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Decreasing Iron Content In Fertilizer-Grade Phosphoric Acid Using Ion Exchange Method

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ABSTRACT

In Egypt, concentrated wet-process phosphoric acid is produced from phosphate concentrate by the conventional dihydrate process in which phosphate concentrate leached with sulfuric and weak phosphoric acids. It is an important intermediate product for production of phosphatic fertilizers. The produced acid contains iron ranging from 2.0 % to 4.0 % Fe_2O_3 as inorganic impurity and 48% P_2O_5. Ion-exchange method is used to reduce the concentration of ferric ions content. Ferric ions affect the quality of produced fertilizers as they combine with P_2O_5 and form insoluble compounds. Decreasing Fe_2O_3 content to less than 1.0% was achieved by reaction of fertilizer-grade phosphoric acid with strong acid cation exchanger (Dowex-50). The following optimum reaction conditions were determined: 30°C reaction temperature, 30 min. raction time, 1.25 weight ratio of cation-exchange resin to acid and 28 % P_2O_5 from acid concentration. These conditions lead to removal of 80.3 % from Fe_2O_3 in the treated acid. Reduction of ferric ions to ferrous ions is a must for higher Fe_2O_3 removal efficiency. Also, regeneration conditions of loaded resin were systematically studied.   © 2006 Trade Science Inc. - INDIA
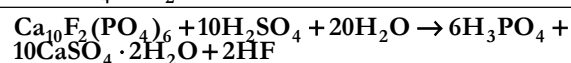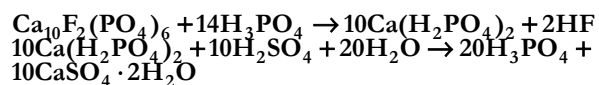
KEYWORDS

Phosphoric acid;
Ion exchange;
Decreasing iron.

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INTRODUCTION

Phosphoric acid is an important intermediate for production of fertilizers. It is mainly produced by Dihydrate Process in which phosphate rock leached with sulfuric and weak phosphoric acids to produce phosphoric acid and calcium sulfate dihydrate (phosphogypsum) as a by-product. The primary reaction for the Dihydrate process is as follows[5]

$$Ca_{10}F_2(PO_4)_6 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$$
$$10Ca(H_2PO_4)_2 + 10H_2SO_4 + 20H_2O \rightarrow 20H_3PO_4 + 10CaSO_4 \cdot 2H_2O$$

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$$

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 48-54% P_2O_5 either through a single or a double-stage 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[5].

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[5] up to 3%-4% in Egyptian phosphate[1,3,4,11]. During the reaction, most of iron impurities present in the phosphate rock (50-95%) reacts and ends 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.

Different techniques can be used to remove iron impurity from wet-process phosphoric acid. Among these techniques are precipitation, ion exchange and solvent extraction. Precipitation of iron from phosphoric acid can 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[2,7].

$$K^+ + 3Fe^{3+} + 8H_3PO_4 + 4H_2O \rightarrow Fe_3KH_{14}(PO_4)_8 \cdot$$
$$4H_2O + 10H^+$$
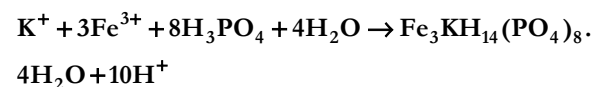
Also, ammonium salts can form analogous compounds. The disadvantage of this process is high P_2O_5 losses. For decreasing Fe_2O_3 content in phosphoric acid by 1%, the corresponding P_2O_5 losses will be about 2.4%. On lab-scale[15] precipitated the impurities from slightly ammoniated acid by addition 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[20], 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.

Found[12] 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. In the following are given the applied suitable conditions:

Amount of ammonium salt   : 0.3-2%
Clarification time   : 4-8 day
Clarification temperature   : Ambient - 82°C

Reported[8] that Fe, Al, Ca and Ti were removed from crude phosphoric acid by adding iso-propanol and 0.06-0.12 mole NH_3/mole P_2O_5. Fe content was decreased[21] from 0.48% to 0.005% treated the phosphoric acid with soluble compounds of Na and F to remove Al as Na_3AlF_6. The iron content is decreased

CHEMICAL TECHNOLOGY
An Indian Journal

Full Paper

to acceptable level by addition of ammonia. Iron is precipitated as crystalline salt, principally in the form of $NH_4Fe_3H_8(PO_4)_6 \cdot 6H_2O$. Found[16] that the metallic impurities (mainly Fe, Al and Mg) were removed from technical-grade phosphoric acid by precipitation with ammonia at 52-108ºC 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%. Adjusted[19] 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%.

