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# REMOVAL OF UNWANTED METALS AND MATERIALS IN PHOSPHORIC ACID BY MEANS OF MAGNETIC SEPARATION

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# Removal of Unwanted Metals and Materials in Phosphoric Acid by Means of Magnetic Separation

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# PERSPECTIVE

The Florida phosphate industry has always had a problem with unacceptable high levels of metallic impurities in the phosphate rock used in the manufacture of phosphoric acid. This problem is becoming increasingly critical as mining has moved south from Polk County and the average total impurity content of the phosphate rock has increased. The three impurities that are of most concern are iron, aluminum, and magnesium. While high levels of any one of these metals creates specific operating problems, a combined total that exceeds a certain level makes it impossible to make on grade DAP(fertilizer grade diammonium phosphate).

Phosphoric acid producers also have to contend with scale formation in all piping and equipment due to the very nature of the process and the phosphoric acid itself This piping scale is controlled today by having two parallel pipe lines so that one can be washed with water to remove the scale while the other one is used for the acid.

This project was to develop an economical process for removing iron from phosphoric acid by means of magnetic separation. A second possibility that would be investigated was aluminum removal by paramagnetism. The other half of the project effort was directed toward eliminating scale formation in the phosphoric acid piping by magnetic means.

The project demonstrated that it is possible to partition the iron in the acid and lower the iron in a portion of the acid. However it was not possible to formulate a practical economical application for this technology at this time.

The project also demonstrated that it is possible to dissolve the scale using a magnetic field but it will require additional research before a practical application for this technology can be proposed.

A practical iron removal scheme has much to offer to the industry since it would allow the production of on grade DAP without the need for adding supplemental nitrogen. It could also allow the use of lower grade phosphate rock, reducing the quantity of rock that has to be discarded as unusable, and thereby reducing the number of acres that must be mined each year.

Elimination of and/or control of scale formation could equate to better operating rates and this increased efficiency would better position the industry to compete in the world phosphate fertilizer market.

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# EXECUTIVE SUMMARY

This research was directed toward the appropriate use of magnetism to effect a separation of unwanted materials from phosphoric acid. Two types of magnetism are involved: (1) paramagnetic substances have one or more unpaired electrons, and these substances will be attracted into a magnetic field; and (2) diamagnetic substances have no unpaired electrons and these substances will be repelled, weakly, by a magnetic field. The goal of this research was to use diamagnetics to prevent or minimize sodium fluorosilicate scale formation in phosphoric acid and to use paramagnetism to reduce the concentration of iron and/or chromium in phosphoric acid.

Sodium fluorosilicate, a by-product of the production of phosphoric acid, is a nuisance material because of the tendency to build up in pipes and the need to remove the material from pipes. Samples of scale from the industry were analyzed and were tested in the presence and absence of magnetic fields (1200 and 2000 gauss). Enhanced solubility was demonstrated in the presence of a magnetic field. The effect is ascribed to an increase in entropy as a result of the field, which in turn results in an increase in the solubility of the scale. At room temperature, the solubility of fluorosilicate scale was 1.70 g/100 g, and at 50 ° C in the presence of a magnetic field it was increased by about 25-28%. The results were obtained at flow rates of about 100 mL/sec, and it is anticipated that the diamagnetism effect would be enhanced at higher flow rates. The control should be effected by the use of one 2,000- gauss magnet for each inch in diameter of stainless steel pipe.

The second phase was concerned with removing iron and/or chromium from phosphoric acid using paramagnetism. Some magnetic attraction designs were tested using this technique. The best approach was a two-step process applied to 54% industrial-grade phosphoric acid with 1.37 % iron, and 81.9 ppm chromium: a hydrocyclone was used as a first-stage separation of solids, and in the second stage, the supernatant was passed through a magnetic field to effect further separation. A total of 78 % iron was removed in the two-stage process without discernable loss of phosphoric acid (no statistically significant difference between the initial and final acid sample). In addition about 13 % of the chromium was removed, again without discernable loss of phosphorus.

The designs that have been described here could easily be adapted to a phosphoric acid plant to minimize scale formation and have the material precipitate at a later stage that would be more convenient for removal by hydrocyclones. The design for removing iron and chromium probably would need little modification to effect the separation, but design features such as recycling would need to be factored into the process.

# INTRODUCTION

Three observations are pertinent concerning separations (Hirschbein, et al., 1982).

First, methods for separating chemical species are a critical part of chemistry.

Second, magnetic interactions/properties can lead to separations that are impractical or impossible to achieve by other means.

Third, magnetic separations are uncommonly used in chemistry. Hirschbein and coauthors (1982) ascribe the evident neglect of magnetic separations among chemists to lack of familiarity with magnetic separation. It is possible that the absence of suitable equipment can be a significant factor as well.

## Basis

Molecules and materials can be divided into two electronic categories: those with unpaired electrons and those with spin-paired electrons. Those in the first category are attracted to regions of a magnetic field (magnetic susceptibility is positive), and the substance or material experiences an apparent change in weight per gram of substance. Members of the second group are repelled from a magnetic field (susceptibility is negative), and the substance or material experiences a negative change in apparent mass in high -field magnetic regions.

Typically materials are in one of four magnetic categories (Table 1, Table 2). The main categories for our purposes are **paramagnetism** (substance is drawn into a magnetic field, or appears to be heavier in a magnetic field than it really is), typical of iron, and **diamagnetism** (substance is repelled by a magnetic field and appears to be lighter than it actually is), typical of aluminum, magnesium, calcium ions and their compounds.

# Table 1

## Magnetic Properties Of Selected Materials (cf. Selwood, 1956; Cullity, 1972)

| Category | Explanation | Apparent mass g/g |
|---|---|---|
| Ferromagnetics Fe, Ni, Co | Parallel alignment magnetic fields of individual atoms | Fe, 400 |
| Ferrimagnetics $CrO_3$. $Fe_3O_4$ | many but not all of Subunits interact; cancellation of interaction effects | $Fe_3O_4$, 122 |
| Paramagnetic $O_2$ (l), $CuCl_2$ | material behaves as collection of independent spins | $O_2$ 7.65<br>$CuCl_2$ 0.29<br>$NiSO_4$ 0.85 |
| Diamagnetic Cu | paired electron spins weakly repelled | Cu - 0.002<br>NaCl - 0.015<br>$H_2O$ - 0.022 |

# Table 2

## Classes Of Magnetic Behavior

| Class of magnetism | Sign of $\chi$ | Magnitude, cgs | Field dependence* |
|---|---|---|---|
| Diamagnetic | negative | $1 \times 10^{-6}$ | Independent |
| Paramagnetic | positive | $1\text{-}100 \times 10^{-6}$ | Independent |
| Ferromagnetic | positive | $10^{-2}$ to $10^{2}$ | Dependent |
| Anti-ferromagnetic | positive | $1\text{-}100 \times 10^{-6}$ | Often dependent |

***relative to field, H**

## Utility

Chemists have long used magnetism and magnetic fields for diagnostic purposes: magnetic susceptibility, using one modification of the Gouy method, has long been used as a means of characterizing coordination entities, bond type (with perhaps questionable results), and geometry (better results) (cf. Martin and Martin, 1964; Wang and Martin, 1992). Nuclear magnetic resonance (NMR) has notably useful diagnostic strengths and has revolutionized organic structure analysis, and USF's Department of Chemistry has a state-of-the-art instrument. Electron spin resonance has been useful to an understanding of a range of chemical problems.

Chemical technology has used certain aspects of magnetism for separation, but most examples have been limited to the involvement of paramagnetic samples. Professor Gregory Bitton, at the University of Florida, effected separation of iron-containing bacteria and other species by filtering water samples through steel wool surrounded by a suitable magnetic field. 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 (Kolm, et al., 1975; Hirschbein, et al., 1982).

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 $\mu$m), 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 (Roy, et al., 1979).

Stack gases, especially from the steel industry [basic oxygen furnaces and sintering plants (Price and Abercrombie, 1979)], 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. (In this connection, it is unfortunate that mercury vapor is diamagnetic.)

Water purification has been achieved by adding a flocculating agent to precipitate dissolved or suspended paramagnetic species, and removing paramagnetic particulate material.

Other examples of the use of HGMS techniques to paramagnetism can be cited:

removal of catalyst-derived impurities (catalysts contain paramagnetic materials, some, e.g. Rainey Ni or Fisher-Tropsch are ferro- or ferri-magnetic);
design of catalyst supports to facilitate separations of magnetically responsive catalysts;

separation of infected red blood cells; erythrocytes infected by malarial parasites contain oxidized products and are more paramagnetic than cells with iron in the lower oxidation state.

While there are interesting and useful examples, the fact remains that the majority of chemical substances are diamagnetic, and comparatively few persons seem to have considered the possibility of separations involving diamagnetic species.

## Background

The reasons for the paucity of examples involving diamagnetism are open to speculation, but may be suggested from information provided in a review by Carpenter (1991), and include:

1. Historical caution: The United States Federal Trade Commission once alleged claims of fraudulence on the part of individuals who were emphasizing diamagnetism; the case was not proven.

2. Poor literature coverage: many fail to cover the patent literature, and some significant patents were awarded for use of HGMS and diamagnetism; and

3. Intellectual inertia.

Nevertheless, three significant facts should be considered:

Magnetic interactions can achieve separations that are either impractical or impossible to achieve by other techniques; magnetic separations are infrequently used in chemistry; simple methods for generating very high magnetic field gradients have been developed; efficient magnetic structures (and also superconducting magnets) have become commercially available. These structures are relatively inexpensive; technical improvements have taken place in matrix design; imaginative creative activities utilizing HGMS and diamagnetism have occurred (Carpenter, 1991).

The latter point deserves much more emphasis than is possible here, but all separation schemes depend upon partitioning species between two different regions of space. For distillation, the species separated are molecules and Region A, say, is a liquid and Region B is a gas.

For HGMS schemes, Region A is a high magnetic field and region B is a low magnetic field, but the object being separated, a diamagnetic, is a particulate or a highly associated species, rather than a molecule.

On that basis, water softening, i.e., nonchemical removal of scale, becomes an attractive HGMS separation process, as Carpenter (1991) has described.

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 (Frazier and Kim, 1989). 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 (Lowe, 1980) and solvent extraction (Nair et al., 1980), (b) electrochemical methods (Ramp, 1976) and (c) chemical methods (Hem, 1968). A magnetic method is developed in this research for iron separation from WPA thanks to paramagnetic property of iron. In this report, we summarize the iron removal from WPA under magnetic field by different fluid-transportation methods.

Magnetic separation can be used for two useful purposes: (1 ) to limit scale formation in phosphoric acid plants and (2) to limit undesired metals in phosphoric acid.

The first purpose would be achieved through use of diamagnetism to remove scale and/or prevent scale formation in pipes using principles described by Benson and co-workers (1994). The effect of a magnetic field is to increase the entropy of a system and in practical terms this means that suspended particles should become more soluble in the presence of a magnetic field. The effect should persist for a period of time (the so-called “memory” effect) until equilibrium is restored. It would mean that scale, e.g., fluorosilicate scale, would be more soluble in pipes treated with a magnetic field and then would precipitate at a later, more convenient location.

The second purpose would be achieved primarily through paramagnetism and the tendency of iron compounds to be attracted to a magnetic field. The possibility that separation by a combination of paramagnetism and diamagnetism using a fluid cyclonic unit remains to be considered and applied. Another implication is that fluorosilicate scale with iron impurities might be treated to improve the purity of the scale and convert it to a product of commerce.

## MAGNETIC TREATMENT OF SCALE

### Scale source

Chunks of scale (weighing about 13.3 pounds) from a phosphoric acid plant were provided by Mr. J. Harold Falls, Chief Chemist, CF Industries, Plant City. The samples consisted of layers of white and gray materials.

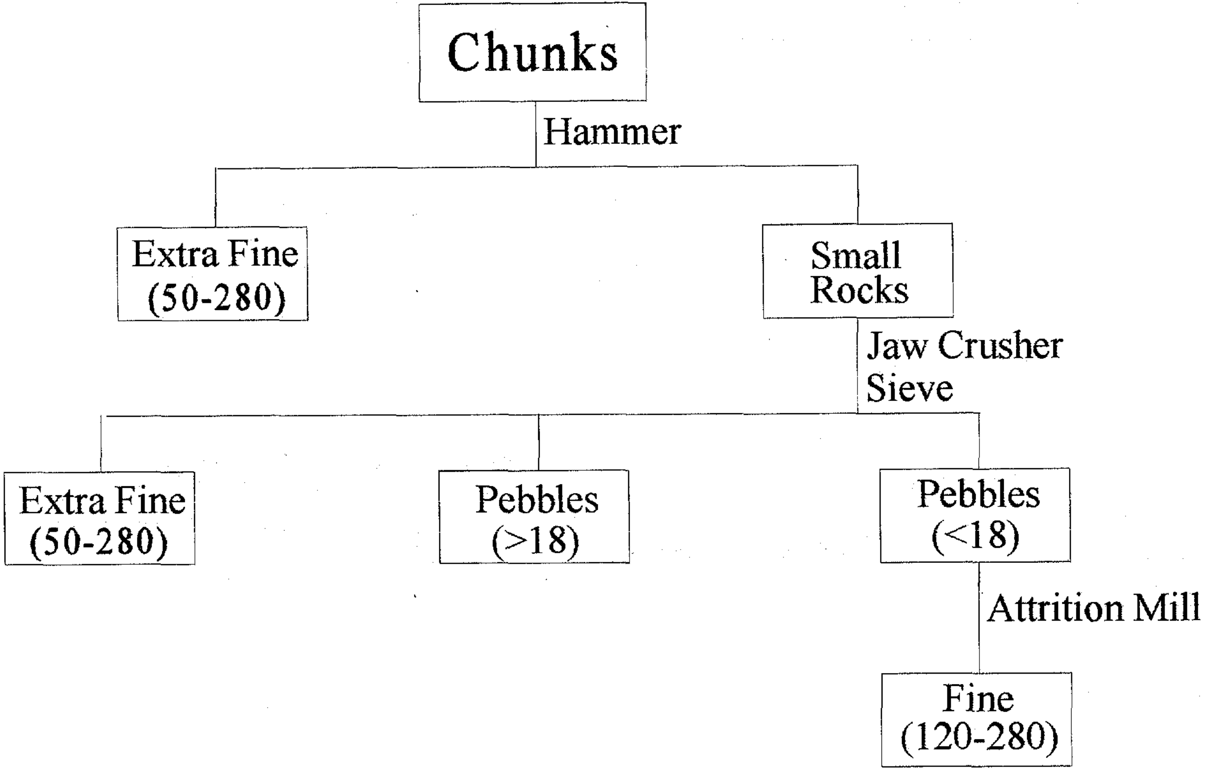
The scale lumps were washed in water, then washed as clean as possible in distilled water, dried on paper towels, and allowed to air dry. Samples were crushed into three sizes: small rocks were produced by hitting the samples (in clean plastic) with a hammer. The small rocks were subjected to a Braun jaw crusher (Chipmunk model) to produce pebbles. The latter were placed in an attrition mill ("coffee grinder") to produce fine material that passed through a size 50 mesh. The ultrafine was (mainly) the result of the simple hammer treatment. The waste was the material that was used to clean out the attrition mill and was set aside for future use.

The process is summarized in Fig. 1, and the weight distribution is summarized in Table 3.

**Table 3**

**Summary Of Distribution Of Material**

| Sample Designation | Stage | Mesh | Weight, g |
|---|---|---|---|
| Small pebbles | Pre-chipmunk | <18 | 3,571 |
| Pulverized scale | Post-attrition | 50-280 | 2,184 |
| Extra fine scale | Pre-chipmunk | 120- >280 | 156 |
| Waste material | | | 165 |
| Total sample | | | 6,078 |



PHOSPHORIC ACID SCALE SIZE REDUCTION

**FIGURE 1**

## Characterization of scale

The majority of white scale was separated and purified by removing the gray layer and polishing white layer surface. White scales were used for the investigation of magnetic treatment on scale suspension either in the solubility and the iron removal. Sample solutions for total iron measurement were prepared by treating the ground scale in 3 HCl : 1 $HNO_3$ solution and dissolved in water. White layer contained less total iron content than gray layer did. The white layer contained about 30-46.9 ppm total iron and the gray layer had total iron up to 1611 ppm. The scale from filter cloth contained 16.17 % total iron. Iron content distribution showed that smaller particle scale contained higher iron than larger one did because of small powdery gray material mixed with smaller particle scale.

***X-ray fluorescence*** -- Material was mounted, as a representative crystal, and subjected to EDAX (energy dispersive x-ray) fluorescence in the Electron Microscopy Laboratory (College of Engineering) by Alicia Slater-Haase. Using 20 kV, 40.0 degrees, and VFS = 4096, the elements detected were (atom %, weight %) sodium (40.7,35.6), silicon (54.7, 58.5), phosphorus (3.0, 3.5), calcium (0.45, 0.69), sulfur (0.23, 0.28), and potassium (0.91, 1.4).

***Fluoride analysis*** -- About 0.5 g of powdered scale was dissolved in 200 mL of deionized water, using a Cole-Parmer (model 8845-3) ultrasonic cleaning bath. Subsequent dilutions were made so that the activity of a fluoride ion was in an optimum range (10-100 ppm) for measurement by the ion-selective method (Clesceri et al., 1989). Two standard fluoride ion solutions (10 and 100 ppm, prepared from Fisher 1000 ppm fluoride standard) were used for calibration. Measurements were made using a fluoride ion-selective electrode (Fisher 13-620-522) and an Orion silver-silver chloride double junction reference electrode (model 90-02) attached to an Orion expandable ion analyzer (model EA 920). Exactly 25.0 mL of sample and 25.0 mL of buffer were used, and the fluoride activity was recorded. Sample weights (and % fluoride) were 0.5 150 g (61.8,63.6); 0.5015g (63.1% and 60.8%). Mean fluoride content was 62.3 ± 1.3%. Calculated for $Na_2SiF_6$: F, 60.6%, Na, 24.5%; Si, 14.9%. Found: F, 62.3±1.3% (USF); Na, 22.02; Si, 13.46% (SGS Commercial Testing & Engineering Co.).

***Calorimetric iron measurement*** --The solubility of scale in water was low ( < 1 g/100 g $H_2O$) and the iron content was very low in the white part of the scale. Sample measurement of total iron content with or without magnetic treatment was a challenge. It was found that the scale sample amount affects iron measurement. Less sample amount lead higher iron content result due to the lower portion of linear calibration curve. Those samples can not be measured by atomic absorption spectrometry because of the high concentration of scale (saturated solutions), and the relative standard deviation was very high at 1 ppm iron level. The thiocyanate calorimetric method was used to measure iron. The solid weight of scale sample was 2 grams. The sample was digested with aqua regia ($3HCl:HNO_3$) and diluted to 100 mL for totally dissolved, at pH =1± 0.1. The solution either was measured directly or was measured after concentration when the iron content was too low to be measured accurately. The measurable iron concentration for the thiocyanate method was 3-5 p.m. (Marczenko, 1986). For those solutions in which the iron concentration less than 1 ppm, the concentration process was needed.

