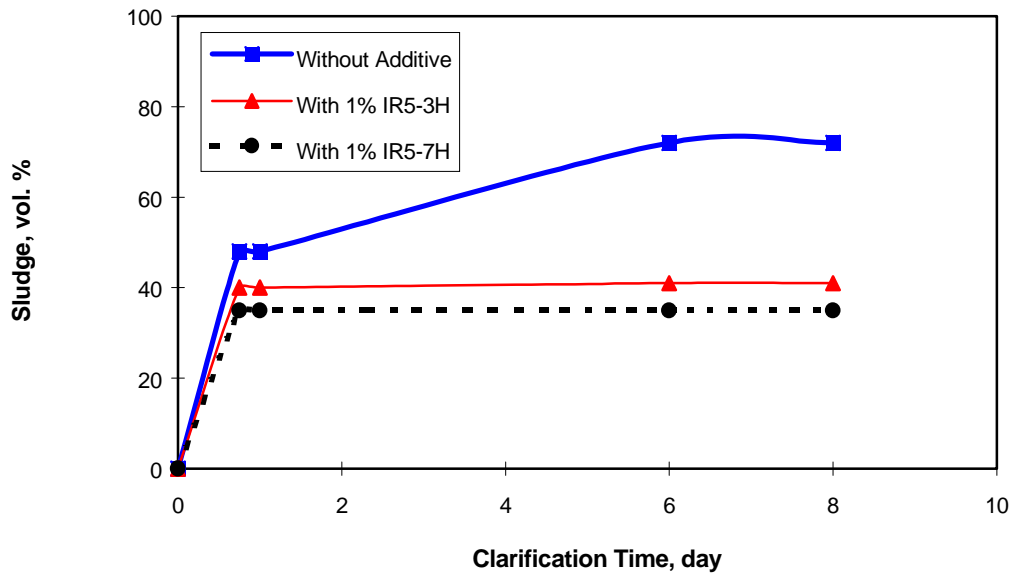
Figure 16. Effect Of IR5-3H and IR5-7H Additives on Sludge Volume Percentage from 52% P_2O_5 Plant (A) Acid at Different Clarification Times.
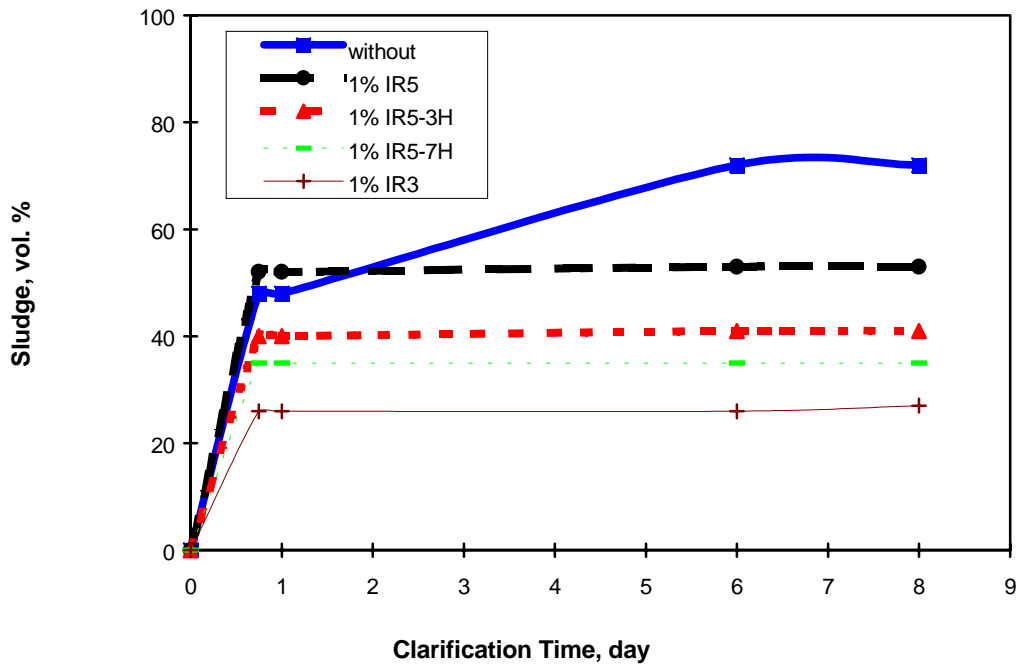
Figure 17. Effect of IR3, IR5, IR5-7H and IR5-3H Additives on Sludge Volume Percentage from 52% P_2O_5 Plant (A) Acid at Different Clarification Times.