Reported[18] that ethanol and aqueous ammonia can be used for purification of phosphoric acid. The raw acid which was 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%). Iron, aluminum and lead can be precipitated by the use of glacial acetic acid[7,17]. Acetic acid can be recovered by distillation.

Cation exchange resin contains free H^+ cations which can be exchanged for Fe^{2+} cations in solution according to the following equation:

$$2(Res.SO_3^-)H^+ + Fe^{2+}(Soln) = (Res.SO_3^-)_2Fe^{2+} + 2H^+ + 2H^+(Soln)$$
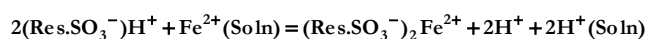
Some authors used this technique for separation of rare earths from phosphoric acid[13,14].

The experimental conditions adjusted to give the equilibrium which is completely displaced from left to right. Then, Fe^{2+} ions are completely fixed on the Dowex-50 cation exchanger.

The factors determining the distribution of ions between an ion-exchange resin and a solution include:

Nature of exchanging ions, in general ions with smaller hydrated volume will usually be absorbed preferentially.

Nature of ion-exchange resin including nature of the functional groups in the resin and the degree of cross-linking: as the degree of cross–linking is increased, resins become more selective towards ions of different sizes[10].

The major goal of this study is to reduce iron content in phosphoric acid by ion exchange method as much as possible, with minimum losses of phosphate values.

EXPERIMENTAL

Raw materials

Pure phosphoric acid grade (85%), pure sulfuric acid grade (98%), ferrous sulfate heptahydrate and ferric sulfate pentahydrate from E-Merck, Germany were used in this study to prepare simulated fertilizer-grade phosphoric acid solutions. Dowex-50 strong acid cation exchanger resin from Dow Co., USA was also used.

Procedure

Different weights from Dowex-50 resin (50-150 gm) were mixed with 100 gram from phosphoric acid of different concentrations (28-42% P_2O_5) in a beaker. Effect of reaction temperature, contact time, concentration of phosphoric acid, resin/acid ratio and iron oxidation state on Fe_2O_3 removal efficiency were systematically studied. Regeneration of resin using sulfuric acid was studied. Samples were chemically analyzed[6] for P_2O_5 and Fe_2O_3 by UV-120-02 Spectrophotometer, Shimadzu, Japan and the percentage of P_2O_5 recovery and Fe_2O_3 removal efficiency were calculated from these assays.

RESULTS

Cation exchange stage

In this stage, the ferric or ferrous ions in simulated phosphoric acid exchange with hydrogen ions in resin Dowex-50. Effects of the following conditions on Fe_2O_3 removal efficiency were systematically studied:

Oxidation state of iron   : Fe^{3+} or Fe^{2+}
Contact time   : 15-180 minutes
Reaction temperature   : 30-80°C
Resin/acid wt. ratios   : (0.5-1.5):1.0
H_3PO_4 concentration   : 28-42 % P_2O_5

Effect of iron oxidation state and resin/acid ratio on Fe_2O_3 removal efficiency

The effect of iron oxidation state on Fe_2O_3 removal efficiency was studied under the following conditions:

H_3PO_4 concentration   : 28% P_2O_5
Contact time   : 15 minute

E.A.Abdel-Aal et al.

Full Paper

Reaction temperature   : 30°C
Resin/acid wt. ratios   : (0.5-1.5):1.0
Oxidation state of iron   : Fe^{3+}, Fe^{2+}

The results are given in figure 1. These results show that oxidation state of iron has a significant effect on Fe_2O_3 removal efficiency. Ferrous iron has higher removal efficiency (35.9-74.9%) compared to ferric iron (7.6-38.0%) at resin / acid ratio ranged from 0.5:1.0 to 1.5:1.0. So, it is preferable to reduce iron in phosphoric acid to ferrous state. The optimum resin/acid wt. ratio is 1.25 that gives about 71.6% Fe_2O_3 removal efficiency. With increasing resin/acid wt. ratio to 1.5:1.0, insignificant increase in Fe_2O_3 removal efficiency was noticed (only 3.3%).