***Chromium measurement*** -- Sample prepared for iron measurement with pH of 1.0 was treated with 0.1 M $KMnO_4$ at near boiling point until the $KMnO_4$ pink color persisted. The excess KMnO4 was reduced to $Mn^{2+}$ by 5% $NaN_3$ solution and the sample solution was boiled for complete decomposition of $NaN_3$. A 5 mL of sample solution was mixed with 2 mL of 0.2% diphenylcarbazide acetone solution and the mixture was measured at 540 nm on a Beakman® Model-25 spectrophotometer. Standard solutions with chromium concentration of 0.2 -1.0 ppm were prepared in the similar way.

***Magnetic susceptibility*** -- Magnetic susceptibility is a quantitative method to describe the magnetic property of a given solid material. If there are any unpaired electrons in elements, this material had positive magnatic susceptibility and was paramagnetic. Those that did not have unpaired electrons had negative magnetic susceptibility and were diamagnetic. The magnetic susceptibility was measured on the magnetic susceptibility balance (Johnson & Matthey Inc., 1401 King Road, West Chester, PA 19380). For the phosphoric acid scale, a mixture of inorganic salts, mainly a sodium hexafluorosilicate, the gram susceptibility ( &) was more useful to describe the magnetic properties of scale. Molar susceptibility, $\chi_m$, was obtained when the molecular weight (MW) was known

$$\chi_m = (\chi_g) \cdot (MW)$$

and the effective magnetic moment was calculated, $\chi_m = (\chi_g) \cdot (MW)$, $\mu_{eff} = 2.83 (\chi_m \cdot T)^2$. The effective magnetic moment was used to estimate the number of unpaired electrons in some elements of samples, $\mu_{eff} = 2.0 [S (S + 1)]^2$. For phosphoric acid scale, Fe(II) (four unpaired electrons) and Fe(III) (5 unpaired electrons) could be identified. Results showed that magnetic susceptibility of scale was related to total iron content. Scale with high iron content had a positive $\chi_g$ value and paramagnetic, such as filter cloth scale and gray layers (Table 4, Dec.95). Scale samples with low iron content had negative $\chi_g$ value and were diamagnetic. White layer scale samples were diamagnetic.

## Table 4
## Properties Of Scale From Different Sources

| Source | Iron content | Magnetic susceptibility ( $\chi_g$ ) |
|---|---|---|
| Filter cloth (Dec., 95) | 16.17 % | $3.48 \times 10^{-5}$, paramagnetic |
| Grey layer (Dec., 95) | 1610 ppm | $4.90 \times 10^{-8}$, paramagnetic |
| White layer (Dec., 95) | 30 ppm | $-2.03 \times 10^{-7}$, diamagnetic |
| Grey layer (May, 95) | 228 ppm | $-3.05 \times 10^{-7}$, diamagnetic |
| White layer (May, 95) | 46.9 ppm | $-3.06 \times 10^{-7}$, diamagnetic |

### Magnets

We borrowed permanent magnets from AquaMagnetics® International, Inc. One set was able to generate a field of 1200 gauss, and another type was able to generate 2000 gauss, [For the sake of comparison, the Earth's magnetic field is 0.5 gauss, and a typical refrigerator magnet has a field of about 100 gauss.]

### Statistical Analyses

The effect of treatments (magnetic field, test versus control samples) was assessed for statistical significance using ANOVA (analysis of variance, Havlicek and Crain, 1988). Two-way analysis of the variance proves the null hypothesis for row effects, which presumes that the means of two or more independent samples are not statistically significantly different. ANOVA calculates F values, which should be equal to unity if the hypothesis is true. The F values become larger than unity, however, when the two sets of data differ significantly. [Then, differences cannot be explained by random error alone, and either the differences are significant or systematic error has occurred.] The probability that the F values greater than unity were obtained by chance was also calculated. 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 (Poly Software, 1992) and an IBM Aptiva computer.

## Preparation of standard scale samples

The data in Table 5 summarize the size distribution that was obtained when the available material was treated. From that study, a standard sample was prepared that was composed of the following sizes and weights (in parentheses): <18 mesh (5 g), 18-3.5 mesh (40 g), 35-60 mesh (20 g), 62-230 mesh (20 g), >230 (15 g). The standard sample (100 g dry weight) was used in each study.

### Table 5

### Poly-Dispersion Of Phosphoric Acid Scale Particles

| Sample # | Size distribution of particle (%) | | | | |
|---|---|---|---|---|---|
| | ≤18 Mesh | 18-35 Mesh | 35-60 Mesh | 60-230 Mesh | ≥230 Mesh |
| 1 | 4.3 | 41.7 | 21.0 | 18.6 | 14.8 |
| 2 | 3.5 | 42.4 | 23.7 | 17.1 | 13.4 |
| 3 | 3.3 | 41.9 | 24.7 | 15.2 | 14.5 |
| Mean | 3.7 | 42.0 | 23.1 | 17.0 | 14.2 |
| Std. deviation | 0.53 | 0.37 | 1.9 | 1.7 | 0.74 |

## Wet sieving process

Aqueous suspensions of scale were sieved completely by sieves with mesh sizes of 18, 35,60, and 230. The largest particles were first separated using the 18 mesh sieve, and collecting the suspension that passed through in a clean plastic bucket. The process was repeated using successively smaller sizes. The remainder of the suspension containing the finest particles was allowed to stand for five hours, when the suspension was collected by careful decanting, All five fractions were dried to constant weight in an oven at 75° C. Pertinent calculations (total suspended solids, fraction weight and weight percent of each fraction) were made using these data.

Sieving phosphoric acid suspension of scale required a modification of the procedure. First, scale suspensions were allowed to stand for ten hours because of the viscosity and density of the phosphoric acid solution. Next, the 1500 mL of phosphoric acid solution was decanted, and the scale was re-suspended in one liter of water before the fractionation was started. After fractionation, the five fractions were rinsed with water (500 mL) to remove any phosphoric acid residue. Samples were then dried as before.

## Effect of magnetic field on scale solubility and particle size distribution

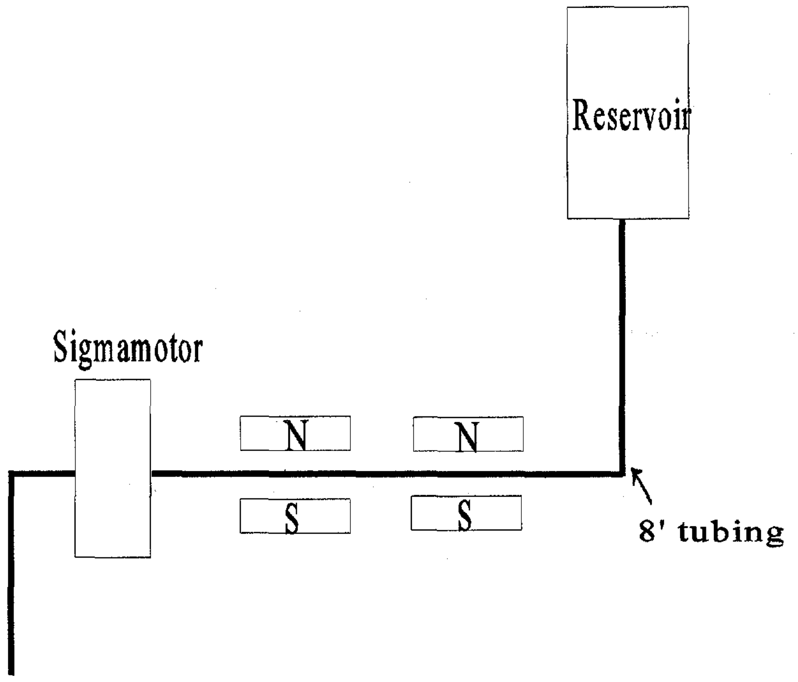
***Magnetic field applied*** -- The magnetic field (for test systems) consisted of two sets of magnets from Aqua Magnetics® International, Inc., Petromag Model and Fuel-Activator, each rated at 1200 gauss. Each set consists of two magnets. Both sets (total of 4 individual magnets) were evaluated to determine the maximum weight that each magnet can lift and the maximum distance that each magnet would attract a metal. The results obtained are summarized in Table 6.

### Table 6

### Properties Of Magnets Used In Study Of Effect Of Diamagnetism

| | Fuel Activator Set | | Petromag Model Set | | MCF |
|---|---|---|---|---|---|
| Maximum weight, g | 444 | 727 | 279 | 248 | 16,229 |
| Maximum distance, mm | 3.1 | 2.2 | 2.5 | 2.5 | 14.5 |
| Nominal field, gauss | 1200 | | 1200 | | 2000 |

***Magnetic treatment of scale aqueous suspension*** -- The phosphoric acid scale was partially soluble in water, and the pH of suspension solution was about 3.5. A suspension of 100 g of standard scale suspended in 1.5 L of de-ionized water was moved through Tygon® tubing (2" o.d. x 3/8" i.d. x 1/16" wall and varying length) using a Sigma motor (Middle point, NY) zero-max finger pump (model T-6S) without the liquid coming in contact with metal (see schematic representation, Fig.2). The results of pumping the fluid without (control) and with a magnetic field (test) were compared. A flow rate of 500 mL/min was used and 3 minutes was needed for the fluid to pass the magnetic field at the optimum rate. [Maximum flow rate was 1250 mL/min at 1 meter water pressure]. Test and control samples of scale were completely separated through 18, 35, 60 and 230- mesh sieves. Samples of sieve suspensions were collected, dried to constant weight at 75°C, a temperature low enough to evaporate the water and keep the scale from being decomposed.



SCHEMATIC OF MAGNETIC TREATMENT IN PARALLEL

**FIGURE 2**

## Table 7

### Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied In Parallel, For One Cycle*

| TRIALS | FIRST TRIAL | | SECOND TRIAL | |
|---|---|---|---|---|
| | Control | Treated | Control | Treated |
| Total (g) | 100 | 100 | 100 | 100 |
| Solid (g) (after suspension) | 84.5 | 85.2 | 86.8 | 86.8 |
| Dissolved solids ($g/100\ g\ H_2O$) | 1.03 | 0.99 | 0.88 | 0.88 |
| pH | 3.34 | 3.23 | -- | -- |
| SIZE DISTRIBUTION | % | % | % | % |
| <18 | 4.7 | 5.3 | 4.9 | 5.1 |
| 18-35 | 45.7 | 47.0 | 42.8 | 42.7 |
| 35-60 | 19.1 | 22.6 | 20.8 | 20.2 |
| 60-230 | 21.8 | 17.1 | 21.0 | 21.0 |
| >230 | 8.7 | 8.0 | 10.6 | 11.0 |
| | ANOVA: F Value = 114.54;<br>Prob.>F = $4.4 \times 10^{-4}$ | | ANOVA: F Value = 5834.17;<br>Prob.>F = $1.762 \times 10^{-7}$ | |

* In the test system, the fluid was passed through the magnetic field (2 X 1200 gauss) in 3 minutes and the magnetic field was between the pump and the reservoir. Tygon tubing: 1/2" o.d. x 3/8" i.d. x 1/16" wall x 8' length.

In the treatment with magnetic field strength of 2 x 1200 gauss, the condition of one cycle and 8 foot tube does not change much scale solubility at the flow rate of 5.4 mL/min (Table 7). It might be due to the short time the suspension spent in the magnetic field. There are several ways to increase the retaining time in the magnetic field. Increasing the tube length and increasing treatment times might be helpful.

***Effect of tubing length*** -- Samples were tested using 21 feet of 5/16" id. Tygon tubing and varying the flow rates. The magnets (2 x 1200 gauss) were either at parallel or at 90° angles to each other as represented by Fig.2 and Fig.3. The suspension was recycled ten times for each.

## TABLE 8

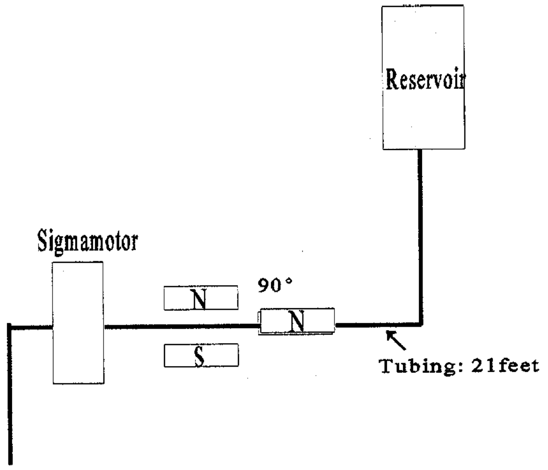
### Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied In Parallel After Ten Cycles*

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g) (after suspension) | 87.4 | 81.0 |
| Dispersed solids (g/100 g $H_2O$) | 0.84 | 1.27 |
| pH | 3.19 | 3.14 |

| SIZE DISTRIBUTION | % | % |
|---|---|---|
| <18 | 3.8 | 3.0 |
| 18-35 | 29.4 | 28.5 |
| 35-60 | 19.6 | 16.4 |
| 60-230 | 24.0 | 26.0 |
| >230 | 23.3 | 26.0 |

ANOVA: F Value = 70.744; Prob.>F =0.00115

* In the test system, the fluid was passed the magnetic field (2 X 1200 gauss) located between the pump and the reservoir in 30 minutes, recycling ten times. Tygon tubing:
1/2" o.d. x 3/8" i.d. x 1/16" wall x 8' length.



SCHEMATIC REPRESENTATION OF MAGNETIC TREATMENT AT 90° ANGLE

**FIGURE 3**

## Table 9

**Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied At A 90 ° Angle And With A Flow Rate Of 5.4 mL/sec***

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 87.2 | 84.8 |
| Dispersed solids<br>(g/100 g $H_2O$) | 0.85 | 1.01 |

SIZE DISTRIBUTION

| | % | % |
|---|---|---|
| <18 | 4.47 | 3.85 |
| 18-35 | 27.75 | 30.76 |
| 35-60 | 19.84 | 20.84 |
| 60-230 | 25.80 | 26.57 |
| >230 | 22.13 | 18.01 |

ANOVA: F Value = 53.538; Prob.>F = 0.00199

* The test sample was passed through a magnetic field (2 X 1200 gauss) applied with the magnets at 90° angle (Fig. 3). Tubing size: 21 feet, 5/16"i.d.

In these conditions with longer tube and ten-cycle treatment, the magnetic field increases the scale solubility in aqueous solutions. The size distribution shifts toward the small size and small particles are easily dissolved. It shows that when the diamagnetic material is exposed in the magnetic field for enough time, the magnetic effect is easily observed. The position of magnets is not significant (Table 8 and Table 9).

## Table 10

## Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied At A 90 ° Angle And A Flow Rate Of 20.6 mL /sec*

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g) (after suspension) | 89.34 | 85.20 |
| SIZE DISTRIBUTION | | |
| | % | % |
| <18 | 6.04 | 4.40 |
| 18-35 | 43.37 | 45.53 |
| 35-60 | 21.99 | 22.06 |
| 60-230 | 19.75 | 19.77 |

| | | |
|---|---|---|
| >230 | 8.84 | 8.39 |

ANOVA: F Value = 502.8; Prob.>F = $2.36 \times 10^{-5}$

* Test sample was passed through a magnetic field (2 X 1200 gauss) with the magnets at 90° angles to each other(Fig.3). Tubing: 21 feet, 5/16 i.d.

## Table 11

## Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied At A 90° Angle And A Flow Rate Of 20.6 mL/sec. After 10 Cycles *

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 90.1 | 86.2 |
| SIZE DISTRIBUTION | | |
| | % | % |
| <18 | 4.44 | 3.83 |
| 18-35 | 39.18 | 40.72 |
| 35-60 | 22.20 | 22.51 |
| 60-230 | 21.09 | 21.35 |
| >230 | 13.10 | 11.60 |

ANOVA: F Value = 560.39; Prob.>F = $1.9 \times 10^{-5}$

* Test sample was passed through a magnetic field (2 X 1200 gauss) with the pairs of magnets placed 90° to each other (Fig 3). Tubing: 21 feet, 5/16 i.d.

When the flow rate of suspension is increased up to 20.6 mL/sec, it is found that the magnetic field does same effect as it does at low flow rate. Both one cycle and ten cycles make the significant increase in scale solubility (Table 10 and Table 11). Small particles are dissolved when large particles are broken under the magnetic field.

***Magnetic treatment of scale in phosphoric acid*** -- 28.5% acid is made from 85% ACS certified phosphoric acid. 100 g scale is suspended in 1.5 L 28.5% acid. The treatment is similar to those in the aqueous suspension. After the treatment, the solid scale are collected and sieved using the wet sieving technique. The treatments are performed at 23 °C, 50 °C and 90 °C.

## Table 12

**Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied In Parallel And At A Flow Rate Of 20.6 mL/sec In 28.5% (as $P_2O_5$) Phosphoric Acid, After 10 Cycles ***

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 77.7 | 76.85 |
| SIZE DISTRIBUTION | | |
| | % | % |
| <18 | 6.31 | 4.36 |
| 18-35 | 45.82 | 43.72 |
| 35-60 | 25.87 | 27.52 |
| 60-230 | 19.43 | 19.73 |
| >230 | 2.57 | 4.68 |

ANOVA: F Value = 295.08; Prob.>F = $6.82 \times 10^{-5}$

* Test sample was passed through a magnetic field (2 X 1200 gauss) with the pairs of magnets parallel to each other (Fig 2). Tubing: 21 feet, 5/16 i.d.

## Table 13

**Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied At A 90° Angle And At A Flow Rate Of 20.6 mL/sec In 28.5% (As $P_2O_5$) Phosphoric Acid After 10 Cycles***

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 77.7 | 76.6 |

| SIZE DISTRIBUTION | % | % |
|---|---|---|
| <18 | 6.31 | 4.20 |
| 18-35 | 45.62 | 43.18 |
| 35-60 | 25.87 | 29.27 |
| 60-230 | 19.43 | 20.47 |
| >230 | 2.57 | 2.89 |

ANOVA: F Value = 201.95 Prob.>F = 0.00014

* Test sample was passed through a magnetic field (2 X 1200 gauss) with the pairs of magnets 90° to each other (Fig 3. ) Tubing: 21 feet, 5/16 i.d.

## Table 14

### Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied At A 90° Angle And A Flow Rate Of 20.6 mL/sec In 28.5% (As $P_2O_5$) Phosphoric Acid After One Cycle*

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g) (after suspension) | 82.4 | 80.8 |

| SIZE DISTRIBUTION | % | % |
|---|---|---|
| <18 | 6.07 | 4.95 |
| 18-35 | 44.54 | 42.45 |
| 35-60 | 23.12 | 24.26 |
| 60-230 | 18.99 | 20.54 |
| >230 | 7.28 | 7.80 |

ANOVA: F Value = 388.07; Prob.>F = 3.95 x 10-5

*Test sample was passed through a magnetic field (2 X 1200 gauss) with the pairs of magnets placed 90 degrees to each other (Fig 3). Tubing: 21 feet, 5/16 i.d.

In the magnetic treatment at 20.6 mL/sec and ten cycles, more scale are dissolved in both control and test than those in one cycle (22.38 vs 17.6 g in control and 23.4 g vs 19.2 g in test). More scale dissolved in test (23.4 g) than in control (22.3 g). This treatment works for the descaling process in phosphate industry (Table 12 and Table 13). While in one cycle treatment, consistent results are obtained although little solid is dissolved in both control and test runs (Table 14).