Using 52% P$_2$O$_5$ Ex-Evaporator Phosphoric Acid (Plant B)

Based on the previous tests, IR3 was selected for testing with acid samples from plants B and C. The results of testing IR3 additive with 52% P$_2$O$_5$ acid of relatively low Fe$_2$O$_3$ content (about 1.8%) are summarized in Table 28 and Fig. 18. The results show that with increasing the amount of IR3 additive, the sludge volume percentage is decreased. The best results are achieved upon using 1% IR3 after 1 day clarification time. However from the economic point of view, using 0.5% is preferable. The decrease in volume of sludge is 60% after 5 days clarification time using 0.5% additive. Chemical composition of the clarified acid and precipitated sludge are given in Tables 29 & 30. Chemical analyses of sludge samples show the following:

- % water-insoluble P$_2$O$_5$ decreases with increasing amount of additive
- % Fe$_2$O$_3$ decreases with increasing amount of additive

This suggests that less amount of Lehr's salt [Fe$_3$KH$_{14}$(PO$_4$)$_8$.4H$_2$O] is formed with increasing the amount of additive.

Also, it is clear that with 0.5 and 1% additive, higher amounts of calcium sulfate and ralstonite (NaMgAlF$_6$.6H$_2$O) are formed as compared to the conditions where no additive is used and with 0.25% additive. The results of P$_2$O$_5$ losses with and without additive are given in Table 31. It is interesting to note that the amount of P$_2$O$_5$ losses has decreased from about 1.7% without additive to about 0.6% with 0.5% additive. In other words, 1.1% increase in P$_2$O$_5$ recovery could be achieved. In addition, sludge weight percentage is decreased with the additive. The decrease in weight percentage of sludge with 0.5% additive can be noticed to be about 61% after 10 days.

**Table 28. Sludge Volume Percentage in Phosphoric Acid (52% P$_2$O$_5$ from Plant B)
With and Without Additives.**

Clarification Time, day	Sludge Volume %			
	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
0	0	0	0	0
0.75	1.00	0.80	0.50	0.25
1.75	6.25	3.90	2.50	1.60
2.75	8.75	6.00	3.25	1.60
3	9.38	6.30	3.50	1.60
4	10.50	8.80	4.00	1.60
5	11.25	9.50	4.50	1.60
6	11.25	9.50	4.50	1.60
7	11.25	9.50	4.50	1.60
8	11.25	9.50	4.50	1.60
9	11.25	9.50	4.50	1.60
10	11.25	9.50	4.50	1.60

Figure 18. Effect of IR3 Amount on Sludge Volume Percentage from 52% P$_2$O$_5$ Plant (B) Acid at Different Clarification Times.

Table 29. Chemical Analysis of the Clarified Phosphoric Acid (52% P$_2$O$_5$ from Plant B) After 10 Days Clarification Time.

Constituent	% in Acid			
	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
P$_2$O$_5$	53.95	53.84	54.13	53.99
Fe$_2$O$_3$	1.63	1.71	1.77	1.79
Al$_2$O$_3$	2.18	2.20	2.21	2.20
MgO	0.74	0.74	0.73	0.73
K$_2$O	0.10	0.06	0.07	0.07
CaO	0.19	0.18	0.17	0.17
SO$_4$	3.32	3.32	3.28	3.28
F	1.25	1.27	1.24	1.25

Table 30. Chemical Analysis of Precipitated Sludge (from 52% P_2O_5 from Plant B) After 10 Days Clarification Time.

Constituent	% in Precipitated Sludge			
	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5	49.61	48.98	43.39	23.24
WS-P_2O_5	24.83	37.67	33.61	19.57
Insoluble P_2O_5	24.78	11.31	9.78	3.67
Fe_2O_3	9.59	5.26	4.94	1.61
Al_2O_3	2.72	2.57	3.46	4.86
MgO	0.73	0.86	1.48	2.37
K_2O	1.22	0.81	0.80	1.76
CaO	2.65	2.00	3.93	14.56
SO_4	5.44	5.20	7.88	23.47
F	2.05	2.17	3.65	8.32

Table 31. P_2O_5 Losses With and Without IR3 Additive After 10 Days Clarification (52% P_2O_5 from Plant B) Time.

Item	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5 Losses, %	3.06	2.52	1.04	0.17
Water-insoluble P_2O_5 Losses, %	1.53	0.58	0.23	0.03
Sludge Volume %	11.25	9.50	4.50	1.60
Dry Sludge, wt. %	3.38	2.82	1.31	0.41

Using 52% P_2O_5 Ex-evaporator Phosphoric Acid With Shaking (Plant B)

Acid with and without IR3 additive has been shaken every 24 hr to determine effect of agitation on sludge formation. The results are given in Table 32 and Fig. 19. The results show that after about 5 days clarification time, without additives, a tremendous increase in sludge volume percentage is obtained (from about 11% to about 31% for the base line). However, the sludge volume percentage with the additive is lower than without additive. The decrease in volume of sludge with 0.5% additive is about 69 and 72% after 5 and 10 days, respectively. Chemical composition of the clarified acid and precipitated sludge are given in Tables 29 and 30. Chemical analyses of sludge samples show the following:

- % water-insoluble P_2O_5 decreases with increasing amount of additive
- % Fe_2O_3 decreases with increasing amount of additive

This may suggest that less amount of Lehr's salt [$Fe_3KH_{14}(PO_4)_8.4H_2O$] is formed with increasing the amount of the additive.