Effect of contact time on Fe_2O_3 removal efficiency

Effect of contact time on Fe_2O_3 removal efficiency was studied under the following conditions:
Oxidation state of iron   : Fe^{2+}
Resin/acid wt. ratio   : 1.25
Reaction temperature   : 30°C
H_3PO_4 concentration   : 28% P_2O_5
Contact time   : 15-180 minute

Each experiment was repeated 3 times and the error bar was depicted. The results are given in figure 2. These results show that the optimum contact time is 30 minutes which gives 80.3% Fe_2O_3 removal efficiency. Further increase in contact time from 30 minutes to 180 minutes has slight increase on Fe_2O_3 removal efficiency.

Effect of reaction temperature

Effect of reaction temperature on Fe_2O_3 removal efficiency was studied under the following conditions:
Oxidation state of iron   : Fe^{2+}
Resin/acid wt. ratio   : 1.25
Contact time   : 30 minute
H_3PO_4 concentration   : 28% P_2O_5
Reaction temperature   : 30-80°C

The results are given in figure 3. These results show that no significant increase in Fe_2O_3 removal efficiency was obtained with increasing reaction temperature from 30°C to 80°C. From economic point of view, the optimum reaction temperature was selected as 30°C which corresponds to 80.3% Fe_2O_3
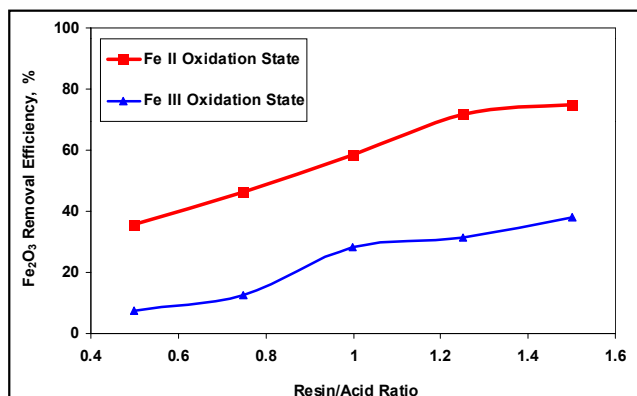

Figure 1: Effect of iron oxidation state and resin/acid ratio on Fe_2O_3 Removal Efficiency
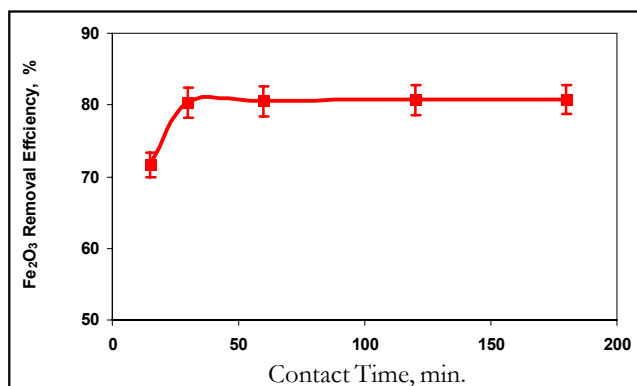

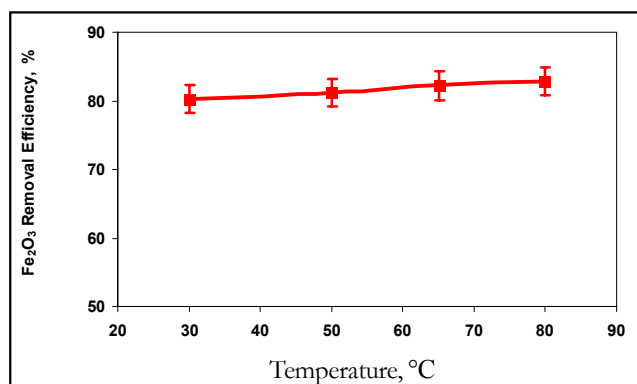Figure 2: Effect of contact time on Fe_2O_3 removal efficiency

Figure 3: Effect of reaction temperature on Fe_2O_3 removal efficiency

removal efficiency.