There is a general trend that after the magnetic treatment, the scale particles shifts toward the smaller size more significantly in phosphoric acid than that in aqueous solution.

The significance between 90° and parallel placement of the magnets (20.6 mL/sec flow rate, 28.5% $P_2O_5$, ten cycles) was determined using ANOVA. The analysis of a two-way row variance resulted in an F value of 634.06 and a probability > F of $1.48 \times 10^{-5}$. Position of the magnets is therefore significant.

## Table 15

## A Comparison Of The Effect Of Treatment On Scale Suspension Caused By A Magnetic Force Of 2 x 1200 Gauss (Data From Table 14) And 2 x 2000 Gauss, Both Applied At A 90° Angle And A Flow Rate Of 20.6 mL/sec In 28.5% (As $P_2O_5$) Phosphoric acid After One Cycle*

| | Control | Test | Test 1[q] | Test 2[q] |
|---|---|---|---|---|
| Total (g) | 100 | 100 | 100 | 100 |
| Solid (g) (after suspension) | 82.4 | 80.8 | 75.9 | 75.6 |
| SIZE DISTRIBUTION | % | % | % | % |
| <18 | 6.07 | 4.95 | 4.74 | 5.03 |
| 18-35 | 44.54 | 42.45 | 49.54 | 49.07 |
| 35-60 | 23.12 | 24.26 | 24.77 | 23.29 |
| 60-230 | 18.99 | 20.54 | 16.73 | 20.11 |
| >230 | 7.28 | 7.80 | 4.22 | 2.51 |

ANOVA: For Control vs. Test, F Value = 388.07; Prob.>F = $3.95 \times 10^{-5}$
Control vs. Test 1[q], F Value = 106.21; Prob.>F = $5.20 \times 10^{-4}$
Test vs. Test 1[q], F Value = 57.68; Prob.>F = $1.7 \times 10^{-3}$

Control vs. Test 2[q], F Value = 102.19; Prob.>F = $5.6 \times 10^{-4}$
Test vs. Test 2[q], F Value = 61.59; Prob.>F = $1.5 \times 10^{-3}$
Test 1[q] vs. Test 2[q], F Value = 327.77; Prob.>F = $5.54 \times 10^{-5}$

* (Data repeated from Table 14) Test sample was passed through a magnetic field (2 X 1200 gauss) with the pairs of magnets placed 90° to each other (Fig 3). Tubing: 21 feet, 5/16 i.d.

[q] Test 1[q] and Test 2[q] were two trials in which the sample was passed through a stronger magnetic field (2 x 2000 gauss, model MC-F magnets from Aqua Magnetics International) with the pairs of magnets placed 90 degrees to each other (Fig 3). Tubing: 21 feet, 5/16 i.d.

Increasing the magnetic field strength to 2000 gauss improves the efficiency of the magnetic treatment as showed in Table 15. At 20.6 mL/sec flow rate, and one-cycle treatment, more solid is dissolved under the magnetic field, especially the small particle. The breaking of larger scale is slower than the dissolving of smaller particle in this condition. The stronger magnet field(2 x 2000 gauss) increases the scale solubility in phosphoric acid significantly ( 1.61 g/100 mL vs 1.28 /100 mL,Table 21), compared with that under weaker field(2 x 1200 gauss).

***Magnetic treatment at high pressure*** -- Test sample was passed through a magnetic field (2 X 1200 gauss) with the pairs of magnets placed parallel to each other and with tubing 50 feet long, 3/8 i.d.The reservoir was placed 13.7 m above the tubing outlet giving a pressure difference of 1.72 atm. The flow rate was 101.5 mL/sec during the first 10 sec, while the average rate was 94 mL/sec. Results are shown in Table 16.

## Table 16

**Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied In Parallel, A High Flow Rate And A Pressure Of 1.72 Atm In 28.5% (As $P_2O_5$) Phosphoric Acid After One Cycle***

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 74.2 | 72.2 |
| SIZE DISTRIBUTION | | |
| | % | % |
| <18 | 6.04 | 5.47 |
| 18-35 | 49.23 | 50.47 |
| 35-60 | 23.43 | 24.76 |
| 60-230 | 17.84 | 15.87 |
| >230 | 3.46 | 3.42 |

ANOVA: F Value = 742.54; Prob.>F = $1.08 \times 10^{-5}$

***Treatment with two separated magnetic fields*** --Test sample was passed through two magnetic fields (1200 gauss each) one of which was on the inlet of the tubing and another one was placed on the lower outlet of the tubing. Tubing was 50 feet long, 3/8 i.d. The reservoir was placed 13.7 m above the tubing outlet giving a pressure difference of 1.72 atm. The flow rate was 101.5 mL/sec during the first 10 sec, while the average rate was 94 mL/sec (Table 17).

## Table 17

### Effect Of Treatment Of Scale Suspension With Two Magnetic Fields Applied Separately, A High Flow Rate And A Pressure Of 1.72 Atm In 28.5% (As $P_2O_5$) Phosphoric Acid After One Cycle*

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 78.9 | 76.0 |
| SIZE DISTRIBUTION | % | % |
| <18 | 4.97 | 5.63 |
| 18-35 | 48.51 | 48.43 |
| 35-60 | 22.35 | 22.20 |
| 60-230 | 20.05 | 20.39 |
| >230 | 4.12 | 3.34 |

ANOVA: F Value =4363.78; Prob.>F $= 3.1489 \times 10^{-7}$

## Table 18

### Effect Of Treatment Of Scale Suspension With Two Magnetic Fields Applied Separately In 28.5% (As $P_2O_5$) Phosphoric Acid After One Cycle*

| | Control | Test |
|---|---|---|
| Total (g) | 100 | 100 |
| Solid (g)<br>(after suspension) | 76.79 | 75.79 |
| SIZE DISTRIBUTION | % | % |
| <18 | 5.17 | 4.84 |
| 18-35 | 48.73 | 49.03 |
| 35-60 | 23.64 | 23.49 |
| 60-230 | 18.52 | 18.43 |
| >230 | 3.96 | 4.19 |

ANOVA: F Value =18825; Prob.>F $=1.69284 \times 10^{-8}$

Scale suspension sample was passed through two magnetic fields (1200 gauss each) one of which was on the inlet of the tubing and another one was placed in the middle of the tubing, which was 8.4 meters below the reservoir. Tubing was 79 feet long, 3/8 i.d., 0.71 $cm^2$ area. The pressure difference was 1.06 atms. The mean linear velocity was 3.2 ft/sec and the flow rate was 70 mL/sec. The difference of suspended solid weights between control and test was 1.22g. In daily production of phosphoric acid plants, flow rate is 63.9 $ft^3$ /min and linear velocity is 5.5 ft/sec for 6" pipes.

## Table 19

### Summary Of Suspended Scale In Water And 28.5% Phosphoric Acid In The Absence (Control) And Presence Of (Treated) A Magnetic Field

| Table | Test Done | Control (g) | Treated (g) | Difference (g) |
|---|---|---|---|---|
| WATER SUSPENSION | | | | |
| 7 | One cycle | 84.5 | 85.2 | 0.7 |
| 7 | | 86.8 | 86.8 | 0.0 |
| 8 | Ten cycles | 87.4 | 81.0 | -6.4 |
| 9 | Angled, slow flow rate, (one cycle) | 87.2 | 84.8 | -2.4 |
| 10 | Angled, high flow rate, (one cycle) | 89.3 | 85.2 | -4.1 |
| 11 | Angled, high flow rate, (ten cycles) | 90.1 | 86.2 | -3.9 |
| PHOSPHORIC ACID SUSPENSION | | | | |
| 12 | Parallel, ten cycles | 77.7 | 76.8 | -0.9 |
| 13 | Angled, ten cycles | 77.7 | 76.6 | -1.1 |
| 14 | Angled, one cycle (2 x 1200 gauss) | 82.4 | 80.8 | -1.6 |
| 15 | Angled, one cycle (2 x 2000 gauss), test 1 | 82.4 | 75.9 | -6.5 |
| 15 | Angled, one cycle (2 x 2000 gauss), test 2 | 82.4 | 75.6 | -6.8 |
| 16 | High pressure, one cycle | 74.2 | 72.1 | -2.1 |
| 17 | High pressure, one cycle | 78.9 | 76.0 | -2.9 |

## Table 20

## Solubility Of Suspended Scale In Water In The Absence(Control) And Presence (Treated) Of A Magnetic Field

| Table | Test done | Control (g/100mL) | Treated (g/100mL) | Difference (%) |
|---|---|---|---|---|
| Water suspension: | | | | |
| 7 | One cycle | 1.03 | 0.99 | -4.17 |
| 8 | Ten cycles | 0.84 | 1.27 | 51.2 |
| 9 | Angled, slow flow rate (one cycle) | 0.85 | 1.01 | 18.8 |
| 10 | Angled, high flow rate (one cycle) | 0.78 | 0.99 | 26.5 |
| 11 | Angled, high flow rate (ten cycles) | 0.66 | 0.92 | 39.4 |

## Table 21

## Scale Solubility In 28.5% Phosphoric Acid In Presence And Absence Of The Magnetic Field

| Method** | Cycles | Magnet field (gauss) | t ( °C) | Control (g/100mL) | Treated (g/100mL) | Difference(%) |
|---|---|---|---|---|---|---|
| Parallel | 1 | 1200 | 90 | 1.41 | 1.47 | 4.26 |
| Perpend. | 1 | 2000 | 90 | 1.41 | 1.57 | 11.3 |
| Parallel | 10 | 1200 | 50 | 1.05 | 1.32 | 25.7 |
| Perpend. | 10 | 2000 | 50 | 1.05 | 1.35 | 28.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Perpend. | 10 | 1200 | 23 | 1.49 | 1.56 | 4.7 |
| Perpend. | 1 | 1200 | 23 | 1.17 | 1.28 | 9.4 |
| Perpend. | 1 | 2000 | 23 | 1.17 | 1.61 | 37.6 |
| Perpend. | 1 | 2000 | 23 | 1.17 | 1.63 | 39.3 |

* Initial total scale weight is 100.0 g with fraction of –18:5.0 g; +18/-35: 40.0 g; +35/-60: 20.0 g; +60/-120: 10.0 g; +120/-230: 10.0 g; -230: 15.0 g. %Difference =(test-control)/control.

**Separation of iron from scale by the magnetic field**

Phosphoric acid scale contained a certain amount of iron and iron content was different for each scale size portion (Table 22). Smaller scale particles (-230 mesh) contained higher iron than larger particle (-18/+35 mesh).

## Table 22
### Effect Of A Magnetic Field On Iron Concentration Of Sample Mesh Size 35-60

SCALE SAMPLE*

| Description | Quantity (mg) | Iron as % $Fe_2O_3$ | Iron as % Fe |
|---|---|---|---|
| Test: initial weight | 298,000 | -- | -- |
| Control | 2,000 | 0.002 | 0.001 |
| Suspended Test | 279,000 | 0.003 | 0.002 |
| Magnetic Attached | 7 | 17.22 | 12.04 |

(*Test submitted to 4 ceramic magnets, fitted in a plastic baffle, 90° apart, for 30 minutes cf. 5.)
("Iron results provided courtesy of J. H. Falls, CF Industries.)

***Magnetic field effect on iron distribution of scale*** -- A 1.5 L of aqueous suspension containing 100g scale was passed through the magnetic field (4 x 1200 gauss) once (Fig. 4). After the treatment, the scale are sieved and dried at 75 C. Iron in each size fraction is measured. Results are shown in Table 23 -Table 26.

# Table 23

## Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied At A 2"i.d. Pipe And Four Magnets At A Flow Rate Of 115 ml/sec*

| | Control | | Test | |
|---|---|---|---|---|
| | Scale | Iron (mg) | Scale | Iron (mg) |
| Total (g) | 100 | 22.49 | 100 | 22.36 |
| Solid (g)<br>(after suspension) | 83.54 | | 81.53 | |
| Size distribution | | | | |
| | % | Iron (mg) | % | Iron (mg) |
| <18 | 6.19 | 0.51 | 5.61 | 0.51 |
| 18-35 | 44.53 | 3.95 | 45.38 | 3.87 |
| 35-60 | 21.45 | 4.66 | 21.50 | 3.79 |
| 60-230 | 21.38 | 4.36 | 23.02 | 5.99 |
| >230 | 6.56 | 4.75 | 4.13 | 3.98 |
| solution | | 4.26 | | 4.22 |

ANOVA:

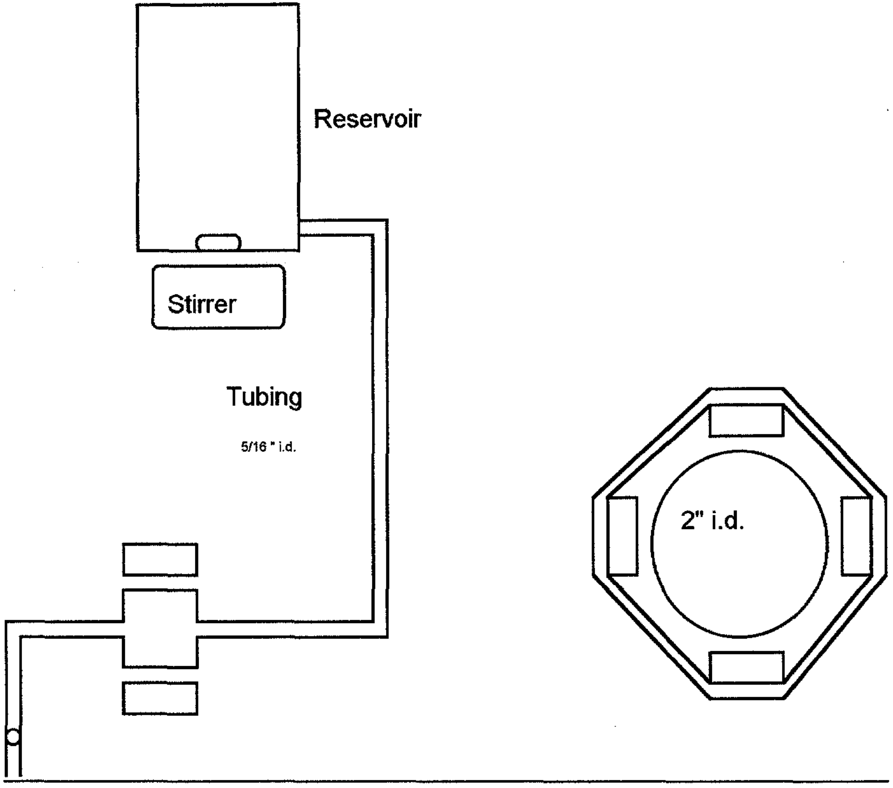
Scale weight change

| | | |
|---|---|---|
| Column: | F Value = 0.018386; | Prob.>F = 0.20262 |
| Row: | F Value = 434.1964; | Prob.>F = $3.16311 \times 10^{-5}$ |

Iron amount change

| | | |
|---|---|---|
| Column: | F Value = 0.003510; | Prob.>F= 0.08990 |
| Row: | F Value = 13.35716; | Prob.>F= 0.01289 |

* The equipment is described in Figure 4 and chromium is below the detection limit in diphenylarbazide method. Test sample was passed through a magnetic field (4 x 1200 gauss) once.



Magnet set
4 x 3000 gauss
2" i.d.  pipe

A SET OF 4 X 3000 GAUSS MAGNETS FROM AQUA MAGNETICS® INTERNATIONAL INC.

**FIGURE 4**

## Table 24

### Effect Of Treatment Of Scale Suspension With A Magnetic Field Applied With A 2"i.d. Pipe And Four Magnets With A Flow Rate Of 115 ml/sec*

| | Control | | Test | |
|---|---|---|---|---|
| | Scale | Iron(mg)** | Scale | Iron(mg)** |
| Total (g) | 100 | 16.54 | 100 | 16.54 |
| Solid (g) (after suspension) | 83.9 | 16.01 | 84.1 | 16.29 |
| Size distribution | % | Iron(mg)** | % | Iron(mg)** |
| <18 | 5.61 | 0.25 | 4.94 | 0.12 |
| 18-35 | 42.55 | 3.82 | 42.20 | 3.41 |
| 35-60 | 25.41 | 1.87 | 24.23 | 1.61 |
| 60-230 | 18.52 | 1.55 | 19.79 | 1.30 |
| >230 | 7.91 | 3.39 | 8.78 | 3.84 |
| Solution | | 5.13 | | 6.01 |

ANOVA:

Scale weight change

| | | |
|---|---|---|
| Column | F Value = 0.00066468; | Prob.>F = 0.03867 |
| Row | F Value = 809.9; | Prob.>F = $9.12 \times 10^{-5}$ |

Iron amount change.

| | | |
|---|---|---|
| Column | F Value = 0.05108; | Prob.>F = 0.3397 |
| Row | F Value = 59.0029; | Prob.>F = $3.826 \times 10^{-4}$ |

* Experiment conditions same as Table 23, ** Iron amount in each scale portion.

## Table 25

### Iron Content In Fluorosilicate Scale After The Magnetic Treatment

| Scale size (mesh) | <18 | 18-35 | 35-60 | 60-120 | >230 | Solution | total |
|---|---|---|---|---|---|---|---|
| Control | | | | | | | |
| weight (g) | 5.16 | 37.06 | 17.89 | 17.83 | 5.47 | 2017 | 83.41 |
| Iron concn.(ppm) | 98.2 | 106.7 | 260.6 | 244.3 | 869 | 2.11 | |
| Iron amount (mg) | 0.51 | 3.95 | 4.66 | 4.36 | 4.75 | 4.26 | 22.49 |
| Test | | | | | | | |
| weight (g) | 4.57 | 37.29 | 17.53 | 18.77 | 3.37 | 2018 | 81.53 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Iron concn.(ppm) | 111.1 | 103.8 | 216.1 | 319.2 | 1180 | 2.09 | |
| Iron amount (mg) | 0.51 | 3.87 | 3.79 | 5.99 | 3.98 | 4.22 | 22.36 |
| Difference in iron | | | | | | | |
| Fe, T - Fe, C (ppm) | +12.9 | -2.9 | -44.5 | +74.9 | +311 | -0.02 | |
| Fe, T - Fe, C(mg) | 0.00 | -0.08 | -0.87 | +1.94 | -0.76 | -0.04 | -0.13 |
| Solid weight(g) | | | | | | | -1.88 |

* T, test: C, control.