Also, it is clear that with 0.5 and 1% additive, higher amounts of calcium sulfate, ralstonite ($NaMgAlF_6.6H_2O$) and potassium sulfate are formed as compared to the sludge formed without additive and with 0.25% additive. The results of P_2O_5 losses with and without additive are given in Table 35. It is interesting to note that the amount of P_2O_5 losses has decreased from 4.75% without additive to 1.41% with 0.5% additive. In other words, about 3.3% increase in P_2O_5 recovery could be achieved. In addition, sludge weight percentage has decreased with the additive. The decrease in weight percentage of sludge with 0.5% additive is about 69% after 10 days.

Table 32. Sludge Volume Percentage In Phosphoric Acid (52% P_2O_5 from Plant B) With and Without Additives (Daily Shaken).

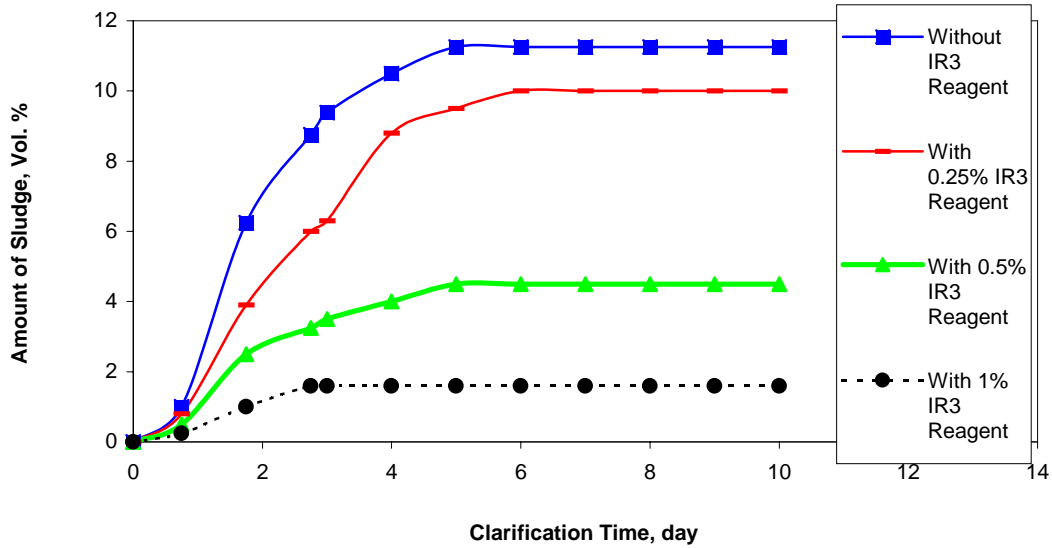| Clarification Time, day	Sludge Volume %			
	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
0	0	0	0	0
0.75	1.00	0.80	0.50	0.25
1.75	4.00	3.20	1.60	1.00
2.75	7.20	4.80	3.20	1.20
3	7.20	4.80	3.20	1.60
4	7.20	4.80	3.20	1.60
5	10.40	6.00	3.20	1.60
6	20.8	12.40	5.00	1.60
7	29.20	16.80	6.00	1.60
8	29.2	24.00	6.80	1.60
9	31.20	28.80	8.80	1.60
10	31.2	28.80	8.80	1.60

Figure 19. Effect of IR3 Amount on Sludge Volume Percentage from 52% P_2O_5 Plant (B) Acid at Different Clarification Times (Daily Shaken Acid).

Table 33. Chemical Analysis of the Clarified Phosphoric Acid (52% P_2O_5 from Plant B) After 10 Days Clarification Time (Daily Shaken).

Constituent	% in Acid			
	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
P_2O_5	54.03	54.13	54.08	53.89
Fe_2O_3	1.03	1.33	1.64	1.80
Al_2O_3	2.16	2.22	2.23	2.22
MgO	0.76	0.75	0.75	0.74
K_2O	Nil	0.02	0.04	0.06
CaO	0.13	0.13	0.16	0.18
SO_4	3.33	3.35	3.34	3.33
F	1.29	1.29	1.26	1.25

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Table 34. Chemical Analysis of Precipitated Sludge from Shaken Phosphoric Acid (52% P$_2$O$_5$ from Plant B) After 10 Days Clarification Time.

Constituent	% in Precipitated Sludge			
	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P$_2$O$_5$	50.76	50.44	48.36	36.96
WS-P$_2$O$_5$	30.81	34.76	33.19	33.73
Insoluble P$_2$O$_5$	19.95	15.68	15.17	3.23
Fe$_2$O$_3$	8.50	7.90	7.31	1.60
Al$_2$O$_3$	2.79	2.78	3.38	3.96
MgO	0.84	0.90	1.34	1.88
K$_2$O	0.78	1.02	0.98	1.63
CaO	1.19	1.52	2.55	7.55
SO$_4$	3.56	4.08	5.76	13.71
F	1.03	2.69	2.73	7.38

Table 35. P$_2$O$_5$ Losses With and Without IR3 Additive After 10 Days Clarification (52% P$_2$O$_5$ from Plant B) Time (Daily Shaken Acid).

