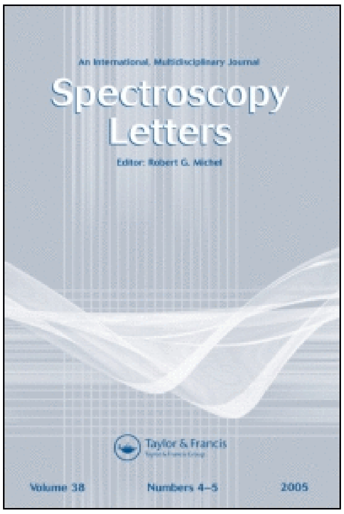

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Iron Removal from Phosphoric Acid by Paramagnetism

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IRON REMOVAL FROM PHOSPHORIC ACID BY PARAMAGNETISM

Key words: Paramagnetism, iron, separation, industrial processes, hydrocyclone

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ABSTRACT

A two-step separation technique was used in the laboratory to purify industrial grade phosphoric acid. Step 1 used a hydrocyclone, and step 2 used paramagetism. A total of 78.4% of the iron was removed without loss of phosphorus, mostly through step 1. In addition, 13% of the initial chromium was removed. Probably recycling or enhanced fields would enhance the removal of iron and chromium.

INTRODUCTION

Filter-grade wet-process phosphoric acid (WPA) with dissolved impurities is produced by the interaction of phosphate rock with sulfuric acid, and the insoluble precipitate $CaSO_4 \cdot 2H_2O$, is removed by filtration. The impurities in wet-process phosphoric acid, which form precipitates during processing, and storage, are iron, aluminum, magnesium, calcium, fluorine, sulfate, etc. Ferric iron precipitates readily at P_2O_5 concentrations about 35 %, and the reports identified ferric iron and aluminum as the major sludge-forming impurities in shipping grades of WPA (1). The interaction between iron and ammonia has been identified as a significant contributor to postprecipitation.

A number of processing techniques are described in the literature for the purification of wet-process acid. These may be classified as (a) physical methods such as crystallization (2) and solvent extraction (3), (b) electrochemical methods (4), and (c) chemical methods (5).

One less-common separation method, magnetic separation, has been used for the separation of paramagnetic material from diamagnetic matrix.. In magnetic filtration, a diamagnetic liquid containing suspended ferro-, ferri-, and para-magnetic particulate is passed through a tube containing magnetic steel wool, and the suspended solid is entrapped on the magnetic steel wool (6,7).

A magnetic method assisted chemical separation of waste by attracting chelating agent- coated paramagnetic particles (8). In this process, magnetic particles were coated with either a selective ion- exchange material or an organic extractant-containing solvent. These coatings selectively separate the metal contaminants (cesium, strontium, and transuranics) onto the particles, which can be recovered from the treatment tank using a magnet.

Similarly, an early large-scale industrial application of high-gradient-magnetic separation (HGMS) involved removal of colored impurities from kaolin clay. The discoloring particles were weakly paramagnetic, with small diameters (ca 1 μm), and the particles could be removed with HGMS to yield beneficiated kaolin clay (aluminosilicate mineral) that was used by the paper industry to enhance brightness (9). Stack gases, especially from the steel industry [basic oxygen furnaces and sintering plants (10)], could be subjected to HGMS and improve the quality of the stack gas emissions. Presumably more fly ash could be removed by this general method, allowing for the presence of paramagnetic substance. Water purification has been achieved by adding a flocculating agent to precipitate dissolved or suspended paramagnetic species, and removing paramagnetic particulate material (10).

In this research, a two- step procedure, involving use of a hydrocyclone, followed by magnetic separation, was tested for removal of paramagnetic impurities from wet-process phosphoric acid.

MATERIALS AND METHODS

Acid source – The 54% (P_2O_5) phosphoric acid was obtained over a several-day period from regular production runs in CF Industries, Plant City, Florida. Acid was high solid content (Table 1).

Iron analyses -- Solid samples were digested with *aqua regia* (3HCl:HNO_3) and diluted to 100 mL when dissolved at pH = 1 ± 0.1. Acid samples were treated with nitric acid to convert all iron into iron(III) and pH was adjusted to 1 ± 0.1. A 5-mL of sample solution was mixed with a 2-mL 20 % NH_4SCN solution. The absorbance of the mixture was measured on a Beckman® Model-25 spectrophotometer at 480 - 490 nm. The measurable iron concentration for the thiocyanate method was 3 - 10 ppm (11).