Effect of phosphoric acid concentration on Fe_2O_3 removal efficiency

Effect of phosphoric acid concentration on Fe_2O_3 removal efficiency was studied under the following conditions:
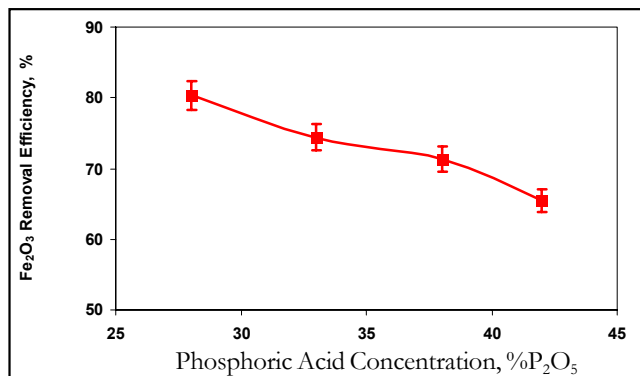Oxidation state of iron   : Fe^{2+}

Full Paper

Figure 4: Effect of phosphoric acid concentration on Fe_2O_3 removal efficiency

Resin/acid wt. ratio : 1.25
Contact time : 30 minute
Reaction temperature : 30°C
H_3PO_4 concentration : 28-42% P_2O_5

The results are given in figure 4. These results show that with increasing phosphoric acid concentration, the Fe_2O_3 removal efficiency is decreased. The optimum concentration of phosphoric acid is 28% at which the obtained Fe_2O_3 removal efficiency is 80.3%. In industry, phosphoric acid is produced in the concentration range of 26% to 30% P_2O_5, so testing lower acid concentration less than 28% P_2O_5 is not preferable.

Optimum conditions

The optimal Fe_2O_3 removal conditions and the results are summarized in TABLE (1). Fe_2O_3 removal efficiency of 80.3 % is obtained. Final Fe_2O_3 content in purified phosphoric acid is 0.38% Fe_2O_3 which corresponds to about 1.2% Fe_2O_3 in concentrated acid (50% P_2O_5 content).

Regeneration stage

In this stage, hydrogen ions in sulfuric acid exchange with ferric or ferrous iron ions loaded in resin Dowex-50. Fe_2O_3 release efficiency was systematically studied under the following conditions:
H_2SO_4 concentration : 10-70 %
Contact time : 15-120 minutes
Reaction temperature : 30-80°C
H_2SO_4 / Resin Ratio : (1.2-2.4):1.0, ml/g

Effect of sulfuric acid concentration on Fe_2O_3 release efficiency

TABLE 1: Optimum conditions and Results of Iron removal Process from Phosphoric acid

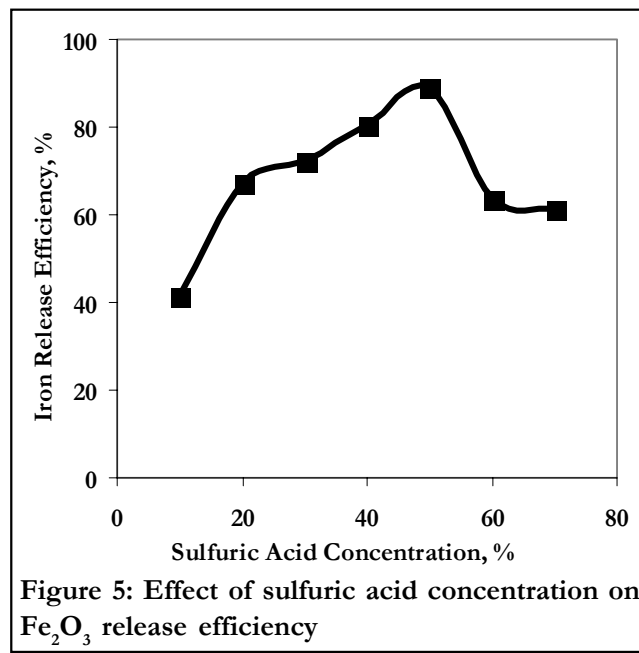| Fe_2O_3 Removal conditions	Value
Oxidation state of iron	Fe^{2+}
Resin/acid wt. ratio	1.25
Contact time, minute	30
Reaction temperature, °C	30
Phosphoric acid concentration, % P_2O_5	28
Results:	
Fe_2O_3 removal efficiency, %	80.3