Item	Without Additive	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P$_2$O$_5$ Losses, %	8.67	6.38	2.58	0.29
Water-insoluble P$_2$O$_5$ Losses, %	3.41	1.99	0.81	0.03
Sludge Volume %	31.2	28.80	8.80	1.60
Dry Sludge, wt. %	9.36	6.94	2.92	0.43

Using 52% P$_2$O$_5$ Ex-evaporator Phosphoric Acid (Plant C)

The results of testing IR3 additive with 52% P$_2$O$_5$ acid from plant C of relatively low Fe$_2$O$_3$ content (about 1.8%) are summarized in Table 36 and Fig. 20. Chemical composition of the clarified acid and precipitated sludge are given in Tables 37 & 38. The results show that with increasing the amount of IR3 additive, the sludge volume percentage is decreased. The best results are achieved upon using 1% IR3 after 1.5 day clarification time. However from the economic point of view, using 0.5% additive is preferable. The decrease in volume of sludge is about 84% after 5 days clarification time using 0.5% additive. In addition, the iron removal efficiency from the acid is about 40%. P$_2$O$_5$ losses with and without additive are given in Table 39. It is interesting to note that with 0.5% additive the amount of P$_2$O$_5$ losses is decreased from 2.0 % to 0.66 %. In other words, 1.3% increase in P$_2$O$_5$ recovery could be achieved. In addition, sludge weight percentage is decreased with the additive. The decrease in weight percentage of sludge with 0.5% additive is about 69% after 5 days.

Table 36. Sludge Volume Percentage in Phosphoric Acid (52% P_2O_5 from Plant C) With and Without Additives.

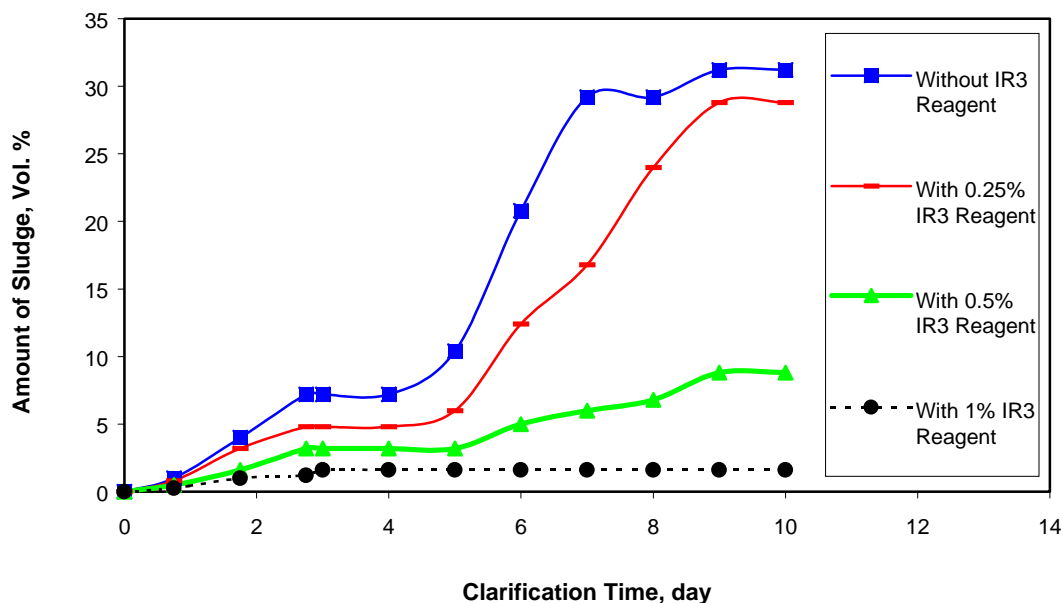| Clarification Time, day	Sludge Volume %				
	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
0	0	0	0	0	0
0.5	9	7	5	2	1.5
0.75	10	8.5	6	2	1.5
1	13	10	8.5	3	2
1.5	21	16	10	3.5	2.5
2	25	20	12	4	2.5
2.5	28	22.5	16	4.5	2.5
3	30	25	17	5	2.5
4	32	25	17	5	2.5
5	32	25	17	5	2.5
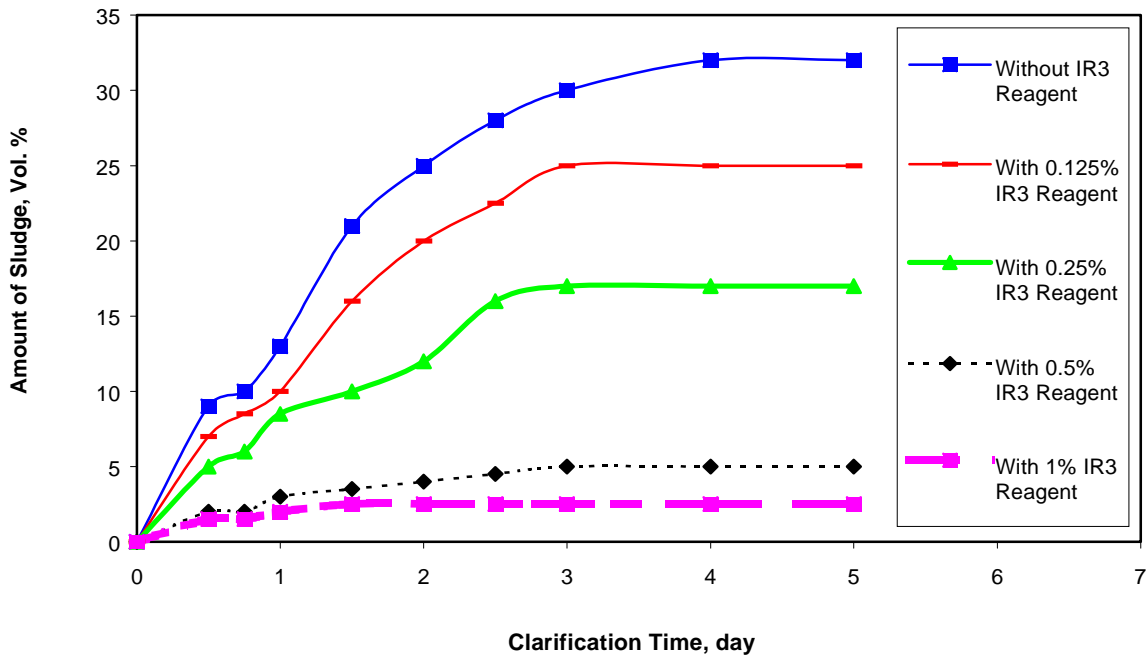
Figure 20. Effect of IR3 Amount Sludge Volume Percentage from 52% P_2O_5 Plant (C) Acid at Different Clarification Times.