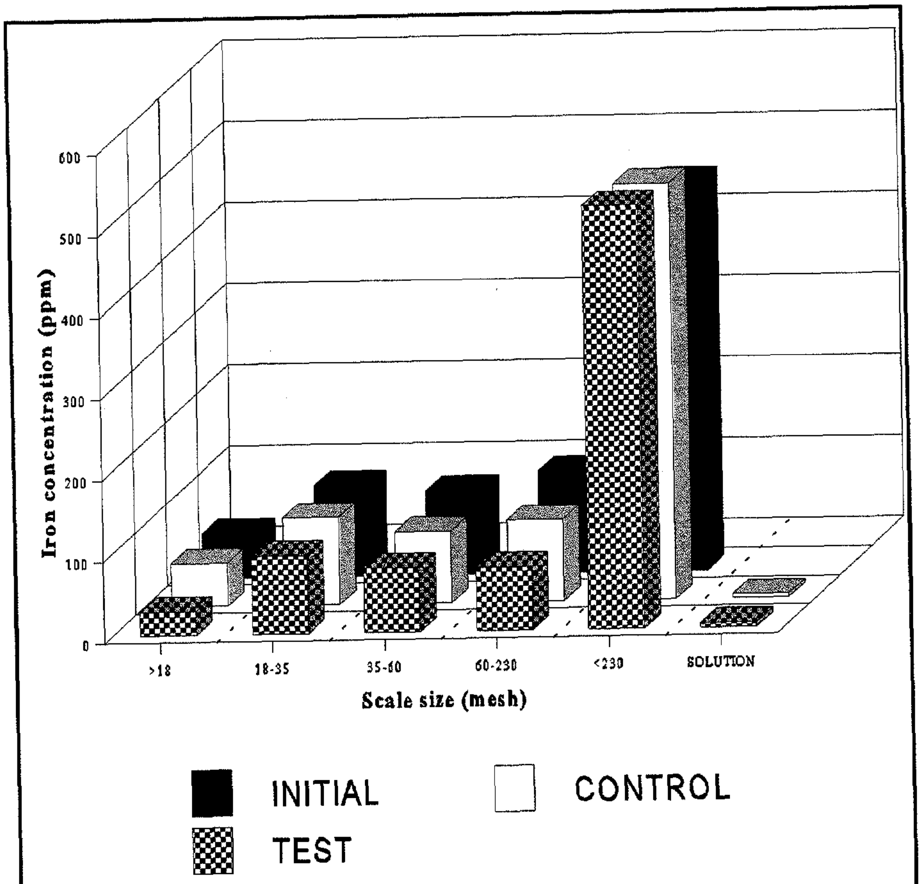
## Table 26

### Iron Content In Fluorosilicate Scale After The Magnetic Treatment (Table 24)

| Scale Size (mesh) | ≤18 | 18-35 | 35-60 | 60-230 | ≥230 | Solution | Total |
|---|---|---|---|---|---|---|---|
| INITIAL | | | | | | | |
| Weight (g) | 5.00 | 40.00 | 20.00 | 20.00 | 15.00 | | 100.0 |
| Iron concn. (ppm) | 54.7 | 111 | 103 | 125 | 478 | | |
| Iron amount (mg) | 0.27 | 4.44 | 2.06 | 2.50 | 7.17 | | 16.54 |
| CONTROL | | | | | | | |
| Weight (g) | 4.71 | 35.70 | 21.31 | 15.54 | 6.63 | 1016 | 83.90 |
| Iron concn. (ppm) | 53.4 | 107 | 87.9 | 99.9 | 511 | 5.06 | |
| Iron amount (mg) | 0.25 | 3.82 | 1.87 | 1.55 | 3.39 | 5.13 | 16.01 |
| TEST | | | | | | | |
| Weight (g) | 4.16 | 35.48 | 20.42 | 16.64 | 7.38 | 1016 | 84.08 |
| Iron concn. (ppm) | 29.5, | 96.2, | 79.0 | 78.0 | 520 | 5.91 | |
| Iron amount (mg) | 0.12, | 3.41, | 1.61 | 1.30 | 3.84 | 6.01 | 16.29 |
| Difference in Iron | | | | | | | |
| Fe,T* -Fe,C- (ppm) | -23.9 | -10.3 | -8.9 | -21.9 | +9 | +0.85 | |
| Fe,T - Fe,C (mg) | -0.13 | -0.41 | -0.26 | -0.25 | 0.45 | 0.88 | 0.28 |
| Fe, T - Fe,I' (ppm) | -25.2 | -14.8 | -24.0 | -47.0 | 42 | | |
| Fe, T - Fe,I (mg) | -0.15 | -1.03 | -0.45 | -1.2 | -3.33 | 6.01 | -0.25 |
| Fe,C - Fe,I (ppm) | -1.3 | -4.0 | -15.1 | -25.1 | 33 | | |
| Fe,C - Fe,I (mg) | -0.02 | -0.62 | -0.19 | -0.95 | -3.78 | 5.13 | -0.53 |

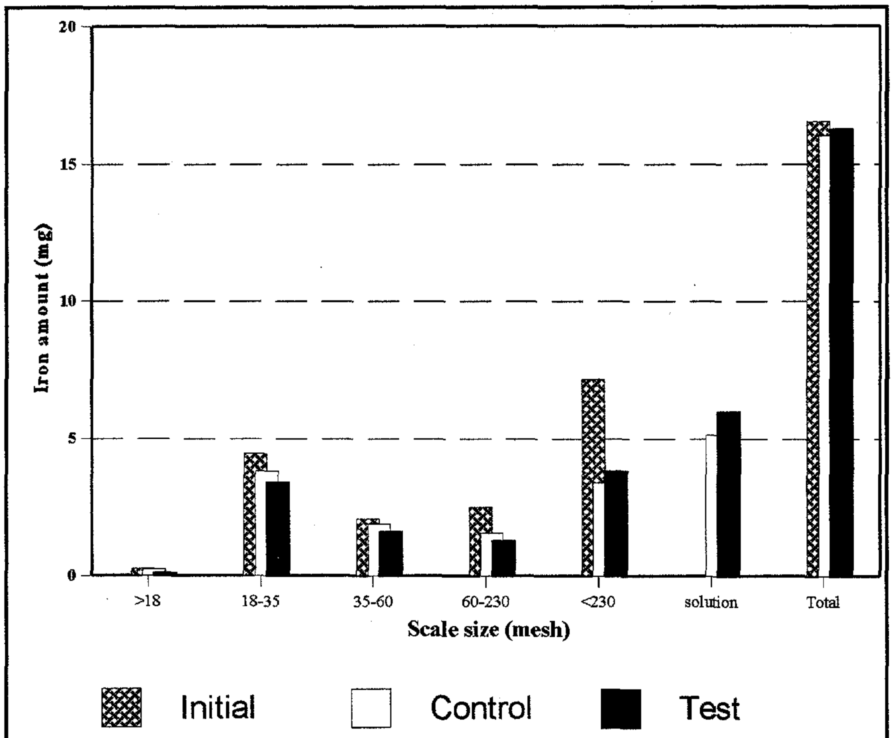
*T - Test, -C - Control, 'I - Initial

After the magnetic treatment, the solubility was consistently higher in the test than that in the control. Iron distribution shifted to the small size (Fig. 6). Iron content was higher(511ppm vs 53.4 ppm) in the smaller scale particle (>230 mesh vs <18 mesh) (Fig.5).



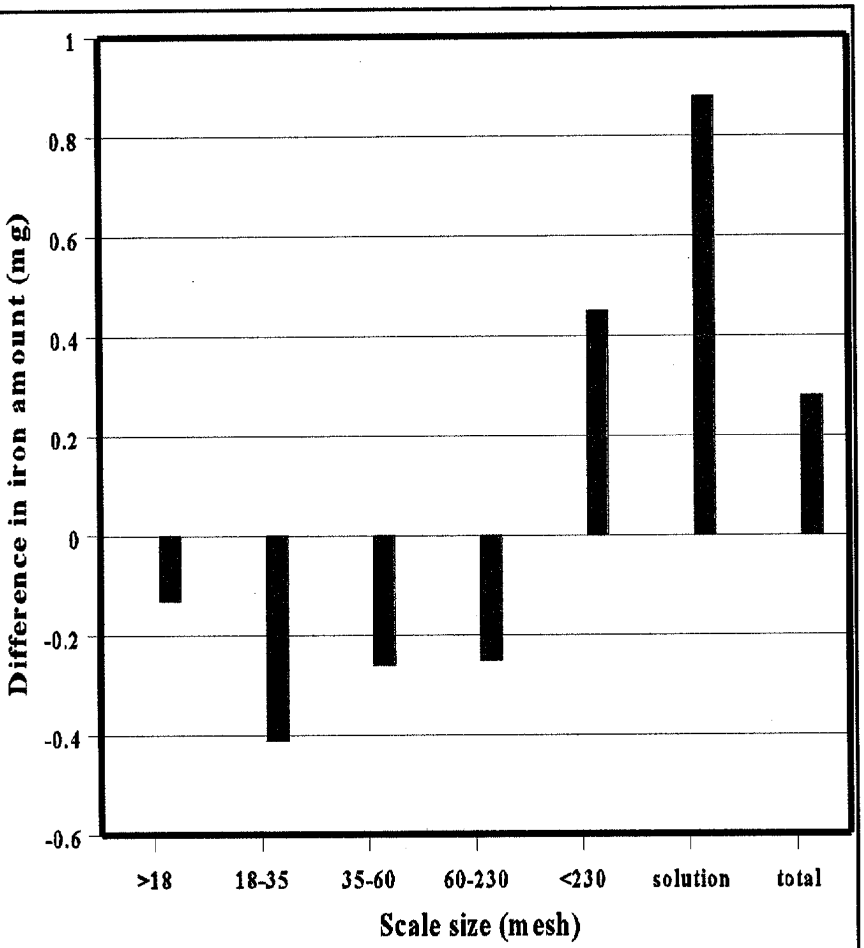
IRON CONCENTRATION DISTRIBUTION WITH FLUOROSILICATE SCALE SIZE

**FIGURE 5**



IRON AMOUNT DISTRIBUTION WITH FLUOROSILICATE SCALE SIZE

**FIGURE 6**

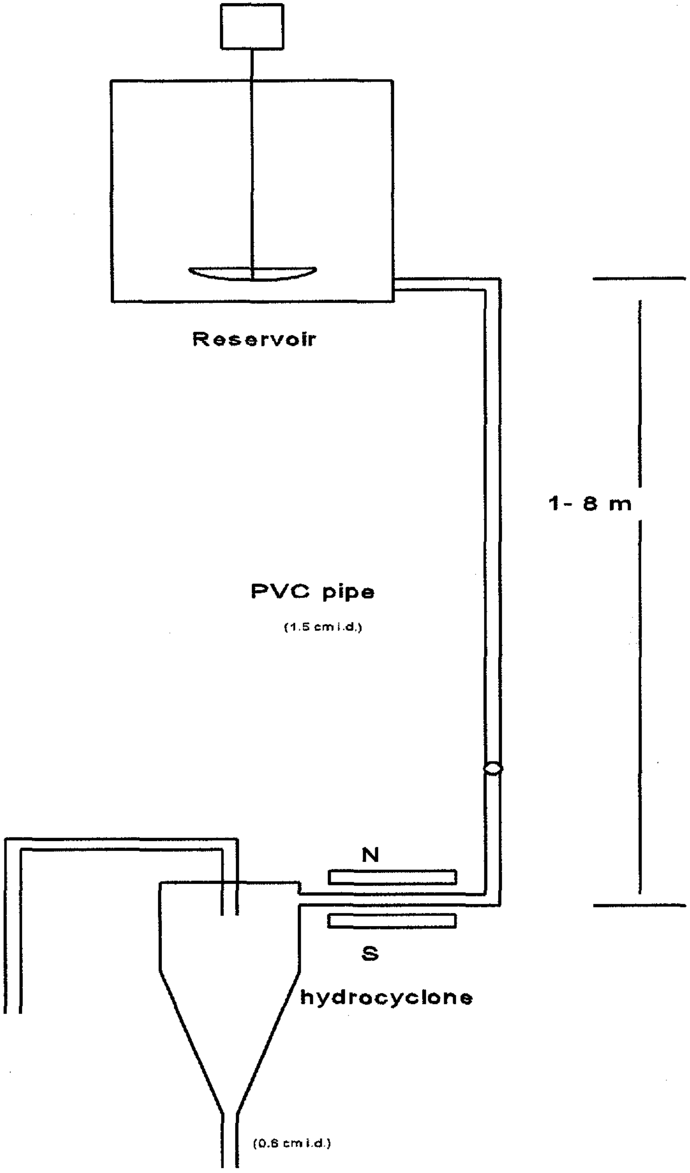


IRON DIFFERENCE IN TEST AND CONTROL (mg)
FOR SODIUM FLUOROSILICATE PASSED THROUGH
A SET OF 4 x 1200 GAUSS MAGNETS

**FIGURE 7**

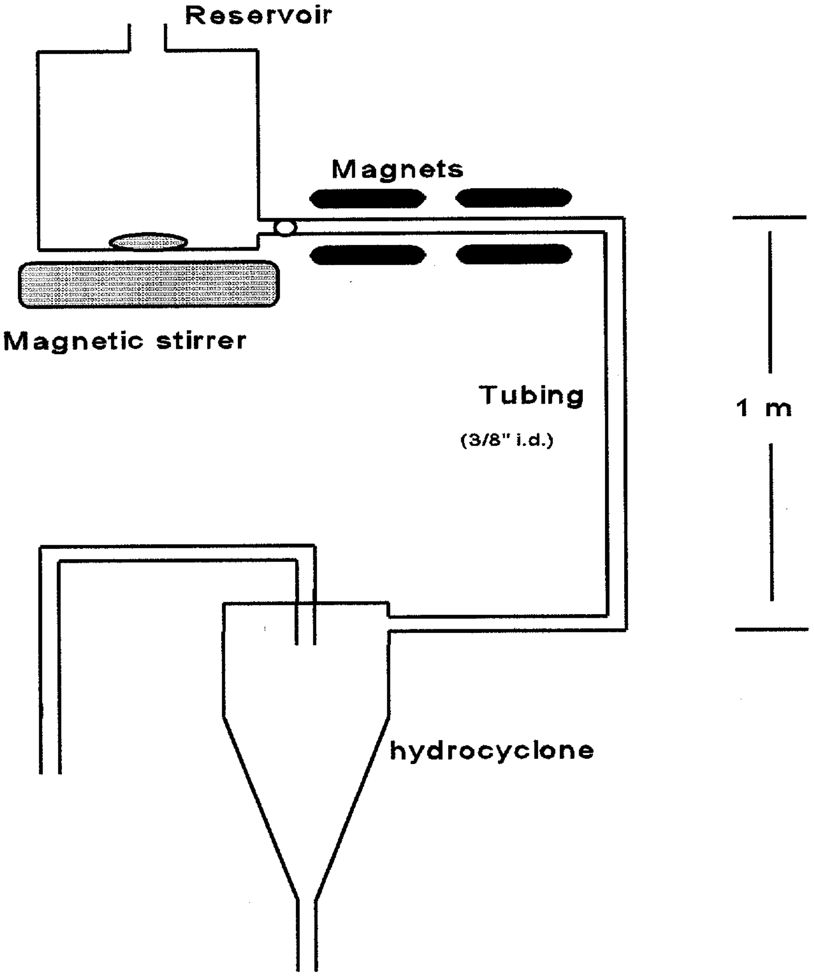
## Separation of iron from scale by magnetic field combined with a hydrocyclone

Three methods were applied, method A, method B, and method C (Fig.8, Fig 9 and Fig 10). In method B and method C, a reservoir was placed one meter above the inlet of hydrocyclone and scale suspension was magnetically stirred. Reservoir and hydrocyclone were connected by Tygon® tubing 3/8" i.d.. Two pairs of magnets (1200 gauss each) were applied on the outlet of the reservoir in method C and one magnetic set with 2" i.d. pipe was applied in method B. The scale suspension was passed through the magnetic field once or 5 times, In method A, the reservoir was placed 8 meters above the inlet of hydrocyclone and the scale suspension was stirred with a mechanical stirrer. The PVC pipe (1" id.) was used to connect reservoir and hydrocyclone and the scale suspension was passed through the magnetic field 5 times. Overflow solid and underflow solid were separated and were dried in a 75 °C oven. Both kinds of scale were investigated for the iron removal [May 1996 (mixture, Tables 27-30) and December 1996 (white part, Tables 31-41)].



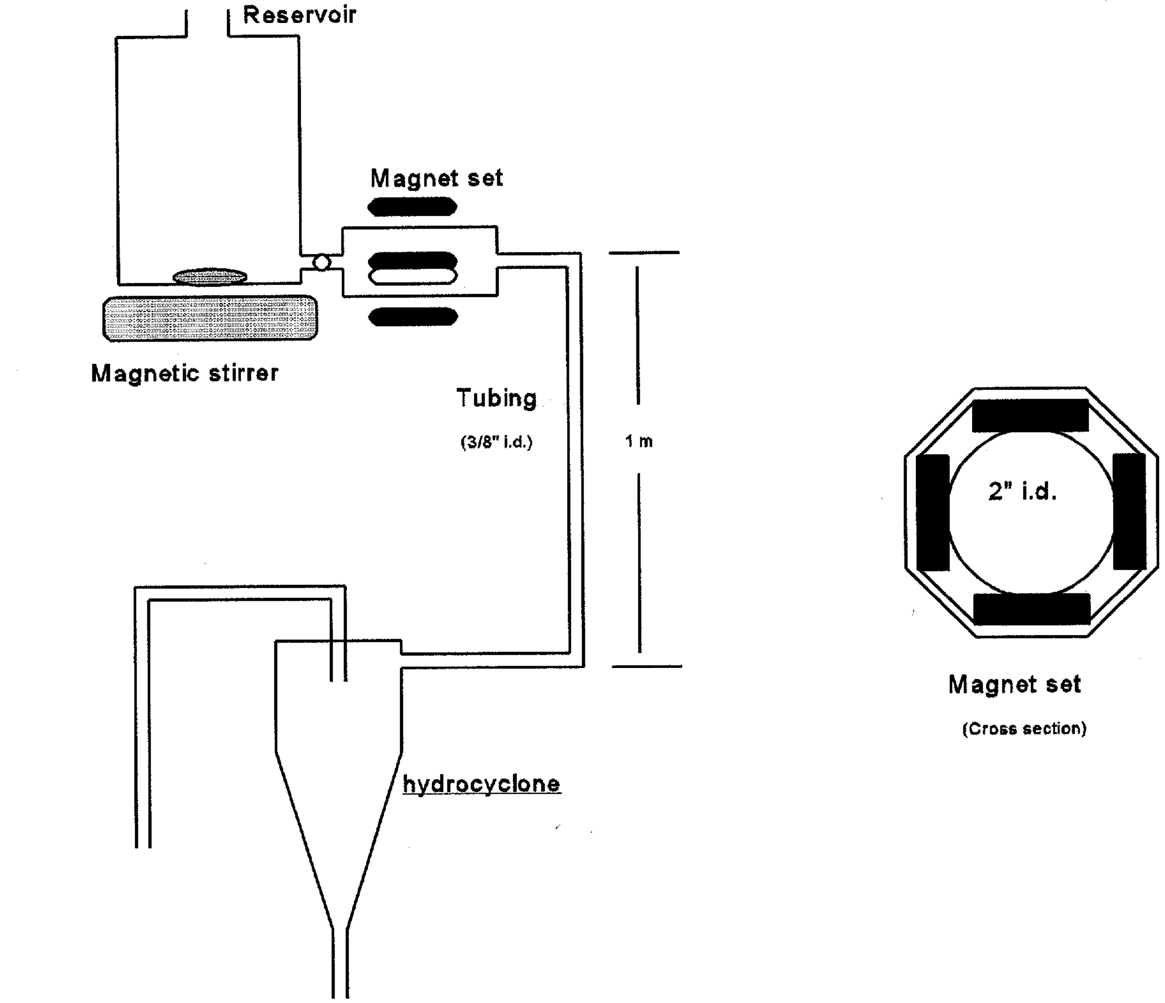
SCHEMATIC OF MAGNETIC TREATMENT BY HYDROCYCLONE, METHOD A.