Chromium analyses -- Samples prepared for iron measurement with pH of 1.0 were treated with 0.1 *M* $KMnO_4$ at near boiling until the color persisted. Excess $KMnO_4$ was reduced to Mn^{2+} by a 5 % NaN_3 solution. The sample solution was boiled for complete decomposition of NaN_3. A 5 mL - sample was mixed with 2 mL of 0.2 % diphenylcarbazide acetone solution, and the mixture 's absorbance was measured at 540 nm on a Beckman® Model-25 spectrophotometer. Standard solutions with chromium concentration of 0.2 - 1.0 ppm were prepared.

Statistical Analyses -- The effect of treatments (magnetic field, test versus control samples) was assessed for statistical significance using ANOVA (12) A probability, p, of less than 0.05 was taken as a criterion that the differences between two independent rows of data (typically size distributions) cannot be explained by random error alone. All ANOVA calculations were performed using PSI-PLOT software (13) and an IBM Aptiva computer.

Solid separation by a hydrocyclone -- Phosphoric acid (54 %) suspension was passed through a hydrocyclone (Fig. 1), and two portions, overflow and underflow (14) were collected. The underflow portion was the solids, and the overflow portion was phosphoric supernatant. The solids were washed, centrifuged, dried at 70 °C, and then weighed. The

TABLE 1. Characteristic of 54 % Phosphoric Acid.

Acid density (g/mL)	1.68
Solid content (%)	9.85 ± 0.61
Iron content in acid suspension (%)	1.37 ± 0.06
Chromium content in acid suspension (ppm)	81.9 ● 2.8
Iron in solid (%)	10.64
Iron in supernatant (%)	0.296 - 0.341
Chromium in supernatant (ppm)	71.03 - 74.64

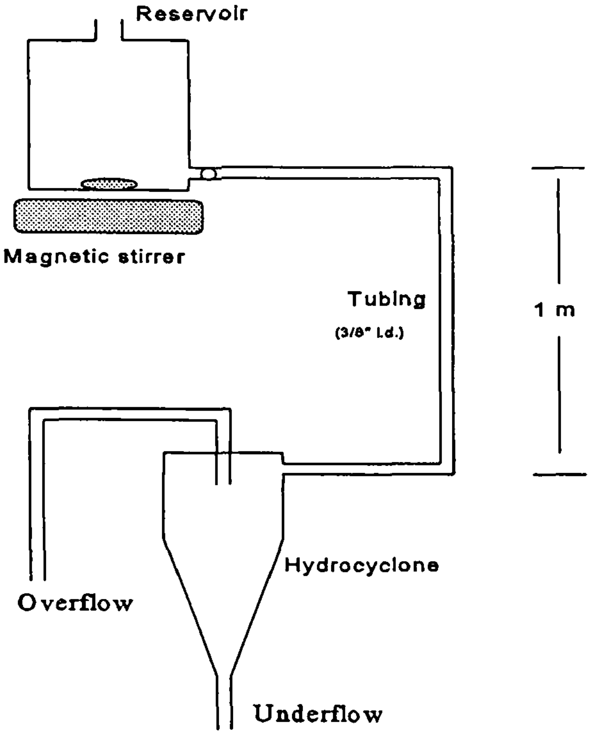

FIG. 1
Schematic representation of hydrocyclone separation of solids from phosphoric acid.

solids were digested with aqua regia and adjusted to pH ~ 1.0 for iron and chromium analysis.

Removal of iron by magnetic separation -- The separation apparatus is schematically described (Fig. 2). A 10-L reservoir and an asymmetric PVC T-pipe were connected by a Tygon® tubing. Eight neodymium magnets (8 x 3000 gauss) were placed ahead of the T-junction of the PVC pipe. The phosphoric acid supernatant was magnetically stirred and passed through the magnetic field. Acid was separated into two portions. The volume ratio of the two portions was adjusted by changing the outlet diameter. It was assumed that paramagnetic materials were attracted by the magnets toward the upper PVC wall and flowed further along the PVC pipe. Diamagnetic materials were repulsed by the magnets and moved toward the lower PVC wall so that they were flowed out just after the T-junction and were separated from paramagnetic material. Acid samples from both portions were treated for the iron and chromium measurement.

RESULTS AND DISCUSSION

Acid characteristics -- Our 54 % phosphoric acid had a 9.85 % solids content (Table 1). Supernatant acid contained low iron (0.3 - 0.35 %) and solid contained 10.64 % iron. Chromium concentration was in the range of 71 -74 ppm in the supernatant, which was slightly lower than that in the suspension. If solid in the acid suspension was completely removed, the iron content was significant reduced from 1.37 % to 0.30 %.