Table 37. Chemical Analysis of the Clarified Phosphoric Acid (52% P_2O_5 from Plant C) After 5 Days Clarification Time.

Constituent	% in Acid				
	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
P_2O_5	55.77	55.94	55.61	56.08	55.67
Fe_2O_3	1.63	1.62	1.71	1.82	1.81
Al_2O_3	1.30	1.31	1.31	1.31	1.30
MgO	0.38	0.38	0.38	0.38	0.37
K_2O	0.06	0.05	0.07	0.14	0.16
CaO	0.02	0.01	0.01	0.02	0.03
SO_4	3.46	3.16	3.21	3.39	3.34
F	0.56	0.55	0.56	0.55	0.54

Table 38. Chemical Analysis of Precipitated Sludge After 5 Days Clarification Time (52% P_2O_5 from Plant C).

Constituent	% in Precipitated Sludge				
	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5	41.30	38.52	34.49	38.43	40.29
WS-P_2O_5	14.56	9.07	9.75	20.36	25.20
Insoluble P_2O_5	26.74	29.45	24.74	18.07	15.09
Fe_2O_3	14.47	12.42	11.86	7.50	6.67
Al_2O_3	1.83	1.88	1.83	1.62	1.60
MgO	0.36	0.48	0.46	0.41	0.41
K_2O	2.04	2.02	2.07	1.09	0.84
CaO	7.74	9.31	11.84	10.83	9.85
SO_4	12.58	15.22	19.15	17.98	16.85
F	2.96	2.99	3.43	2.94	2.70

Table 39. P_2O_5 Losses With and Without IR3 Additive After 5 Days Clarification Time of 52% acid from Plant C.

Item	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5 Losses, %	2.30	1.86	1.22	0.66	0.56
Water-insoluble P_2O_5 Losses, %	1.49	1.42	0.88	0.31	0.21
Sludge Volume %	32	25	17	5	2.5
Dry Sludge, wt. %	3.10	2.69	1.97	0.95	0.77

Using 52% P$_2$O$_5$ Ex-Evaporator Phosphoric Acid with Shaking (Plant C)

Acid with and without IR3 additive is shaken every 24 hr to determine effect of agitation on sludge formation. The results are given in Table 40 and Fig. 21. In addition, chemical composition of the clarified acid and precipitated sludge are given in Tables 41 and 42. The results suggest that no significant change in sludge volume percentage is obtained compared to acid without agitation (Table 36). The sludge volume percentage is less with additive. The decrease in volume of sludge with 0.5% additive is about 84% after 5 days. In addition, the iron removal efficiency from the acid is about 40%. P$_2$O$_5$ losses with and without additive are given in Table 43. It is interesting to note that, even with shaking, the amount of P$_2$O$_5$ losses decreases from 2.32 % to0.58 % with 0.5% additive. In other words, 1.7 % increase in P$_2$O$_5$ recovery may be achieved. In addition, sludge weight percentage has decreased in presence of the additive. The decrease in weight percentage of sludge with 0.5% additive is about 65% after 10 days.

Table 40. Sludge Volume Percentage in Phosphoric Acid (52% P$_2$O$_5$ from Plant C) With and Without Additives (Daily Shaken).