**FIGURE 8**



SCHEMATIC OF MAGNETIC TREATMENT BY HYDROCYCLONE, METHOD B.

**FIGURE 9**



SCHEMATIC OF MAGNETIC TREATMENT BY HYDROCYCLONE, METHOD C

**FIGURE 10**

## Table 27

## Magnetic Treatment Of -18/+35 Mesh Scale By A Hydrocyclone, 5-Cycle Run, In Method A*

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 100.0 | 100.0 | 0 |
| Underflow (g) | 79.0 | 81.2 | -2.2 |
| Overflow (g) | 0.2500 | 0.1081 | -0.1419 |
| Total solid (g) | 79.3 | 81.3 | -2.0 |
| Solution pH | 3.4 | 3.4 | 0 |
| $\text{Iron}_{\text{overf}}$ (ppm) | 2700 | 11000 | |
| $\text{Iron}_{\text{underf}}$ (ppm) | 79.4 | 81.5 | |
| $\text{Iron}_{\text{soln}}$ (ppm) | 0.68 | 0.69 | |
| $\text{Iron}_{\text{overf}}$ (mg) | 0.68 | 1.183 | |
| $\text{Iron}_{\text{under}}$ (mg) | 6.273 | 6.618 | |
| $\text{Iron}_{\text{soln}}$ (mg) | 2.734 | 2.781 | |
| Total iron (mg) | 9.687 | 10.579 | -0.892 |

* $\text{Iron}_{\text{overf}}$ represents iron amount in overflow scale solid, $\text{Iron}_{\text{underf}}$ represents iron amount in underflow scale solid and $\text{Iron}_{\text{soln}}$ represents iron amount in solution. Difference is test amount *vs.* control amount.

## Table 28

## Magnetic Treatment Of -35/+60 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method A

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 100.0 | 100.0 | |
| Overflow (g) | 0.0381 | 0.2664 | |
| Underflow (g) | 78.6 | 79.8 | -1.2 |
| Total solid (g) | 78.6 | 80.1 | -1.5 |
| Solution pH | 3.41 | 3.43 | |
| $\text{Iron}_{\text{overf}}$ (ppm) | 11000 | 3800 | |

| | | | |
|---|---|---|---|
| Iron$_{underf}$ (ppm) | 115.1 | 161.7 | |
| Iron $_{soln}$ (ppm) | 0.853 | 0.898 | |
| Iron$_{overf}$ (mg) | 0.42 | 1.00 | |
| Iron$_{underf}$ (mg) | 9.05 | 12.90 | |
| Iron$_{soln}$ (mg) | 3.31 | 3.59 | |
| Total iron (mg) | 12.79 | 16.49 | -3.7 |

## Table 29

### Magnetic Treatment Of -60/+230 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method A

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 80.0 | 80.0 | |
| Underflow (g) | 42.8 | 49.7 | - 6.9 |
| Iron$_{underf}$ (ppm) | 113.6 | 151.4 | |
| Iron$_{soln}$ (ppm) | 0.802 | 0.687 | |
| Iron $_{underf}$ (mg) | 4.862 | 7.525 | |
| Iron$_{soln}$ (mg) | 3.238 | 2.769 | |
| Total iron (mg) | 8.100 | 10.294 | -2.194 |

## Table 30

## Magnetic Treatment Of -230 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method A

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 70.0 | 70.0 | |
| Overflow (g) | 11.62 | 10.69 | |
| Underflow (g) | 25.00 | 26.45 | |
| Total solid | 36.62 | 37.14 | -0.5 |
| Solution pH | 3.53 | 3.58 | |
| $\text{Iron}_{\text{overf}}$ (ppm) | 1480 | 1706 | |
| $\text{Iron}_{\text{underf}}$ (ppm) | 488 | 541 | |
| $\text{Iron}_{\text{soln}}$ (ppm) | 2.25 | 1.98 | |
| $\text{Iron}_{\text{overf}}$ (mg) | 17.202 | 18.232 | |
| $\text{Iron}_{\text{underf}}$ (mg) | 12.198 | 14.299 | |
| $\text{Iron}_{\text{soln}}$ (mg) | 9.00 | 7.92 | |
| Total iron (mg) | 38.400 | 40.451 | -2.051 |

From Table 27-30, Method A works for both larger particles (-18/+35) and small particles (-230 mesh). Under the magnetic field, more scale dissolved than in absence of the field. Iron content in the solid (underflow portion) is lowered by the magnetic treatment.

## Table 31

## Magnetic Treatment Of -18/+35 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method B

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0005 | 50.0002 | +0.0003 |
| underflow (g) | 39.1756 | 39.7551 | -0.5795 |
| Solution pH | 3.16 | 3.16 | |

| | | | |
|---|---|---|---|
| Iron$_{\text{underf}}$ (ppm) | 22.7 | 25.2 | |
| Iron $_{\text{underf}}$ (mg) | 0.889 | 1.002 | |
| Iron $_{\text{soln}}$ (ppm) | 0.382 | 0.422 | |
| Iron $_{\text{soln}}$ (mg) | 0.577 | 0.637 | |
| Total Iron (mg) | 1.476 | 1.639 | -0.163 |

## Table 32
## Magnetic Treatment Of -18/+35 Mesh Scale By A Hydrocyclone, 5-Cycle Run, Method B

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0008 | 50.0002 | +0.0006 |
| Underflow (g) | 40.4848 | 40.5643 | -0.0795 |
| Solution pH | 3.30 | 3.32 | |
| Iron$_{\text{under}}$ (ppm) | 14.7 | 17.5 | |
| Iron$_{\text{under}}$ (mg) | 0.595 | 0.710 | |
| Iron$_{\text{soln}}$ (ppm) | 0.36 | 0.35 | |
| Iron$_{\text{soln}}$ (mg) | 0.537 | 0.522 | |
| Total iron (mg) | 1.132 | 1.232 | -0.100 |

Two parallel treatments show that iron in scale is lowered after the magnetic treatment. Scale solubility is increased under the field.

## Table 33
## Magnetic Treatment Of -120/+230 Mesh Scale By A Hydrocyclone, 5-Cycle Run, In Method B

| Component | Test | Control | Difference |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Scale input (g) | 50.0000 | 50.0000 | 0 |
| Solution pH | 3.26 | 3.28 | |
| Underflow (g) | 35.5162 | 37.3876 | -1.8714 |
| Overflow (g) | 2.9800 | 2.0023 | +0.9777 |
| Total solid (g) | 38.4962 | 39.3899 | -0.8937 |
| Iron$_{underf}$ (ppm) | 20.7 | 26.7 | |
| Iron$_{overf}$ (ppm) | 42.9 | 49.0 | |
| Iron$_{overf}$ (mg) | 0.128 | 0.098 | |
| Iron$_{underf}$ (mg) | 0.735 | 0.998 | |
| Iron$_{soln}$ (ppm) | 0.67 | 0.71 | |
| Iron$_{soln}$ (mg) | 1.013 | 1.070 | |
| Total Iron (mg) | 1.876 | 2.166 | -0.290 |

For –120/+230 mesh scale particle, the magnetic effect on the solubility is more significant than that for –18/+35 mesh particle(Table 33 *vs.* Table 32)

## Table 34
## Magnetic Treatment Of -230 Mesh Scale Particle By A Hydrocyclone, One-Cycle Run, Method B

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0027 | 49.9982 | +0.0045 |
| Overflow (g) | 17.6837 | 17.7048 | |
| Underflow (g) | 21.7023 | 21.7400 | |
| Total solid (g) | 39.3860 | 39.4468 | -0.0608 |
| Solution pH | 3.27 | 3.28 | |
| Iron$_{overf}$ (ppm) | 60.2 | 62.5 | |
| Iron$_{underf}$ (ppm) | 33.3 | 36.6 | |
| Iron$_{soln}$ (ppm) | 0.84 | 0.88 | |
| Iron$_{overf}$ (mg) | 1.065 | 1.107 | |

| | | | |
|---|---|---|---|
| Iron$_{underf}$ (mg) | 0.723 | 0.796 | |
| Iron$_{soln}$ (mg) | 1.275 | 1.325 | |
| Total iron (mg) | 3.063 | 3.228 | -0.165 |

## Table 35

### Magnetic Treatment Of -230 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method B

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0010 | 50.0000 | +0.0010 |
| Solution pH | 3.34 | 3.32 | |
| Overflow (g) | 18.8454 | 18.8313 | |
| Underflow (g) | 20.8184 | 20.9841 | |
| Total solid (g) | 39.6638 | 39.8154 | -0.1516 |
| Iron$_{overf}$ (ppm) | 67.4 | 53.5 | |
| Iron$_{underf}$ (ppm) | 38.3 | 45.6 | |
| Iron$_{soln}$ (ppm) | 1.14 | 1.25 | |
| Iron$_{overf}$ (mg) | 1.270 | 1.007 | |
| Iron$_{underf}$ (mg) | 0.797 | 0.957 | |
| Iron$_{soln}$ (mg) | 1.722 | 1.888 | |
| Total iron (mg) | 3.789 | 3.852 | -0.063 |

Results from treatments of –18/+35, -120/+230, and –230 mesh scale show that in method B, the magnetic field affects smaller particles more significantly than larger particle.

In method C, all fractions of scale are used in the magnetic treatment for 5-cycle run. 50 g of each fraction of scale is suspended in 1.5 L of water. Results are listed in Table 36 – Table 41.

## Table 36

### Magnetic Treatment Of -230 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method B

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0094 | 50.0130 | -0.0036 |
| Overflow (g) | 17.5272 | 16.7505 | |
| Underflow (g) | 21.2977 | 22.4185 | |
| Total solid (g) | 38.8249 | 39.1690 | -0.3441 |
| Solution pH | 3.20 | 3.20 | |
| $\text{Iron}_{\text{overf}}$ (ppm) | 146 | 73.1 | |
| $\text{Iron}_{\text{underf}}$ (ppm) | 48.6 | 47.7 | |
| $\text{Iron}_{\text{soln}}$ (ppm) | 1.19 | 1.23 | |
| $\text{Iron}_{\text{overf}}$ (mg) | 2.559 | 1.224 | |
| $\text{Iron}_{\text{underf}}$ (mg) | 1.035 | 1.069 | |
| $\text{Iron}_{\text{soln}}$ (mg) | 1.801 | 1.855 | |
| Total iron (mg) | 5.395 | 4.307 | +1.088 |

## Table 37

## Magnetic Treatment Of -120/+230 Scale Particle By A Hydrocyclone, 5-Cycle Run, Method C

| | Test | Control | Difference |
|---|---|---|---|
| Scale input | 50.0038 | 50.0042 | -0.0004 |
| Overflow (g) | 5.5043 | 5.2129 | |
| Underflow (g) | 34.0850 | 34.5594 | |
| Total solid (g) | 39.5893 | 39.7723 | -0.1830 |
| Solution pH | 3.29 | 3.30 | |
| $\text{Iron}_{\text{overf}}$ (ppm) | 37.7 | 34.6 | |
| $\text{Iron}_{\text{underf}}$ (ppm) | 28.0 | 35.7 | |
| $\text{Iron}_{\text{soln}}$ (ppm) | 0.51 | 0.52 | |
| $\text{Iron}_{\text{overf}}$ (mg) | 0.208 | 0.180 | |
| $\text{Iron}_{\text{underf}}$ (mg) | 0.954 | 1.234 | |
| $\text{Iron}_{\text{soln}}$ (mg) | 0.770 | 0.785 | |
| Total iron (mg) | 1.932 | 2.199 | -0.119 |

## Table 38

## Magnetic Treatment Of -230 Scale Particle By A Hydrocyclone, 1-Cycle Run, Method C

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0018 | 50.0112 | -0.0094 |
| Overflow (g) | 17.0192 | 21.3897 | |
| Underflow (g) | 22.2986 | 18.7357 | |
| Total solid (g) | 39.3178 | 40.1254 | -0.8076 |
| Solution pH | 3.23 | 3.31 | |

| | | | |
|---|---|---|---|
| Iron$_{overf}$ (ppm) | 55.6 | 49.2 | |
| Iron$_{underf}$ (ppm) | 37.4 | 45.6 | |
| Iron$_{soln}$ (ppm) | 1.09 | 1.03 | |
| Iron$_{overf}$ (mg) | 0.946 | 1.052 | |
| Iron$_{underf}$ (mg) | 0.834 | 0.854 | |
| Iron$_{soln}$ (mg) | 1.647 | 1.556 | |
| Total iron (mg) | 3.427 | 3.462 | -0.035 |

## Table 39

### Magnetic Treatment Of -230 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method C

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0278 | 50.0285 | -0.0007 |
| Overflow (g) | 18.3611 | 19.5231 | |
| Underflow (g) | 21.0488 | 21.0927 | |
| Total solid (g) | 39.4099 | 40.6158 | -1.2059 |
| Solution pH | 3.24 | 3.26 | |
| Iron$_{overf}$ (ppm) | 73.6 | 52.3 | |
| Iron$_{underf}$ (ppm) | 39.2 | 40.7 | |
| Iron$_{soln}$ (ppm) | 1.28 | 1.04 | |
| Iron$_{overf}$ (mg) | 1.351 | 1.021 | |
| Iron$_{underf}$ (mg) | 0.825 | 0858 | |
| Iron$_{soln}$ (mg) | 1.934 | 1.570 | |
| Total iron (mg) | 4.110 | 3.449 | +0.190 |

## Table 40

## Magnetic Treatment Of -35/+60 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, Method C

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0028 | 50.0033 | -0.0005 |
| Overflow (g) | 1.0821 | 0.6246 | |
| Underflow (g) | 38.5300 | 39.0009 | |
| Total solid (g) | 39.6121 | 39.6255 | -0.0134 |
| Solution pH | 3.33 | 3.32 | |
| $\mathrm{Iron}_{\mathrm{overf}}$ (ppm) | 47.1 | 42.8 | |
| $\mathrm{Iron}_{\mathrm{underf}}$ (ppm) | 13.9 | 14.5 | |
| $\mathrm{Iron}_{\mathrm{soln}}$ (ppm) | 0.49 | 0.50 | |
| $\mathrm{Iron}_{\mathrm{overf}}$ (mg) | 0.051 | 0.027 | |
| $\mathrm{Iron}_{\mathrm{underf}}$ (mg) | 0.536 | 0.566 | |
| $\mathrm{Iron}_{\mathrm{soln}}$ (mg) | 0.740 | 0.759 | |
| Total iron (mg) | 1.327 | 1.352 | -0.025 |

## Table 41

## Magnetic Treatment Of -60/+120 Mesh Scale Particle By A Hydrocyclone, 5-Cycle Run, In Method C

| Component | Test | Control | Difference |
|---|---|---|---|
| Scale input (g) | 50.0007 | 50.0000 | +0.0007 |
| Overflow (g) | 1.6013 | 1.6536 | |
| Underflow (g) | 37.0192 | 37.3991 | |
| Total solid (g) | 38.6205 | 39.0527 | -0.4322 |
| Solution pH | 3.30 | 3.31 | |
| $\mathrm{Iron}_{\mathrm{overf}}$ (ppm) | 34.2 | 30.8 | |
| $\mathrm{Iron}_{\mathrm{underf}}$ (ppm) | 17.0 | 13.1 | |

| | | | |
|---|---|---|---|
| Iron $_{\text{soln}}$ (ppm) | 0.54 | 0.66 | |
| Iron $_{\text{overf}}$ (mg) | 0.055 | 0.051 | |
| Iron $_{\text{underf}}$ (mg) | 0.629 | 0.490 | |
| Iron $_{\text{soln}}$ (mg) | 0.814 | 1.001 | |
| Total iron (mg) | 1.498 | 1.542 | -0.044 |

## Table 42

### Summary Of Solid Weight Change Of Scale In Water With A Magnetic Field And Without A Magnetic Field, Room Temperature (23°C)

| Scale Particle Size (Mesh) | Table #, Method | Input (g) | Test Weight (g) | Control Weight (g) | ΔW (g) | Change % |
|---|---|---|---|---|---|---|
| -18/+35 | 27, a | 100 | 79.0 | 81.2 | -2.0 g | - 2.0 |
| -35/+60 | 28, a | 100 | 78.6 | 80.1 | -1.5 g | - 1.5 |
| -120/+230 | 29, a | 80 | 42.8 | 49.7 | -6.9 g | - 8.6 |
| -230 | 30, a | 70 | 36.62 | 37.14 | -0.5 g | - 0.7 |
| -18/+35 | 31, b | 50 | 39.1756 | 39.7551 | -0.5795 g | - 1.16 |
| -18/+35 | 32, b | 50 | 40.4848 | 40.5643 | -0.0795 g | - 0.16 |
| -120/+230 | 33, b | 50 | 38.4962 | 39.3899 | -0.8937 g | - 1.79 |
| -230 | 34, b | 50 | 39.3860 | 39.4468 | -0.0608 g | - 0.12 |
| -230 | 35, b | 50 | 39.6638 | 39.8154 | -0.1516 g | - 0.30 |
| -230 | 36, b | 50 | 38.8249 | 39.1690 | -0.3441 g | - 0.69 |
| -120/+230 | 37, c | 50 | 39.5890 | 39.7723 | -0.1830 g | - 0.37 |
| -230 | 38, c | 50 | 39.3178 | 40.1254 | -0.8076 g | - 1.62 |
| -230 | 39, c | 50 | 39.4099 | 40.6158 | -1.2059 g | - 2.41 |
| -35/+60 | 40, c | 50 | 39.6121 | 39.6255 | -0.0134 g | - 0.03 |
| -60/+120 | 41, c | 50 | 38.6205 | 39.0527 | -0.4322 g | - 0.86 |

*$\Delta W = W_{\text{test}} - W_{\text{control}}$ ; Change (%) $= \Delta W \times 100\% / W_{\text{input}}$

ANOVA

| | | |
|---|---|---|
| Column | F Value = 5.6262; | Prob.>F = 0.06514 |
| Row | F Value = 268.8915; | Prob.>F = 3.2267 x $10^{-14}$ |

From results of magnetic treatment combined with a hydrocyclone, scale solubility in the aqueous solution is increased (Table 42). This is consistent with results obtained with the pump method. When the diamagnetic scale passed the magnetic field, it is decomposed into smaller particles and some of these small particles are dissolved.