Figure 5: Effect of sulfuric acid concentration on Fe_2O_3 release efficiency

Effect of sulfuric acid concentration on Fe_2O_3 release efficiency was studied under the following conditions:
Oxidation state of iron : Fe^{2+}
H_2SO_4 / Resin ratio : 1.6:1.0, ml/g
Reaction temperature : 30°C
H_2SO_4 concentration : 10-70%
Contact time : 15 minute

The results are given in figure 5. These results show that with increasing sulfuric acid concentration, the Fe_2O_3 release efficiency is increased. The optimum concentration was 50% at which 89% iron release efficiency was obtained. Further increase in sulfuric acid concentration leads to decrease in Fe_2O_3 release efficiency.

Effect of contact time on Fe_2O_3 release efficiency

Effect of contact time on Fe_2O_3 release efficiency was studied under the following conditions:
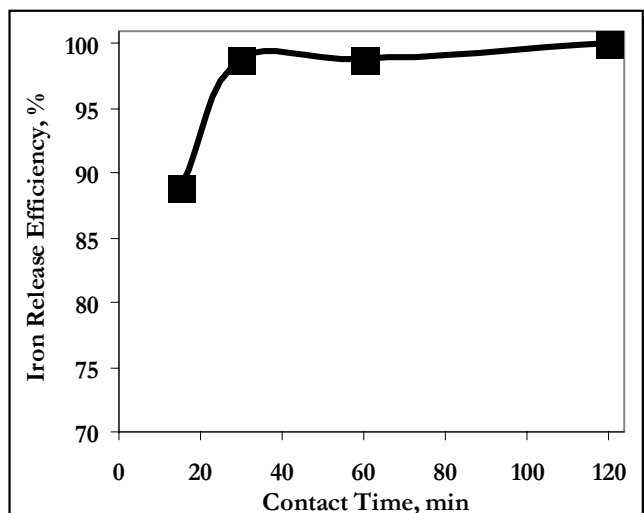Oxidation state of iron : Fe^{2+}

Figure 6: Effect of contact time on Fe$_2$O$_3$ release efficiency

Figure 7: Effect of sulfuric acid / resin ratio on Fe$_2$O$_3$ release efficiency

H$_2$SO$_4$ / Resin ratio	: 1.6:1.0, ml/g
Reaction temperature	: 30°C
H$_2$SO$_4$ concentration	: 50%
Contact time	: 15-120 minute

The results are given in figure 6. These results show that with increasing contact time the Fe$_2$O$_3$ release efficiency is increased. The optimum contact time is 30 minutes at which the 98.8% Fe$_2$O$_3$ release efficiency is obtained. Further increase in contact time from 30 minutes to 120 minutes has insignificant increase in Fe$_2$O$_3$ release efficiency.

Effect of sulfuric acid / resin ratio on Fe$_2$O$_3$ release efficiency

Effect of sulfuric acid / resin ratio on Fe$_2$O$_3$ release efficiency was studied under the following conditions:

Oxidation state of iron	: Fe^{2+}
Reaction temperature	: 30°C
H$_2$SO$_4$ concentration	: 50 %
Contact time	: 30 minute
Acid / Resin Ratio	: (1.2-2.4):1.0, ml/g