Clarification Time, day	Sludge Volume %				
	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
0	0	0	0	0	0
0.5	9	7	5	2	1.5
0.75	9	8	5	2	1.5
1	10	9	5.5	3	2
1.5	15	14	7	3.5	2.5
2	22.5	19	9	4	2.5
2.5	29	24.5	13.5	4.5	2.5
3	30	25.5	15	5	2.5
4	30	26	16	5	2.5
5	31	26	16	5	2.5
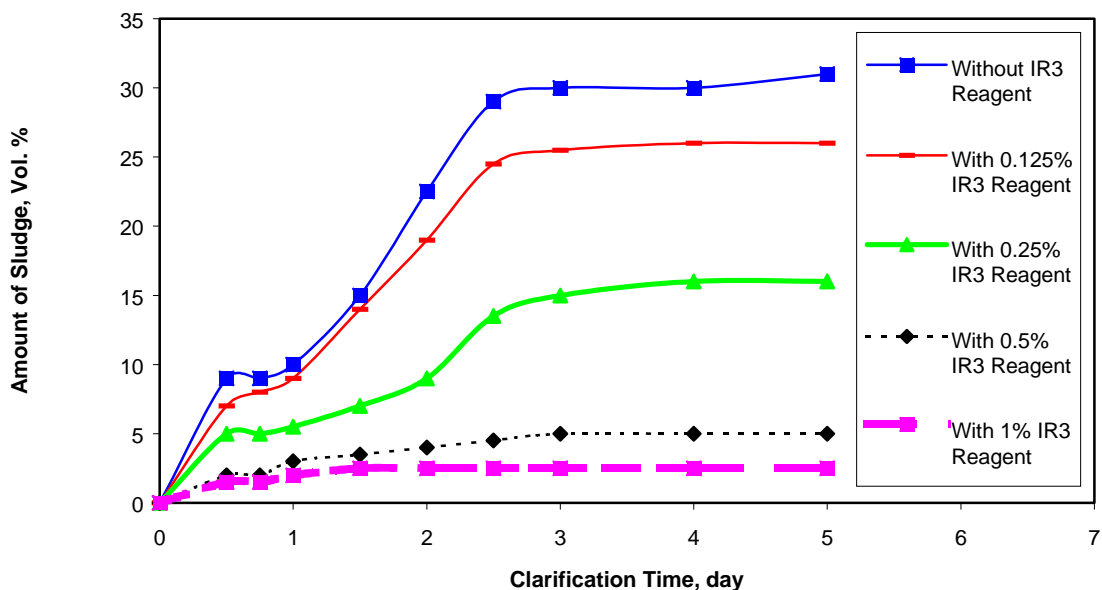
Figure 21. Effect of IR3 Amount on Sludge Volume Percentage from 52% P$_2$O$_5$ Plant (C) Acid at Different Clarification Times (Daily Shaken Acid).

Table 41. Chemical Analysis of the Clarified Phosphoric Acid (52% P$_2$O$_5$ from Plant C After 5 Days Clarification Time (Daily Shaken).

Constituent	% in Acid				
	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
P$_2$O$_5$	56.00	56.22	55.86	55.70	55.95
Fe$_2$O$_3$	1.37	1.49	1.60	1.81	1.82
Al$_2$O$_3$	1.31	1.31	1.31	1.32	1.31
MgO	0.39	0.38	0.38	0.38	0.38
K$_2$O	0.02	0.03	0.08	0.10	0.15
CaO	0.03	0.02	0.02	0.02	0.03
SO$_4$	3.46	3.24	3.21	3.32	3.33
F	0.56	0.56	0.55	0.55	0.55

Table 42. Chemical Analysis of Precipitated Sludge from Shaken Phosphoric Acid (52% P_2O_5 from Plant C) After 5 Days Clarification Time.

Constituent	% in Precipitated Sludge				
	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5	44.31	42.27	40.68	31.94	30.49
WS-P_2O_5	19.57	11.64	14.95	8.68	9.16
Insoluble P_2O_5	24.74	30.63	25.73	23.26	21.33
Fe_2O_3	16.03	15.49	15.07	11.21	10.65
Al_2O_3	1.76	1.73	1.70	1.77	1.76
MgO	0.29	0.31	0.32	0.40	0.42
K_2O	2.25	2.54	2.00	1.77	1.60
CaO	5.41	6.67	7.43	12.87	13.13
SO_4	8.89	10.96	12.14	20.76	20.56
F	2.21	2.57	2.99	5.48	6.01
Methanol Solids	93.02	94.81	90.13	95.96	95.94

Table 43. P_2O_5 Losses With and Without IR3 Additive After 5 Days Clarification Time of 52% P_2O_5 from Plant C (Daily Shaken Acid).

Item	Without Additive	With 0.125% IR3	With 0.25% IR3	With 0.5% IR3	With 1% IR3
Total P_2O_5 Losses, %	2.32	2.07	1.42	0.58	0.44
Water-insoluble P_2O_5, %	1.29	1.50	0.90	0.42	0.31
Sludge Volume %	31	26	16	5	2.5
Dry Sludge, wt. %	2.91	2.73	1.94	1.01	0.80

RECOVERY OF % P_2O_5 FROM SLUDGE

The four precipitating reagents (IR3, IR5, IR5-7H and IR5-3H) were tested for extraction of phosphoric acid from sludge. The sludge was obtained from one of Florida phosphoric acid plants and it contained 44.7% P_2O_5 content. A sludge sample from 52% P_2O_5 ex-evaporator phosphoric acid was pulped with water with and without calculated amount of the reagent. The extracted phosphoric acid was then separated from the solids. The reagent was regenerated from the solids and recycled to another batch. After regeneration, the precipitated residue was chemically analyzed. Then, P_2O_5 recovery and Fe_2O_3 removal efficiency were calculated. The obtained results are summarized in Table 44 and Fig. 22. The results show that with addition of the reagents, the iron removal efficiency is increased. IR3 reagent gives the highest iron removal efficiency at all dosages tested. Also, with addition of the reagents, P_2O_5 recovery is increased by up to about 23% depending to type and amount of reagent used.