## Table 43
### Iron Concentration (ppm) In Underflow Portion Of The Treated Scale

| Table Number | Iron (ppm), Test | Iron (ppm),Control | Difference (%)* |
|---|---|---|---|
| 27, -18/+35, a | 79.4 | 81.5 | - 2.58 |
| 28, -35/+60, a | 115.1 | 161.7 | - 28.82 |
| 29, -120/+230, a | 113.6 | 151.4 | - 24.97 |
| 30, -230, a | 488 | 541 | - 9.80 |
| 31, -18/+35, b | 22.7 | 25.2 | - 9.92 |
| 32, -18/+35, b. | 14.7 | 17.5 | - 16.00 |
| 33, -120/+230, b | 20.7 | 26.7 | - 22.47 |
| 34, -230, b, 1 cycl. | 33.3 | 36.6 | - 9.02 |
| 35, -230, b | 38.3 | 45.6 | - 8.40 |
| 36, -230, b | 48.6 | 47.7 | +1.89 |
| 37, -120/+230, c. | 28.8 | 35.7 | - 19.33 |
| 38, -230, c, 1 cycl.. | 37.4 | 45.6 | - 17.98 |
| 39, -230, c | 39.2 | 40.7 | - 3.69 |

| | | | |
|---|---|---|---|
| 40, -35/+60, c | 13.9 | 14.5 | - 4.14 |

* Difference % = (Iron $_{test}$ -Iron $_{control}$) / Iron $_{control}$

ANOVA

Column F Value = 6.67796; Prob.>F = 0.04595
Row F Value = 199.7436; Prob.>F = $1.8729 \times 10^{-13}$

## Table 44
## Iron Amount (mg) In Underflow Portion of The Treated Scale

| Table No. | Iron (mg), Test | Iron(mg),Control | Difference* | Difference %* |
|---|---|---|---|---|
| 27 | 6.273 | 6.618 | - 0.345 | - 5.21 |
| 28 | 9.05 | 12.90 | - 3.85 | - 29.84 |
| 29 | 4.862 | 7.525 | - 2.663 | -35.39 |
| 30 | 12.198 | 14.299 | - 2.101 | - 14.69 |
| 31 | 0.889 | 1.002 | - 0.113 | - 11.28 |
| 32 | 0.595 | 0.710 | - 0.115 | - 16.20 |
| 33 | 0.735 | 0.998 | - 0.263 | - 26.35 |
| 34 | 0.723 | 0.796 | - 0.073 | - 9.17 |
| 35 | 0.797 | 0.957 | - 0.160 | - 16.72 |
| 36 | 1.035 | 1.069 | - 0.034 | - 3.18 |
| 37 | 0.954 | 1.234 | - 0.280 | - 22.69 |
| 38 | 0.834 | 0.854 | - 0.020 | - 2.34 |
| 39 | 0.825 | 0.858 | - 0.033 | - 3.85 |
| 40 | 0.536 | 0.566 | - 0.030 | - 5.30 |

* Difference = Iron $_{test}$ - Iron $_{control}$ ; Difference % = Difference x 100% / Iron $_{control}$

ANOVA

Column F value = 4.8639; Prob.>F = 0.09207
Row F Value = 48.7574; Prob.>F = $1.508 \times 10^{-8}$

## Table 45
## Iron Concentration (ppm) In Overflow Portion Of The Treated Scale

| Table Number | Iron (ppm), Test | Iron (ppm), Control | Difference ( % ) |
|---|---|---|---|
| 27 | 2700 | 11000 | - 75.45 |
| 28 | 11000 | 3800 | |
| 29 | 1480 | 1706 | -13.25 |
| 33 | 42.9 | 49.0 | - 12.45 |
| 34 | 60.2 | 62.5 | -3.68 |
| 35 | 67.4 | 53.5 | 25.98 |
| 36 | 146 | 73.1 | 99.73 |
| 37 | 37.7 | 34.6 | 8.96 |
| 38 | 55.6 | 49.2 | 13.01 |
| 39 | 73.6 | 52.3 | 21.30 |
| 40 | 47.1 | 42.8 | 10.05 |
| 41 | 34.2 | 30.8 | 11.04 |

Difference % = $(\text{Iron}_{test} - \text{Iron}_{control}) \times 100\% / \text{Iron}_{control}$

ANOVA

Column F Value = 0.0111; Prob.>F = 0.1641
Row F Value = 2.7175; Prob.>F = 0.1120

# Table 46

## Iron Amount In Overflow Portion Of The Hydrocyclone-Treated Scale

| Table No | Iron(mg), Test | Iron(mg),Control | Difference* (mg) | Percent Difference |
|---|---|---|---|---|
| 27 | 0.68 | 1.183 | -0.503 | - 42.52 |
| 28 | 0.42 | 1.00 | -0.58 | - 58.00 |
| 30 | 17.202 | 18.232 | -1.03 | - 5.65 |
| 33 | 0.128 | 0.098 | 0.03 | 30.61 |
| 34 | 1.065 | 1.107 | -0.042 | - 3.79 |
| 35 | 1.27 | 1.007 | 0.263 | 26.12 |
| 36 | 2.559 | 1.224 | 1.335 | 109.1 |
| 37 | 0.208 | 0.180 | 0.028 | 15.56 |
| 38 | 0.946 | 1.052 | -0.106 | -10.08 |
| 39 | 1.351 | 1.021 | 0.33 | 32.32 |
| 40 | 0.051 | 0.027 | 0.024 | 88.89 |
| 41 | 0.055 | 0.051 | 0.004 | 7.84 |

* Difference = $\text{Iron}_{\text{test}}$ - $\text{Iron}_{\text{control}}$; Difference % = Difference x 100% / $\text{Iron}_{\text{control}}$

ANOVA

| | | |
|---|---|---|
| Column | F Value = 0.01545; | Prob.>F = 0.1933 |
| Row | F Value = 295.172; | Prob.>F = $1.212 \times 10^{-11}$ |

Impurity iron in scale is attracted during the scale decomposition process by the magnetic field. Iron is moved to the overflow portion by the hydrocyclone. Larger scale particles from the underflow of the magnetic treatment contains less iron than that in the overflow portion.

## Table 47

## Iron Amount In Overflow Suspension Of -230 Mesh Scale

| Table No., Method | Iron (mg), Test | Iron (mg), Control | Difference* (mg) | Difference % |
|---|---|---|---|---|
| 30, a, 5cycl. | 26.202 | 26.152 | 0.050 | 0.19 |
| 34, b, 1 cycl. | 2.340 | 2.432 | -0.092 | - 3.78 |
| 35, b, 5 cycl. | 2.992 | 2.895 | 0.097 | 3.35 |
| 36, b, 5 cycl. | 4.360 | 3.079 | 0.281 | 9.13 |
| 38, c, 1 cycl. | 2.593 | 2.613 | -0.020 | -0.77 |
| 39, c, 5 cycl. | 3.285 | 2.591 | 0.694 | 26.79 |

* Difference = Iron $_{test}$ - Iron $_{control}$ ; Difference % = Difference x 100% / Iron $_{control}$

ANOVA (One way)

F Value = 0.003723; Prob.>F = 0.094897

## Table 48

## Iron Amount In Overflow Suspension Of -120/+230 Scale

| Table no., Method | Iron (mg), Test | Iron (mg), Control | Difference* (mg) | Difference % |
|---|---|---|---|---|
| 29, a, 5 cycl. | 3.238 | 2.769 | 0.469 | 16.94 |
| 33, b, 5 cycl | 1.141 | 1.168 | -0.027 | -2.31 |
| 37, c 5 cycl. | 0.978 | 0.965 | 0.013 | 1.35 |

* same as in table 47.

ANOVA (One Way)

F Value =0.02690; Prob.>F =0.24466

# Table 49

## Iron Amount Of Overflow Suspension Of The Treated Scale

| Table Number | | | Iron (mg), Test | Iron (mg), Control | Difference* (mg) |
|---|---|---|---|---|---|
| 27, | a, | -18/+35 | 3.414 | 3.964 | -0.550 |
| 28, | a, | -35/+60 | 3.730 | 4.590 | -0.86 |
| 29, | a, | -120/+230 | 3.238 | 2.769 | 0.469 |
| 30, | a, | -230 | 26.202 | 26.152 | 0.050 |
| 31, | b, | -18/+35 | 0.959 | 1.059 | -0.100 |
| 32, | b, | -18/+35 | 0.537 | 0.522 | 0.015 |
| 33, | b, | -120/+230 | 1.141 | 1.168 | -0.027 |
| 34, | b, | -230 | 2.340 | 2.432 | -0.092 |
| 35, | b, | -230 | 2.992 | 2.895 | 0.097 |
| 36, | b, | -230 | 4.360 | 3.079 | 0.281 |
| 37, | c, | -120/+230 | 0.978 | 0.965 | 0.013 |
| 38, | c, | -230 | 2.593 | 2.613 | -0.020 |
| 39, | c, | -230 | 3.285 | 2.591 | 0.694 |
| 40, | c , | -35/+60 | 0.791 | 0.786 | 0.005 |

* Difference = Iron $_{test}$ - Iron $_{control}$

ANOVA

One Way: F Value = 0.000804, Prob.>F = 0.0448

Two Way:
Column F Value = 0.2636, Prob.>F = 0.7675

Row F Value = 655.05. Prob.>F = $8.645 \times 10^{-6}$

## Conclusion

***Separation of iron from scale*** -- The experiments of magnetic treatment show that there are changes in the iron amount in all methods (A, B, and C). The general trend observed was that under the magnetic field there is more iron in the overflow portion (solution and overflow solid) than in the absence of a magnetic field. More iron was dissolved in the presence of a magnetic field than in its absence. The total iron was matched in test and control samples.

From Tables 43 and 44, it is seen that in all methods used, the iron content of the underflow part of the sample with magnetic treatment was much less than that of the control samples, It is concluded that the magnetic field (4 x 1200 gauss) has some positive effects for iron removal from the scale sized smaller than 18 mesh. ANOVA (Analysis of Variance) showed that probability of identity is less than 4.60% in iron concentration between test and control samples and less than 9.21% in the iron amount between test and control samples. These magnetic separation methods are able to remove iron from scale in a certain degree. The removed iron goes into solution and overflow suspension.

In overflow suspension, the iron amount in the test samples was greater than that in the control samples (Tables 45-49). The results are not as significant as these in underflow suspension. The probability of identity is about 16-19 %(Tables 45-46). When both iron in overflow suspension and in solution are considered, it is hard to tell the difference between test and control because of the high probability of identity (76.75% in Table 49). This is due to the iron measurement error in the solution samples, and possibly solution sample contamination during the separation process.

The magnetic field we used (4 x 1200 gauss) played an important role in iron removal from sodium fluorosilicate scale by the hydrocyclone. It enhanced the iron removal without costing extra energy. We got a significant iron content difference between test samples and control samples. However, in those methods (A, B, and C), iron in scale cannot be completely removed. The reasons may be that the sample spent a short time (1 minute for one cycle) in a magnetic field and the magnetic field strength was too weak (about 4 x 1200 gauss). Increasing the number of cycles the sample suspension passes through the field may help better iron separation. The difference of iron content of the overflow suspension was increased with increasing cycle number (0.694 mg VS. -0.020 mg, and 0.281 mg vs. -0.092 mg in Table 47). Further investigations of increasing time samples spend in the magnetic field are in progress.

## Table 50
## Scale Weight Change In Water Under A Magnetic Field In Method C

| Scale Size (meshes) | Input (g) | Test (g) | Control (g) | ΔW* (g) | ΔW% | T (°C) |
|---|---|---|---|---|---|---|
| 18-35 (5 cycle) | 50.000 | 17.280 | 19.376 | -2.096 | 4.2 | 90 |
| 18-35 (1 cycle) | 50.000 | 24.256 | 28.745 | -4.489 | 8.98 | 90 |
| 18-35 (1 cycle) | 50.000 | 20.136 | 22.673 | -2.538 | 5.08 | 90 |
| 18-35 (5 cycle) | 50.000 | 29.997 | 30.620 | -0.623 | 1.25 | 50 |
| 35-60 (1 cycle) | 50.000 | 18.112 | 18.400 | -0.288 | 0.58 | 90 |
| 60-120 (5 cycle) | 50.000 | 29.296 | 30.116 | -0.820 | 1.64 | 90 |
| -230 (1 cycle) | 50.000 | 36.419 | 37.470 | -1.051 | 2.1 | 95-96 |
| -230 (5 cycle) | 50.000 | 35.005 | 34.769 | +0.236 | 0.5 | 55 |

* $\Delta W = W_{test} - W_{control}$; $\Delta W\% = \Delta W \times 100\% / W_{input}$

***Effect of magnetic field on scale solubility*** -- In all hydrocyclone treatments, the solubility of scale in water was increased under the magnetic field, compared with the control and is summarized in Table 42. Analysis of the variance (ANOVA) shows that there is a significant difference in scale solubility. For column comparison, probability is less than 6.51% and means 93.49 % difference. For small particles, e.g., -230 mesh scale, change in scale solubility in water with five-cycle run magnetic field treatment is more significant than one-cycle run treatment (Table 36 vs. Table 34 in method b and Table 39 vs. Table 38 in method c). The results are consistent with those in Table 19. The results show that magnetic field increases the scale solubility in both water solution and phosphoric acid solution, presumably due to the increase of scale entropy, S, and the unstablization of the sodium fluorosilicate lattice under the magnetic field (Benson, et al, 1994).

In comparing a 1-cycle- run with a 5-cycle- run, we observed more effect from the 1- cycle- run magnetic treatment than five-cycle run for 18-35 mesh scale, and -230 mesh scale (2.1% *vs.* 0.5% for -230 mesh, and 8.98%, 5.08% *vs.* 4.2% for 18-35 mesh, Table 50). There is a kinetic mechanism that under a magnetic field, scale is dissolved in water faster than in the absence of the field. For 1- cycle-run treatment, the equilibrium has not been reached and scale solubility is dependent on the rate of transition from solid scale to aqueous solution. In a magnetic field, the transition rate is faster, and more solid scale is dissolved compared to the control. After 5-cycle- runs, equilibrium is approached, and more solid scale is dissolved and scale solubility difference between the test and the control is less than the difference in the one-cycle- run process ( 8.98 % for 1 cycle *vs.* 4.20% for 5 cycle, 8-35 mesh, at 90°C, Table 50). At a high temperature (90°C), scale is dissolved faster and it takes less time to reach equilibrium compared with the process at room temperature. However, at room temperature, solubility difference between the test and the control samples after a 5-cycle- run was more significant than that after the one-cycle- run process (2.41% *vs.* 1.62%, for -230 mesh, in method C; 0.69% *vs.* 0.12, for -230 mesh, in method B Table 42).

Magnetic effect on solubility was also investigated at higher temperatures, e.g., 50°C and 90°C. The results are listed in Table 50. Preliminary results gave us the confidence that the magnetic effect on scale solubility at a high temperature is more significant than that at room temperature. Since $\Delta S >$ 0 for scale solubility, high temperature has a high $T\cdot \Delta S$ value and makes the free energy change, $\Delta G$, more negative (thermodynamically, $\Delta G = \Delta H - T\cdot \Delta S$), and then make scale more soluble in water. We assume a similar result will be observed with phosphoric acid. Since $\Delta S_{test} > \Delta S_{control}$ in the treatment, T affects more effective to solubility under magnetic field than in absence of the field. For a larger scale (-18/+35 meshes), solubility change for the 5-cycle- run was 1.25% (50°C) and 4.2% (90 °C) (Compared to 0.16 -1.16%, 25 °C Table 42). Treatment at 90°C was more effective than that at 50°C and 23°C. For 60-120 mesh, the solubility difference is 1.64 % at 50 °C, Table 50, compared with 0.86% at 23°C, Table 42).

Concerning scale solubility change and iron removal, we have made some assumptions.Iron species tend to coexist with smaller scale particles and they are located at an interstitial position in the $Na_2SiF_6$ lattice. When $Na_2SiF_6$ scale is dissolved, the iron species in scale goes into the solution whether they are dissolved or not. Under the magnetic field treatment, more small scale particles were observed because of high entropy and a less stable lattice and those small particles are easily dissolved in solution because of their higher specific surface area. It is consistent that the scale shifts to smaller particles under the magnetic field. The more significant effect would be observed if the stronger magnetic field was applied also. Small-size particles were more likely to be dissolved in magnetic field so that the overflow solid after magnetic treatment was less than the control one (18.3611 g *vs.* 19.5231 g, Table 41), while the underflow solid was not changed significantly.

# MAGNETIC TREATMENT OF PHOSPHORIC ACID

## Acid source

The phosphoric acid was obtained over a several-day period from regular production runs. Three kinds of phosphoric acid were used. One acid is 54% ($P_2O_5$) with high solid content. The other two are a 28% acid with low solid content. The iron content of acids are different (Table 51, Table 52). Table 51 shows the characteristics of the 28% acid samples received from two different plants in Florida. As seen, the density is the same but the iron content in solid and the concentration of iron in the acid greatly differs in percentage. This could be due to the different techniques in processing. Table 52 shows the characteristics found for the 54% phosphoric acid. As seen, the data increased as expected.

## Acid characteristics

***Separation and determination of iron in phosphoric acid*** -- Centrifugation was used to separate solids from phosphoric acid suspension (~5 % solid). 45 mL of the acid sample was placed in the plastic centrifuge tube and was centrifuged for 30 minutes at 4000 rpm. The solution was decanted and the wet solid was centrifuged again. The solid was collected and weighed. The solids were digested with aqua regia and adjusted to pH ~ 1.0 for iron measurement. In one acid sample (CF Industries, 7-9-96) with a Fe% ~1.0 g/100 mL, there was less solid found (1.9-2.3 %), and the solid contained less iron (Fe %: 0.5-0.7%) than that (Fe%: 9.29 ± 0.16 % for dark brown solid and 5.36 ± 0.04 % for white solid) in another acid sample (IMC-Agrico), which had an iron content of Fe% - 0.6 g/100 mL.

### Table 51

**Characteristics Of Industrial Phosphoric Acid From Two Plants In Florida**

| Acid Source | CF Industries, Inc.(1996) | IMC-Agrico, Inc.(1992-93) |
|---|---|---|
| Density (g/mL) | 1.33 | 1.33 |
| Iron concentration in acid (%) | 0.75 - 0.83 | 0.5 |
| Iron content in solid (%) | 0.5 - 0.7 | 5.36 ± 0.04 (white, majority)<br>9.26 ± 0.16 (brown, slight amount) |
| Solid content (%) | 1.9 -2.3 | > 2.8 |

The sample tested for table 52 was obtained from CF Industries on February 7, 1997. Prior to this date, 28% phosphoric acid was being tested. As previously stated, there was an increase in the observational data.

## Table 52

**Characteristic of 54% phosphoric acid (CF Industries, 2-10-97)**

| | | |
|---|---|---|
| Acid density | 1.68 g/mL | |
| Solid content | 9.85 ± 0.61 % | |
| Iron content in acid suspension | 1.37 ± 0.06% | |
| Chromium content in acid suspension | 81.9 ± 2.8 ppm | |
| Iron in solid | 10.64 % | |
| Iron in supernatant | 0.341 % (mag), | 0.296 % (non-mag) |
| Chromium in supernatant | 72.9 ppm<br>74.64 (ppm) (mag), | <br>71.03 (ppm) (non-mag) |

## Removal of unwanted metals and materials in phosphoric acid by means of magnetic separation

***Magnetic Treatment Sedimentation under magnetic field; static test.*** The phosphoric acid(28 %) suspension was placed under a magnetic field with a 4 x 1200 gauss magnet set. The control was set without the magnetic field. The samples from the test and control were taken and were measured for iron content. There was no significant difference between control and test results after 16 days treatment. The iron concentration for control was 0.618% and test was 0.614%.

***Magnetic Treatment, Pump method*** -- The acid suspension was passed through the magnetic field (4X 1200 gauss strength) by the sigmamotor pump (Fig 2). The suspension was allowed to circulate for a certain period. Table 53 indicates that the iron content in the phosphoric acid was decreased with treatment time or time in the magnetic field. When under the magnetic field, the iron precipitated because paramagnetic particles were attracted to the magnetic field. The difference between time zero and 13 hours was statistically significant (using a t-test, $P = 0.0028$), though the difference between zero and 6 hours was not ($P = 0.126$).