Separation technique. Solid removal by a hydrocyclone method -- A two-step technique was used to remove iron and chromium. In Step 1, solid was separated from acid by a hydrocyclone (1), and most of iron was removed. This treatment reduced iron content in acid to 0.3 % from 1.4 % (Fig 3). The iron existed in both solid form and acid-dissolved form. In the hydrocyclone treatment, larger solid particles were forced to the underflow fraction, and acid fluid was pumped out of overflow outlet (Fig. 1).

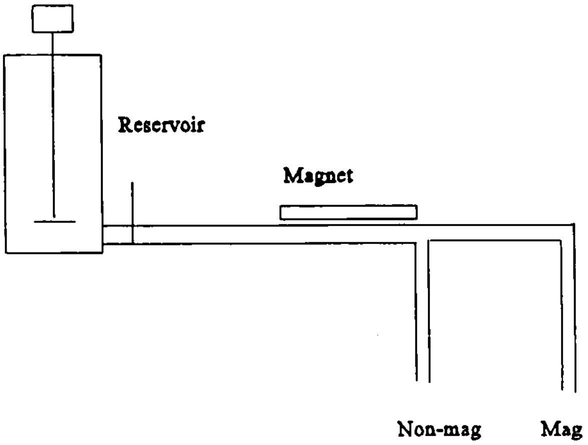

FIG. 2
Schematic representation of an non-symmetric T-tube configuration.

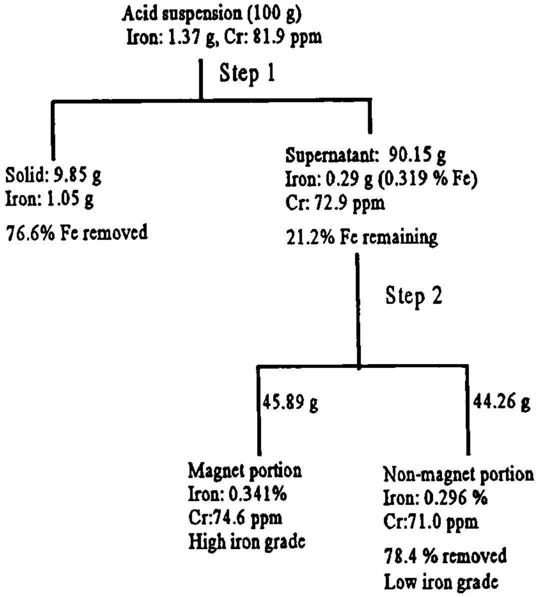

FIG. 3
Summary of two-step separation of iron and chromium from industrial-grade phosphoric acid.

TABLE 2. Magnetic Treatment of 54 % Phosphoric Acid by the Asymmetric T-tube.

	Magnet portion	Non-magnet portion	Difference*
Acid volume (mL)	2700	2800	
Phosphate(P_2O_5)	49.73	50.37	
Iron content (%)	0.341 ± 0.020	0.296 ± 0.005	15.2 %, p** =3.x 10^{-9}
Chromium content (ppm)	74.64 ± 1.80	71.03 ± 2.76	5.1 %, p**=0.00468

* Difference = (Iron, mag. - Iron, non-mag) x 100%/(Iron, non-mag).

** Student's t-test, magnet vs. non-magnet.

Several forms of iron compounds, $FePO_4 \cdot 2H_2O$, $FeH_3(PO_4)_2 \cdot 4H_2O$, and $Fe_3H_9(PO_4)_6 \cdot H_2O$, are suspended in wet-processed phosphoric acid (15) and those compounds go with other solid materials to underflow fraction of a hydrocyclone.

Iron removal by a magnetic separation -- Step 2 was a magnetic separation. Magnetic fields did remove paramagnetic impurities from wet-processed phosphoric acid in this research without affecting the phosphate content. Different methods were tried, with varying fluid transportation conditions and strength of the magnetic field (16) .The percentage of iron removal from acid varied with the treatment method (16). The highest efficiency of iron separation achieved, described here was 15.2 % (Table 2) with a horizontal asymmetric T-tube method. The chromium separation was achieved up to 32.9 % (Table 2).

Figure 3 summarizes iron removal from the 54 % phosphoric acid. In this treatment of acid suspension, a hydrocyclone under magnetic field removed the majority of solid and 76.6 % iron from acid, and the asymmetric T-tube method further removed another 15.2 % of iron from supernatant acid. In the horizontal PVC Y-tube, percentage of iron removal from acid was up to 4.1 % (16). The magnetic field with alternate magnet positions worked much better than random magnet positions, because the former was better at keeping the paramagnetic particles along the magnetic side wall of the tube.

We anticipate that stronger fields would yield better separation. Unfortunately, speed may be a factor. Diamagnetic separations are favored by faster speeds, but paramagnetic separations are favored by slower speeds, and better separations than we have achieved may require recycling , higher fields, and perhaps compromise on flow rates.

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