Table 44. Effect of Reagent Addition on P_2O_5 Recovery and Fe_2O_3 Removal Efficiency From Sludge (Sludge formed in 52% P_2O_5 Acid).

Conditions	Fe_2O_3 Removal Efficiency, %	P_2O_5 Recovery, %
Baseline, Sludge + Water	19.9	70.3
Sludge + 2% IR3 + Regenerated Reagent + Water	33.1	92.1
Sludge + 3% IR3 + Regenerated Reagent + Water	45.1	88.8
Sludge + 4% IR3 + Regenerated Reagent + Water	52.7	88.8
Sludge + 2% IR5 + Regenerated Reagent + Water	30.6	91.6
Sludge + 3% IR5 + Regenerated Reagent + Water	40.9	89.7
Sludge + 4% IR5 + Regenerated Reagent + Water	48.4	90.0
Sludge + 2% IR5-7H + Regenerated Reagent + Water	26.0	93.2
Sludge + 3% IR5-7H + Regenerated Reagent + Water	37.4	91.3
Sludge + 4% IR5-7H + Regenerated Reagent + Water	47.6	91.5
Sludge + 3% IR5-3H + Regenerated Reagent + Water	29.6	93.0

Most importantly, the obtained acid in presence of 1.0% IR3 contains very low iron content as shown in Table 45.

Table 45. P_2O_5 and Iron Content in Recovered Acid from IR3 Treated Sludge.

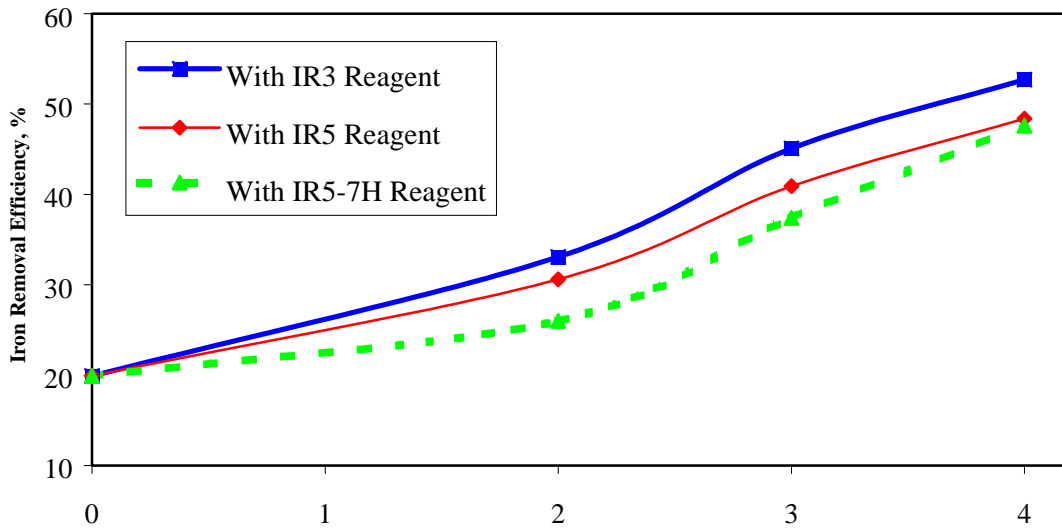| Item	Test 1	Test 2
Treatment	Sludge pulped with water	Sludge pulped with water and reagent
% P_2O_5 in Recovered Acid	24.9	25.0
% Fe_2O_3 in Recovered Acid	0.526	0.055

Figure 22. Effect of IR3, IR5 and IR5-7H Amounts on Iron Removal Efficiency.

QUALITY OF DAP PREPARED FROM TREATED PHOSPHORIC ACID

Quality of diammonium phosphate fertilizers prepared from phosphoric acid mixed with different proportions of IR3 reagent ranging from 0.02% to 0.5% is given in Table 46. It should be mentioned that these are preliminary bench scale ammoniation tests. More controlled tests need to be conducted in a pilot setting to produce more reliable results.

Table 46. %P_2O_5 in DAP Prepared from Treated Phosphoric Acid.