## Table 53
### Effect Of Magnetic Field On Iron In Phosphoric Acid Using The Pump Method

| Treatment time (hours) | Total iron content (%) |
|---|---|
| 0 | 0.657 ± 0.009 |
| 6 | 0.642 ± 0.001 |
| 13 | 0.614 ± 0.007 |

***Magnetic treatment - Hydrocyclone method*** -- The phosphoric acid(28%) suspension was passed through the magnetic field (4 pairs magnets) and two portions of suspension (overflow and underflow) were collected (Fig. 9). Both the underflow portion and overflow portions were filtered and the filtrates were analyzed for total iron content. The results are shown in table 54. Two types of samples were used: low-solid suspension (essentially the supernatant, separated from the solid which settled to the bottom of the container) and high-solid suspension (which consisted of the total acid, with all solids dispersed).

The iron content in the underflow fraction, which contained larger particles, was greater than that in the overflow fraction (Table 54). In the presence of a magnetic field, more iron was transferred to underflow by the hydrocyclone. The mechanism is presumably a combination of paramagnetism and the fluid dynamics of iron. The situation is complicated because there are several forms of iron compounds suspended in wet-processed phosphoric acid (Frazier, 1992). Two major iron forms in the 28.5% ($P_2O_5$) acid at 25°C are $FeH_3(PO_4)_2 \cdot 4H_2O$, and $Fe_3H_9(PO_4)_6 \cdot H_2O$ When the temperature was increased to 75°C only $FePO_4 \cdot 2H_2O$ was observed in 28.5%($P_2O_5$) acid suspension (Frazier, 1992). Like the temperature effect, we assumed that the magnetic field may change the iron composition in the $Fe_2O_3$-$(NH_4)_2O$-$P_2O_5$-$H_2O$ system, affect the solubility of iron compounds, and then affect the sludge precipitation. An additional contributor to postprecipitation could be the breakdown of iron- and aluminum-fluorine complexes during the magnetic treatment, evolving fluoride and freeing additional iron and aluminum for sludge formation.

Table 54 shows the results of the placing the acid in a magnetic field and passing it through the hydrocyclone also. The results show that, as previously stated, the underflow portion obtains more of the iron particles. This is due to the magnetic field and the fluid dynamics of iron on that field.

## Table 54

### Results Of Treatment Of Iron In Phosphoric Acid With A Magnetic Field(2 X 1200 Gauss) In Combination With A Hydrocyclone (cf. Fig 9)

| Sample | Portion | Volume (mL) | Total Iron Concentration, % | $P_2O_5$ ( %) | P* | Significant* |
|---|---|---|---|---|---|---|
| INITIAL | ----- | 3000 | 0.657 ± 0.009 | 27.0 | | |
| LOW- SOLID SUSPENSION | | | | | | |
| | Overflow | 2100 | 0.595 ± 0.012 | 27.5 | 0.0018 | Yes |
| | Underflow | 900 | 0.673 ± 0.014 | 27.0 | 0.1646 | No |
| HIGH- SOLID SUSPENSION | | | | | | |
| | Overflow | 2000 | 0.680 ± 0.011 | 27.4 | 0.0132 | Yes |
| | Underflow | 1000 | 0.736 ± 0.010 | 27.1 | 0.0006 | Yes |

**P = probability based upon null hypothesis and yes or no [Is there a significant difference between the initial concentration (low-solid suspension) and overflow or underflow, based upon Student's t-test]. For both suspensions, the difference between overflow and underflow was statistically significant.**

Table 54a shows similar findings as table 54. The different number of cycles were used to see which amount would give the best results. The only difference is that table 54 deals with the phosphoric acid only whereas the following table shows results from working with a phosphoric acid suspension. The results are consistant with those obtained above, showing that the underflow gets more of the iron than the overflow area.

# Table 54a

## Results Of Treatment Of Phosphoric Acid Suspension With A Magnetic Field (2 x 1200 Gauss) In Combination With A Hydrocyclone. (cf. Fig.9)

| Portion | Initial | Overflow | Underflow |
|---|---|---|---|
| 1-CYCLE | | | |
| Volume (mL) | 2000 | 1460 | 540 |
| $P_2O_5$ (%) | 27.0 | 27.5 | 27.0 |
| Iron (g/100 mL) | 0.675 ± 0.005 | 0.613 ± 0.015 | 0.733 ± 0.015 |
| Iron (g) | 12.52 | 7.91 | 4.14 |
| 10-CYCLE | | | |
| Volume (mL) | 2000 | 1390 | 490 |
| $P_2O_5$ (%) | 27.0 | 27.3 | 27.0 |
| Iron (g/100mL) | 0.675 ± 0.005 | 0.684 ± 0.006 | 0.767 ± 0.010 |
| Iron (g) | 12.42 | 9.03 | 3.99 |

Student's t-Test (For Iron Concentration In Solution)

| | | |
|---|---|---|
| 1-CYCLE TREATMENT | | |
| Overflow *vs.* Initial: | t = -6.629, | Prob. = 0.00269 |
| Underflow *vs.* Initial | t = 6.470, | Prob. = 0.00294 |
| Underflow *vs.* Overflow | t = 9.837, | Prob. = 0.00060 |
| 10-CYCLE TREATMENT | | |
| Overflow *vs.* Initial | t = 2.129, | Prob. = 0.10028 |
| Underflow *vs.* Initial | t = 14.205, | Prob. = 0.00014 |
| Underflow *vs.* Overflow | t = 12.496, | Prob. = 0.00024 |

Table 54b is similar to those shown above except the magnetic field changed. The results obtained show that the underflow portion gets more of the iron than the overflow portion, staying consistant with previous experiments done. It also shows that as the cycles increase, more iron was removed from the acid.

## Table 54b

### Results Of Treatment Of Phosphoric Acid Suspension With A Magnetic Field (2 x 2000 Gauss) In Combination With A Hydrocyclone (cf. Fig.9)

| Portion | Volume (mL) | Solution | | $P_2O_5$ (%) | Solid | |
|---|---|---|---|---|---|---|
| | | Iron conc. (g/100 mL) | Iron amount (g) | | Solid amount (g) | Iron amount (g) |
| INITIAL | 2000 | 0.899 ± 0.009 | 15.55 | 27.6 | 82.50 | 0.320 |
| 1-CYCLE | | | | | | |
| Underflow | 500 | 0.886 ± 0.004 | 4.870 | 27.3 | 32.81 | 0.132 |
| Overflow | 1500 | 0.898 ± 0.008 | 10.596 | 28.0 | 72.65 | 0.287 |
| 10-CYCLE | | | | | | |
| Underflow | 400 | 0.941± 0.005 | 4.705 | 27.5 | 26.50 | 0.107 |
| Overflow | 1600 | 0.912 ± 0.016 | 10.31 | 27.7 | 73.63 | 0.270 |

Student's t-Test

1-CYCLE TREATMENT

| | | |
|---|---|---|
| Underflow *vs.* Initial | t = -2.1794, | Prob. = 0.09480 |
| Overflow *vs.* Initial | t = -1.6512, | Prob. = 0.17405, NS* |
| Underflow *vs.* Overflow | t = -0.2673, | Prob. = 0.80248, NS* |

10-CYCLE TREATMENT

| | | |
|---|---|---|
| Underflow *vs.* Initial | t = 7.0654, | Prob. = 0.00212 |
| Overflow *vs.* Initial | t = 1.2452, | Prob. = 0.28103, NS* |
| Underflow *vs.* Overflow | t = 3.0597, | Prob. = 0.03767 |

***NS = not significant**

Table 55 shows the results obtained from the acid when placed in a magnetic field of 4000 gauss, passed through a hydrocyclone, and only done for one cycle.Once again, the underflow is seen to have a greater amount of iron than the overflow has. The phosphate value is not changed in the magnetic treatment combined with a hydrocyclone.

## Table 55

## Results Of Treatment Of 28% acid Suspension With A Magnetic Field (2 x 2000 Gauss) In Combination With A Hydrocyclone (Fig. 9), One-Cycle run.

| Portion | Solution | | | Solid | |
|---|---|---|---|---|---|
| | Volume (mL) | Iron Conc. (g/100 mL) | Iron Amount (g) | Solid Amount (g) | Iron Amount (g) |
| Initial | 6400 | 1.080 ± 0.008 | 69.12 | 154.1 | 1.11 |
| Underflow | 2200 | 1.120 ± 0.002 | 24.64 | 72.5 | 0.44 |
| Overflow | 4200 | 1.017 ± 0.003 | 42.71 | 131.2 | 1.00 |

Iron mass balance: Initial 70.23 g, Treatment 68.79 g

STUDENT'S t-TEST

for iron concentration in solution

| | | | | |
|---|---|---|---|---|
| Underflow | *vs.* | Initial | t = 8.023, | Prob. = 0.00131 |
| Overflow | *vs.* | Initial | t = -12.677, | Prob. = 0.00022 |
| Underflow | *vs.* | Overflow | t = 55.678, | Prob. = $6.23 \times 10^{-7}$ |

* A hydrocyclone had an inlet diameter of 1.8 cm, an overflow outlet ("vortex finder") diameter of 1.8 cm, and an underflow orifice diameter of 0.4 cm. The connecting Tygon® tubing was 1" diameter. The WPA suspension was magnetically stirred.

The results in table 56 were obtained when the treatment of the acid was achieved by using a different setting than those above. The hydrocyclone was changed to a medium size, the height was changed to 1.0 m and the magnetic field stayed the same. Again the results support the fact that the underflow receives more iron than the overflow.

## Table 56

### Magnetic Treatment Of 28% Phosphoric Acid With A Hydrocyclone, Medium Size, h = 1 m , 2 X 2000Gauss

| Portion | Solution | | | $P_2O_5$ | Solid | |
|---|---|---|---|---|---|---|
| | Volume (mL) | Iron Conc. (g/100mL) | Iron Amount (g) | (%) | Solid Amount (g) | Iron Amount (g) |
| Initial | 1960 | 1.014 ± 0.013 | 19.87 | 27.5 | 52.12 | 0.255 ± 0.003 |
| Underflow | 705 | 0.988 ± 0.013 | 6.97 | 28.0 | 20.90 | 0.138 ± 0.001 |
| Overflow | 1255 | 1.018 ± 0.009 | 12.78 | 27.6 | 31.63 | 0.107 ± 0.001 |

Iron balance: Initial 20.13 g; Treated 20.00 g

STUDENT t-TEST

| | | |
|---|---|---|
| Underflow *vs.* Initial | t = -2.3879 | Prob. = 0.07534 |
| Overflow *vs.* Initial | t = 0.4532 | Prob. = 0.67388 |
| Underflow *vs.* Overflow | t = -3.2222 | Prob. = 0.03222 |

Table 57 shows the results of what occurred when the height condition changed from 1.0 m to 1.2 m. All other conditions remained the same.

## Table 57

### Magnetic Treatment Of 28% Phosphoric Acid By A Medium Size Hydrocyclone, h = 1.2 m, 2 X 2000 Gauss

| Portion | Solution | | | | Solid | |
|---|---|---|---|---|---|---|
| | Volume (mL) | Iron Conc. (g/100 mL) | Iron Amount ( g ) | $P_2O_5$ (%) | Solid Amount ( g ) | Iron Amount ( g ) |
| Initial | 1970 | 1.028 ± 0.002 | 20.25 | 27.5 | 58.83 | 0.382 ± 0.005 |
| Underflow | 575 | 1.012 ± 0.003 | 5.82 | 27.9 | 16.67 | 0.052 ± 0.001 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Overflow | 1395 | 0.999 ± 0.008 | 13.94 | 28.0 | 41.66 | 0.038 ± 0.003 |

Iron balance: Initial 20.63 g; Treated 19.85 g

STUDENT'S t-TEST

| | | |
|---|---|---|
| Underflow *vs.* Initial | t = -8.4853 | Prob. = 0.001058 |
| Overflow *vs.* Initial | t = -5.8523 | Prob. = 0.004253 |
| Underflow *vs.* Overflow | t = 2.5885 | Prob. = 0.060779 |

Table 58 shows the results obtained with the first experiment done on the 54% phosphoric acid sample. Here the difference is 3.15% between the different flow portions.

## Table 58

## Hydrocyclone Treatment Under A Magnetic Field of 54% Phosphoric Acid

| | Initial | Overflow | Underflow | Difference |
|---|---|---|---|---|
| Supernatant Volume (mL) | 6000 | 3500 | 2500 | |
| $P_2O_5$ (%) | 50.4 | 49.8 | 49.7 | |
| Iron content (g/100 mL) | | 0.495 ± 0.005 | 0.480 ± 0.015 | 3.15% |

Student's t -test (overflow *vs.* underflow):

t = 2.3522, Prob. = 0.04049

* Difference = (Iron, overflow - Iron, underflow ) x 100% / (Iron, underflow)

***Vertical symmetric way*** -- The phosphoric acid solution was suspended and passed down a Y-tube with a magnet present, an arrangement that was supposed to induce a separation on the basis of paramagnetism. We used four 1200 gauss magnets. The system is represented schematically in Fig, 11. The design was changed in two ways: vertical treatment was used, and the input volume was made about the same as the sum of the two output volumes by changing the diameters of the tubes. This way, the residence time in the magnetic field would increase, and there should be a pressure drop. Results are considered in Table 59.

## Table 59

## Effect Of A Magnetic Field Using The Y-Tube Attraction Method, As Indicated In Fig.11, With CF Industries Sample ( 7-9-96) Acid

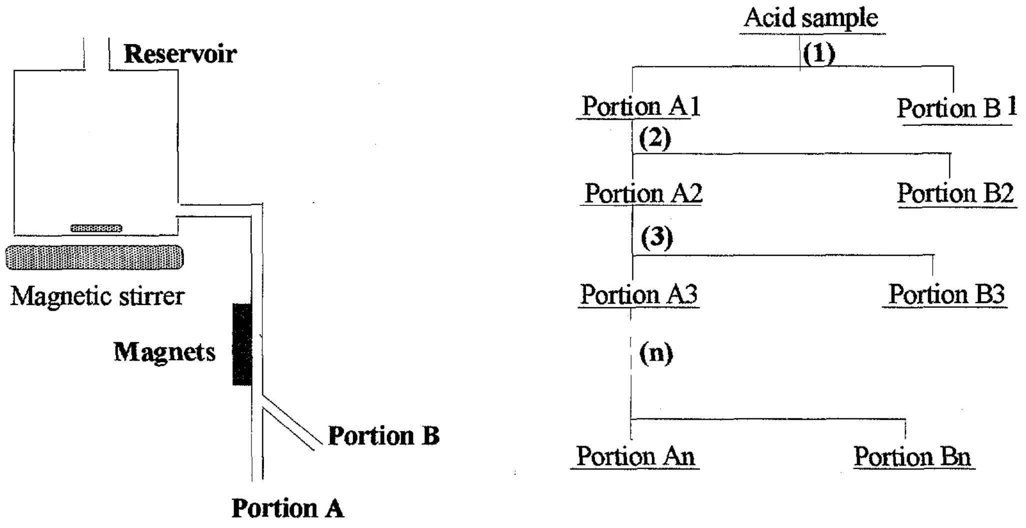
| Sample | Iron Content, % |
|---|---|
| INITIAL | 1.09± 0.02 |
| 1- CYCLE TREATMENT | |
| $A_1$ portion | 1.123 ±0.010 |
| $B_1$ portion | 1.102 ± 0.009 |
| 5- CYCLE TREATMENT | |
| $A_5$ portion | 1.134 ± 0.011 |
| B portion ($B_1$, $B_2$, ... $B_5$) | 1.119 ± 0.013 |
| 10- CYCLE TREATMENT | |
| $A_{10}$ portion | 1.123 ± 0.011 |
| B portion ($B_1$, $B_2$, ... $B_{10}$) | |
| B (FURTHER TREATMENT) | |
| 10- CYCLE | |
| A portion | 1.134±0.015 |
| B fraction (combined) | 1.139 ± 0.010 |

The results from table 60 show what happened when the acid was filtered before going through the magnetic field. There is indication that some of the iron may have been removed during the filtering process therefore making the results lower than what was previously obtained.

## Table 60

## Effect Of A Magnetic field Using The Y-Tube Attraction Method (Fig 11) With Filtered Acid Sample (IMC-Agrico)

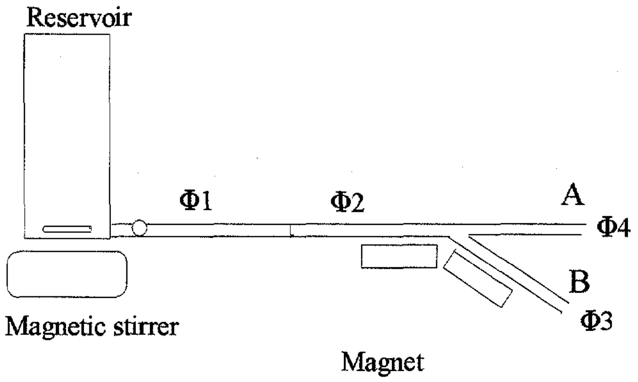
| Sample | Iron content, % | |
|---|---|---|
| Initial | 0.740 ± 0.011 | |
| 1- cycle treatment | | |
| $A_1$ portion | 0.747 ± 0.015 | |
| $B_1$ portion | 0.722 + 0.011 | |
| 5- cycle treatment | | |
| $A_5$ portion | 0.757 + 0.015 | |
| B portion | 0.757 +0.015 | ($B_1$, $B_2$, ...$B_5$) |
| B collection (5- cycle) further treatment | | |
| 5- cycle | | |
| B ($B_1$, $B_2$, ...$B_5$) | 0.784 ± 0.020 | |
| A | 0.702 ± 0.010 | |



SCHEMATIC REPRESENTATION OF MAGNETIC TREATMENT OF IRON IN PHOSPHORIC ACID USING AN ATTRACTION METHOD

**FIGURE 11**

***Horizontal asymmetrical way*** -The magnetic apparatus was set horizontally and the reservoir was placed 10 cm above the outlet (Fig. 12). Two magnets with 2000 gauss each were used. The 28% phosphoric acid suspension with 4-5% of solid was passed through the magnetic field once. The solid content was measured for each portion before and after the magnetic treatment. In methods B and C, solid content in phosphoric acid suspension was increased after the magnetic treatment (Table 61).



SCHEMATIC REPRESENTATION OF MAGNETIC TREATMENT OF INDUSTRIAL-GRADE PHOSPHORIC ACID USING A Y-TUBE ATTRACTION METHOD(HORIZONTAL ASYMMETRICAL WAY)

**FIGURE 12**

(Procedure A: $\phi1$ = 25 mm; $\phi2$ = 18 mm; $\phi3 = \phi4$ = 18 mm; Procedure B: $\phi1 = \phi2$ =25 mm, $\phi3 = \phi4$=18mm; Procedure C: $\phi1 = \phi2$ = 7 mm, $\phi3 = \phi4$ = 5 mm; where $\phi n$ is the diameter at the position indicated.)