The results are given in figure 7. These results show that with increasing acid / resin ratio, the Fe$_2$O$_3$ release efficiency is increased. The optimum ratio was 1.6:1.0 at which the Fe$_2$O$_3$ release efficiency is 98.8 %. Further increase in the acid / resin ratio has insignificant effect on increase of Fe$_2$O$_3$ release efficiency.
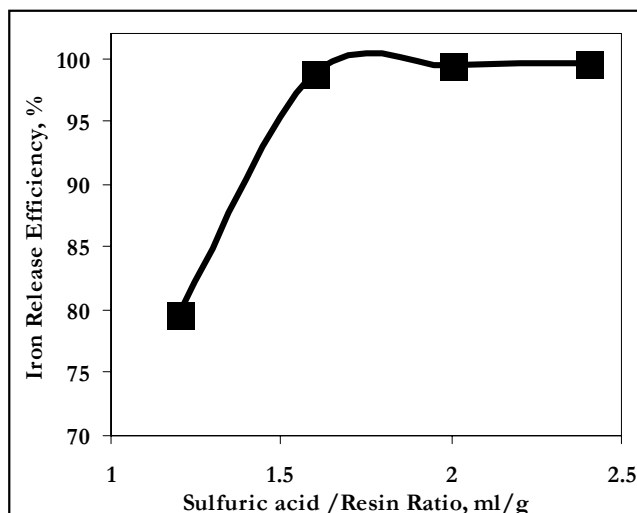
Effect of reaction temperature on Fe$_2$O$_3$ release

efficiency

Effect of reaction temperature on Fe$_2$O$_3$ release efficiency was studied under the following conditions:

Oxidation state of iron	: Fe^{2+}
Acid / Resin .Ratio	: 1.6:1.00
H$_2$SO$_4$ concentration	: 50 %
Contact time	: 30 minute
Reaction temperature	: 30-80°C

The results are given in figure 8. These results show that with increasing temperature the Fe$_2$O$_3$ release efficiency is slightly increased. From technical

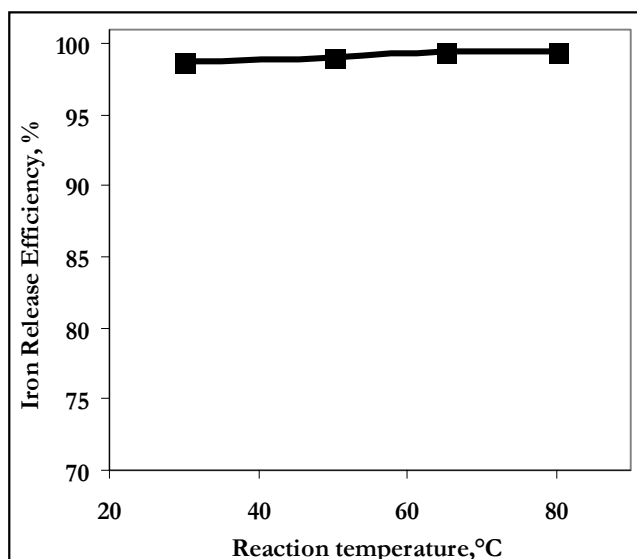**Figure 8: Effect of reaction temperature on Fe$_2$O$_3$ release efficiency**

Full Paper

and economical point of view, the optimum temperature is 30°C at which the Fe_2O_3 release efficiency is 98.8 %.Further increase in temperature has a slight effect on increase of Fe_2O_3 release efficiency.

Optimum conditions

The optimum regeneration conditions and the results are summarised and given in TABLE (2). 98.8% Fe_2O_3 release efficiency was achieved.

TABLE 2: Optimum conditions and results of cation exchanger regeneration process

Regeneration conditions	Value
Reaction temperature,°C	30
Contact time, minutes	30
Sulfuric acid concentration %	50
Sulfuric acid / rsesin ratio, ml/g	1.6;1.0
Results:	
Fe_2O_3 release efficiency, %	98.8

CONCLUSION

The results show that the cation-exchanger can be used for the effective removal of iron from crude phosphoric acid. Fe_2O_3 removal efficiency of 80.3 % was achieved under the following conditions:

Oxidation state of iron   : Fe^{2+}
Resin/acid wt. ratio   :   1.25
Contact time, minute, minute :   30
Reaction temperature, °C   :   30
Phosphoric acid concentration, %P_2O: 28

Regeneration of loaded resin was also studied. Fe_2O_3 release efficiency of 98.8 % was achieved under the following conditions:

Reaction Temperature,°C   : 30
Contact Time, minute   : 30
Sulfuric Acid Concentration, % : 50
Sulfuric Acid/Resin Ratio, ml/g : 1.6:1.0

Application of the cation-exchanger for purification of fertilizer-grade phosphoric acid is considered to be encouraging. Cost benefit analysis and feasibility study will be calculated.

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