Additive	% P_2O_5		
	Total	Citrate-soluble	Water-soluble
Without Additive (Control Test)	51.9	51.4	47.8
With 0.5% IR3 Reagent	52.3	51.2	47.7
With 0.1% IR3 Reagent	52.3	50.8	47.1
With 0.05% IR3 Reagent	51.9	50.1	48.0
With 0.02% IR3 Reagent	52.8	51.7	48.0

COST BENEFIT ANALYSES

RECOVERY OF P_2O_5 FROM POST PRECIPITATED SLUDGE

Treating post-precipitated sludge by the chelating reagent IR3 indicate that 92% of P_2O_5 can be recovered which represents a gain of 22% in P_2O_5 recovery as compared to washing the sludge with water alone. Quantification of the value of such gain depends on many factors such as: a)-Price of recovered P_2O_5 as dilute phosphoric acid, and b)- value of P_2O_5 if used as sludge for one purpose or another. If the difference in the price of ton of P_2O_5 as phosphoric acid and ton of P_2O_5 price as sludge is greater than $60.0 then the process is economical. Note that $60.0 is the cost of treatment one ton of P_2O_5. Thus the cost benefit analyses are left to the reader.

PREVENTION OF FORMATION OF POST PRECIPITATED SLUDGE

A cost of about $4.7/ton P_2O_5 could be incurred for prevention of sludge formation in concentrated phosphoric acid. Such costs could be acceptable to phosphoric acid producers who ship the concentrated acid for a long distance.

For the cost benefit analyses, the following criteria are used:

- Minimum increase in P_2O_5 recovery = 2.0% (see Table 27)
- IR3 reagent consumption = 5 Kg/ ton Acid (55%P_2O_5)
- IR3 reagent consumption = 9 Kg// ton P_2O_5
- Price of ton of P_2O_5 = $395.00
- Cost of 1.0 Kg. of IR3 reagent = $1.40

Thus, the following analyses is conducted:

Cost of IR3 reagent	=	$12.60/ton P_2O_5
Benefits:		
Gain in recovery:		
(2.0% @ $395.00/ton P_2O_5)	=	$7.90/ ton P_2O_5

Net gain = $ - 4.70/ ton P_2O_5

Most importantly, there is a decrease of up to 84% in sludge volume. The benefits due to decrease in sludge handling problems cannot be quantified.

REDUCTION OF IRON IN DILUTE PHOSPHORIC ACID

The use of these chelating reagents to decrease iron content in dilute acids may not be economical since the minimum required amount is about 15.0 Kg/ ton of acid. However, addition of a smaller quantity (2.5 kg/ton acid) may be beneficial in:

- preventing sludge formation during evaporation
- preventing sludge formation during clarification since the concentration of chelating reagent will also increase during evaporation
- increase in P_2O_5 recovery by at least 2.0%.

CONCLUSIONS AND RECOMMENDATIONS

The major goal of this project is to decrease iron content in wet-process phosphoric acid using different precipitating reagents. Reducing the amount of post-precipitated sludge in the acid is another important objective in this study. In order to achieve these goals the following tasks have been conducted:

- Bench scale testing of effect of four different reagents [IR3, IR5, IR5-7H and IR5-3H (Patent Pending)] on removal of iron from phosphoric acid produced from South Florida high iron and magnesium phosphate concentrate. Role of addition point of reagent was studied; specific points involve adding the reagents:
    - To filter acid (25-27% P_2O_5),
    - To partially concentrated acid (42-45% P_2O_5) and
    - To concentrated acid (52-56% P_2O_5).
- Regeneration and recycling of the reagent
- Plant testing using freshly produced concentrated acids for reducing the post-precipitated sludge
- Addition of the reagents to the precipitated sludge to extract phosphoric acid of low Fe_2O_3 content
- Cost benefit analysis

The data obtained in the above studies lead to the following conclusions:

- Addition point of the precipitating reagent is very important as the precipitated iron compound has higher solubility at higher P_2O_5 concentrations.
- Effects of IR3, IR5, IR5-7H and IR5-3H precipitating reagents on iron removal from phosphoric acid have been investigated at different operation conditions.
- The results indicate that up to 60% Fe_2O_3 removal efficiency are achieved depending on the type and amount of the reagent, concentration of acid used and operating conditions.
- Most importantly, precipitating reagent can be regenerated and recycled. The optimum regeneration conditions were obtained. The results reveal that up to 69% of the reagent could be regenerated and recycled.
- Addition of 0.5% IR3 precipitating reagent to freshly concentrated phosphoric acid leads up to 84% decrease in sludge volume percentage depending on acid type and clarification conditions. Decreasing the volume percentage of the sludge (consolidation and compaction) facilitates acid handling as well as decreases the adherent water-soluble P_2O_5 with the sludge. Also, with 0.5% IR3 reagent, the total P_2O_5 losses decreases (or P_2O_5 recovery increases) by about 1.6% - 6.1% depending on acid type and clarification conditions.

- Cost benefit analyses suggest a gain of about $26/ton P_2O_5, if IR3 reagent is used for extraction of phosphoric acid from precipitated sludge. On the other hand, loss of about $4.7/ton P_2O_5 for prevention of sludge formation in concentrated phosphoric acid. Consequently, the handling problems associated with post precipitation of solids with aging can be avoided.

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[*]Cost includes cost of the reagent at the delivery price as quoted by manufacturer. Feeding and handling costs are neglected since only a feeding tank and dosing pump are needed for this application.

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