## Table 61

## Effect Of A Magnetic Field Using The Horizonal Attraction Method, As Indicated In Fig. 12, With 28% CF Industries Phosphoric Acid Suspension.

| Portion | Solution |  | Solid |  |
|---|---|---|---|---|
|  | Iron conc. (%) | Iron amount(g) | Solid amount (g) | Iron amount (g) |
| PROCEDURE A* |  |  |  |  |
| Initial | 1.072 ± 0.006 | 66.84 | 300.4 | 1.718 |
| Magnet side | 1.068 ± 0.031 | 18.42 | 77.66 | 0.398 |
| Other side | 1.100 ± 0.016 | 49.61 | 209.1 | 0.790 |
| PROCEDURE B* |  |  |  |  |
| Initial | 1.009± 0.001 | 60.54 | 292.3 | 1.441 |
| Magnet side | 1.060 ± 0.018 | 10.60 | 60.28 | 0.268 |
| Other side | 1.068 ± 0.031 | 53.40 | 296.0 | 1.360 |
| Procedure C*: |  |  |  |  |
| Initial | 0.964 ± 0.019 | 19.09 | 84.95 | 0.347 |
| Magnet side | 0.904 ± 0.005 | 8.86 | 46.29 | 0.189 |
| Other side | 0.944 ± 0.016 | 9.44 | 48.74 | 0.199 |

* The experiment was done on the apparatus described (Fig. 12). In procedure A, the inlet tube (25 mm i.d.) was tapered to 18 mm i.d. and was connected with two tubes of 18 mm i.d.. In procedure B, the inlet tube was 25 mm i.d. and was connected with two tubes of 18 mm. i.d.. In procedure C, the inlet tube was 7 mm i.d. and outlet tubes were 5 mm i.d.. In B and C, the flow rate (mL/min) of inlet was twice as much as that of outlet.

Table 62 shows the results obtained when using the horizontal attraction method on the acid suspension from CF Industries. There was an uneven flow between the magnetic and nonmagnetic side.

# Table 62

## Effect Of A Magnetic Field Using The Horizontal Attraction Method, As Indicated In Fig. 12, with CF industries phosphoric acid suspension

| | | Solution | | Solid | |
|---|---|---|---|---|---|
| Sample | Volume (mL) | Iron conc. (g/ 100 mL) | Iron amount (g) | Solid amount (g) | Iron amount (g) |
| Initial | 6000 | 1.006 ± 0.005 | 60.36 | 137.0 | 1.06 |
| Magnetic side* | 2585 | 1.006 ± 0.005 | 26.01 | 66.1 | 0.25 |
| Other side | 3415 | 0.993 ± 0.012 | 33.91 | 75.1 | 0.74 |

Iron mass balance: Initial: 61.42 g, Treated: 60.92 g

Student's t-test:

Magnetic side *vs.* Initial: t = -0.02872, Prob. = 0.9785

Other side *vs.* Initial: t = -1.6778, Prob. = 0.1687

Magnetic side vs. Other side t = 1.6064, Prob. = 0.1835

*Procedure A was used

# Table 63

## Magnetic Treatment Of A Phosphoric Acid By The Horizontal Attraction Method, Long Tube, 2 X 2000 Gauss (Fig. 12)

| | Solution | | | Solid | |
|---|---|---|---|---|---|
| Sample | Volume (mL) | Iron conc. (g/100mL) | Iron amount (g) | Solid amount (g) | Iron amount (g) |
| Initial | 6400 | 1.098 ± 0.025 | 70.29 ± 1.57 | | 0.508±0.002 |
| Magnetic side | 3215 | 1.130 ± 0.008 | 36.34 ± 0.19 | | 0.161 ± 0.001 |
| Other side | 3185 | 1.139 ± 0.003 | 36.29 ± 0.08 | | 0.160 ± 0.000 |

Iron mass balance Initial : 70.80 g, Treated: 73.05 g.

Student's t-test:

| | |
|---|---|
| Magnetic side *vs.* Initial | t = 2.1596, Prob. = 0.09693 |
| Other side *vs.* Initial | t = 2.8784, Prob. = 0.04508 |
| Magnetic side vs. Other side | t = -1.9692, Prob. = 0.12028 |

## Table 64

## Summary Of The Phosphoric Acid Treatment By Magnets Combined With A Hydrocyclone

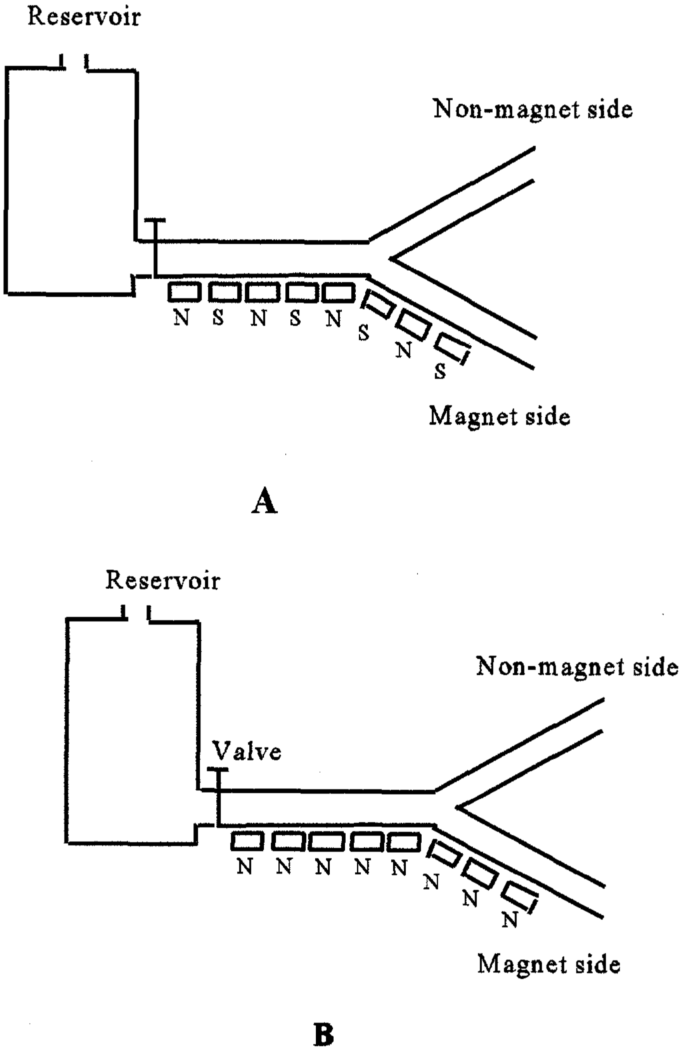
| | Iron concentration (g/ 100 mL) | | |
|---|---|---|---|
| Table, Method | Initial | Underflow | Overflow |
| 54a, 1 cycle | 0.675 $^{+/-}$0.005 | 0.733 $^{+/-}$0.015 | 0.613 $^{+/-}$0.015 |
| 54a, 10 cycle | 0.675 $^{+/-}$0.005 | 0.767 $^{+/-}$0.010 | 0.684 $^{+/-}$0.006 |
| 54b, 1 cycle | 0.899 $^{+/-}$0.009 | 0.866 $^{+/-}$0.004 | 0.898 $^{+/-}$0.008 |
| 54b, 10 cycle | 0.899 $^{+/-}$0.009 | 0.941 $^{+/-}$0.005 | 0.912 $^{+/-}$0.016 |
| 55, 1 cycle | 1.080 $^{+/-}$0.008 | 1.120 $^{+/-}$0.002 | 1.017 $^{+/-}$0.003 |
| 56, 1 cycle | 1.014 $^{+/-}$0.013 | 0.988 $^{+/-}$0.013 | 1.018 $^{+/-}$0.009 |
| 57, 1 cycle | 1.028 $^{+/-}$0.002 | 1.012 $^{+/-}$0.003 | 0.999 $^{+/-}$0.008 |

## Table 65

## Summary of 28% Phosphoric Acid Suspension Treatment By An Asymmetrically Magnetic Attraction Method

| | Iron concentration (g/100 mL) | | |
|---|---|---|---|
| Table, Method | Initial | Magnet side | Non-magnet side |
| 61, A | 1.072 $^{+/-}$0.006 | 1.068 $^{+/-}$0.031 | 1.100 $^{+/-}$0.016 |
| 61, B | 1.009 $^{+/-}$0.001 | 1.060 $^{+/-}$0.018 | 1.068 $^{+/-}$0.031 |
| 61, C | 0.964 $^{+/-}$0.019 | 0.904 $^{+/-}$0.005 | 0.944 $^{+/-}$0.016 |
| 62, B | 1.006 $^{+/-}$0.005 | 1.006 $^{+/-}$0.005 | 0.993 $^{+/-}$0.012 |
| 63, B | 1.098 $^{+/-}$0.025 | 1.130 $^{+/-}$0.008 | 1.139 $^{+/-}$0.003 |

***Horizontally symmetric PVC Y-tube*** -- The treatment process is schematically described in Fig 13. A ½" PVC is used to make the symmetric Y-tube with a 90 degree angle between the two outlets. The one inlet and two outlets were the same size. The Y-tube is horizontally placed and connected to the reservoir by Tygon® tubing. A flow controller is placed on the tubing. The distance between the reservoir and the Y-junction is 10 inches or 75 inches, which was adjusted for the desired flow rate. Magnets (with different strength and numbers) are placed on one side of the Y-tube, which is assigned as the magnet side. Magnets are placed with pole alternating, randomly, and parallel. For phosphoric acid treatment, 5 liters of phosphoric acid (either supernatant or suspension) is passed through the Y-tube once and two portions of acid are collected. Iron and chromium were measured by the colorimetric method.



SCHEMATIC REPRESENTATION OF MAGNETIC TREATMENT OF PHOSPHORIC ACID SUSPENSION USING ½" PVC SYMMETRIC Y-TUBE ATTRACTION METHOD.

**FIGURE 13**

## Table 66
### Magnetic Treatment (4 X 3000 gauss) Of Phosphoric Acid Using A ½" PVC Symmetric Y Tube Attraction Method

| | Control | Magnet side | Non-magnet side | Difference* |
|---|---|---|---|---|
| Aerated acid, supernatant: | | | | |
| Volume (mL) | 2800 | 1365 | 1415 | |
| Iron (g/100 mL) | 0.952 ± 0.003 | 0.971 ± 0.008 | 0.948 ± 0.003 | 2.43 % |

Student's t - test:
magnet *vs.* non-magnet t = 6.802, Prob. = 2.9462 X $10^{-5}$, significant.

* Difference (%) = (Iron, magnet - Iron, non-magnet) X 100 % / Iron, non-magnet.

## Table 67
### Magnetic Treatment (4 X 3000 Gauss) Of 28% Phosphoric Acid Using A ½" PVC Symmetric Y-Tube Attraction Method

| | Control | Magnet side | Non-magnet side | Difference |
|---|---|---|---|---|
| Regular, supernatant: | | | | |
| Volume (mL) | 2960 | 1365 | 1595 | |
| Iron (g/100mL) | | | | |
| 1. | 0.927 ± 0.005 | 0.914 ± 0.008 | 0.904 ± 0.004 | 1.1% |
| 2. | 0.973 ± 0.003 | 0.986 ± 0.007 | 0.972 ± 0.003 | 1.4% |

Student's t - test: mag *vs.* non-mag:
1. t = 1.912, Prob.= 0.104
2. t = 3.306, Prob.= 0.0289

## Table 68

### Magnetic Treatment (4 X 3000 Gauss Plus 2000 Gauss, MCF) Of 28% Phosphoric Acid Using ½" PVC Symmetric Y-Tube Attraction Method

| | Control | Magnet side | Non-mag side | Difference |
|---|---|---|---|---|
| Aerated acid, supernatant: | | | | |
| Volume (mL) | 2750 | 1470 | 1280 | |
| Iron (g/100 mL) | | | | |
| 1. | 0.915 ± 0.003 | 0.948 ± 0.007 | 0.930 ± 0.010 | 1.9% |
| 2. | 0.927 ± 0.00 | 0.945 ± 0.002 | 0.928 ± 0.006 | 1.8% |
| Student's t - test: | | | | |
| mag *vs.* non-mag | | 1. t = 2.43, Prob. = 0.0511 | | significant |
| | | 2. t = 3.95, Prob. = 0.109 | | |
| Regular acid, supernatant: | | | | |
| Volume (mL) | 2960 | 1580 | 1380 | |
| Iron (g/100 mL) | | | | |
| | | 0.922 ± 0.005 | 0.903 ± 0.001 | 2.0% |
| Student's t - test: | | | | |
| mag. *vs.* non-mag. | | t = 6.424, | Prob. = 0.00302 | significant |

## Table 69

### Magnetic Treatment (4 X 3000 Gauss Plus One MCF ) Of 28% Phosphoric Acid Using A ½" PVC Symmetric Y-Tube Attraction Method

| | Control | Magnet side | Non-magnet side | Difference |
|---|---|---|---|---|
| Aerated acid suspension: | | | | |
| Volume (mL) | 2820 | 1330 | 1490 | |
| Iron (g/100mL) | 1.114 ± 0.012 | 1.111 ± 0.015 | 1.103 ± 0.023 | 0.7% |
| Student's t - test: | | | | |
| mag *vs.* non-mag | | t = 0.8929, | Prob. = 0.3870 | Not Significant |
| Regular acid suspension: | | | | |

| | | | | |
|---|---|---|---|---|
| Volume (mL) | 3060 | 1500 | 1560 | |
| Iron (g/100mL) | 1.076 ± 0.020 | 1.102 ± 0.032 | 1.068 ± 0.008 | 3.2 % |
| Student's t - test: | | | | |
| mag. *vs.* non-mag.: | | t = 2.6177, | Prob. = 0.02392 | significant |

## Table 70

## Magnetic Treatment (4 X 3000 Gauss) Of 28% Phosphoric Acid Using A ½" PVC Symmetric Y-Tube Attraction Method

| | Control | Magnet side | Non-magnet side | Difference* |
|---|---|---|---|---|
| **Regular acid suspension:** | | | | |
| Volume (mL) | 3060 | 1520 | 1540 | |
| Iron (g/100mL) | 1.109± 0.058 | 1.134 ± 0.012 | 1.110± 0.036 | 2.2% |
| Student's t-test: | | | | |
| magnet *vs.* non-magnet: | | t = 1.506, | Prob. = 0.16293 | Not Significant |
| Aerated acid suspension: | | | | |
| Volume (mL) | 2800 | 1360 | 1440 | |
| Iron (g/100 mL) | 1.152 ± 0.005 | 1.127 ± 0.034 | 1.089 ± 0.009 | 3.5% |
| Student's t-test: | | | | |
| magnet *vs.* non-magnet: | | t = 2.6737, | Prob. = 0.02334 | significant |

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

# Table 71

## Magnetic Treatment Of 28% Phosphoric Acid Using ½" PVC Y-Tube Attraction Method

| | Control | Magnet side | Non-magnet side | Difference |
|---|---|---|---|---|
| A. 4 x 3000 gauss Neodymium, 2x2000gauss MCF, 1x1200gauss.<br>75 inches long Tygon® tubing | | | | |
| Volume (mL) | 5290 | 3260 | 2030 | |
| Iron (g/100mL) | | 0.910 ± 0.019 | 0.874 ± 0.026 | 4.12 % |
| Student's t-test(mag. *vs.* non-mag.): | | t = 4.83295; Prob. = 2.6545 x $10^{-5}$<br>Significant. | | |
| B. 4 x 3000 gauss Neodymium, 2 x 2000 gauss MCF, 12 x 1200 gauss.<br>75 inches long Tygon® tubing | | | | |
| Volume (mL) | 5230 | 2950 | 2280 | |
| Iron (g/100 mL) | 0.860±0.009 | 0.870±0.013 | 0.863±0.007 | 0.81% |
| Student's t-test (mag. *vs.* non-mag.): | | t = 1.4866; Prob. = 0.1565<br>Not significant. | | |

## Table 72
### Magnetic Treatment Of 28% Phosphoric Acid Using A ½" PVC Y-Tube Attraction Method

| | Control | Magnetic side | Non-magnetic side | Difference |
|---|---|---|---|---|
| Magnets: | 2 x 2000 gauss MCF, 11 x 1200 gauss, 7 x 3000 gauss Neodymium.<br>75 inches long Tygon® tubing | | | |
| Volume (mL) | 4990 | 2520 | 2470 | |
| Iron (g/100 mL) | 0.828±0.007 | 0.869±0.012 | 0.858±0.005 | 1.28 % |
| Student's t-test (mag. *vs.* non-mag.): | | t = 2.5564; Prob. = 0.02112<br>Significant | | |

## Table 73
### Magnetic Treatment Of 28% Phosphoric Acid Using A ½" PVC Y-tube*

| | Magnet side | Non-magnet side | Difference |
|---|---|---|---|
| Acid volume (mL) | 1835 | 1775 | |
| Iron content (g/ 100 mL) | 0.854 ± 0.008 | 0.831 ± 0.004 | 2.77 % |
| Student's t -test | t = 7.4774; | Prob. = $1.317 \times 10^{-6}$ | |

*A 70 inch PVC pipe connects reservoir and Y-junction, 2 X2000 gauss magnets, and 6 x 3000 gauss magnets.

In a shorter Y-tube distance, under 4 x 3000 gauss strength magnetic field, 1.4 -3.5 % iron difference between two portions.( table 66, Table 67, 68, 69, 70, 71, 72, and 73) occurred. In a Y-tube with a long connecting tubing, the fluid rate is reduced. With 4 x 3000 gauss Neodymium, 2 x 2000 MCF (big size magnet) and several 1200 gauss magnets, the iron difference improved up to 4.12 % (Table 71).

In the alternate magnet position (Fig. 13 .A), which is placement of south, north, south, north magnet poles, iron difference is higher (2.97%) than that (-0.80%) in parallel position (Fig. 13. B) in which same side of magnets face the Y-tube (Table 74). The alternate magnet placement strongly keeps pammagnetic particles along the magnetic side wall of tube during their moving down to Y-junction.

## Table 74

### Magnetic Treatment Of 28% Phosphoric Acid By Attraction Using A ½" PVC Y-Tube

| | Control | Magnet side | Non-magnet side | Difference |
|---|---|---|---|---|
| A. Alternately magnetic pole placed (5 x 1200 gauss, 7 x 3000 gauss magnets before the junction, 3 x 3000 gauss magnets after the junction). | | | | |
| Volume (mL) | 5240 | 2635 | 2605 | |
| Iron (g/100 mL) | 0.879 ± 0.006 | 0.902 ± 0.022 | 0.876 ± 0.005 | 2.97 % |
| Student's t-test (mag. *vs.* non-mag.) | | t = 3.4418, | Prob. = 0.0029089 | |
| | | | Significant difference. | |
| ----------------------- | | | | |
| B. Parallel magnetic pole side placed (5 x 1200 gauss, 7 x 3000 gauss magnets before the junction and 3 x 3000 gauss magnets after the junction). | | | | |
| Volume (mL) | 5295 | 2845 | 2450 | |
| Iron(g/100 mL) | 0.886 ± 0.007 | 0.871± 0.003 | 0.878 ± 0.007 | - 0.80 % |
| Student's t - test (mag. *vs.* non-mag.) | | t = -2.3024, | Prob. = 0.035024. | |
| | | | Significant difference. | |

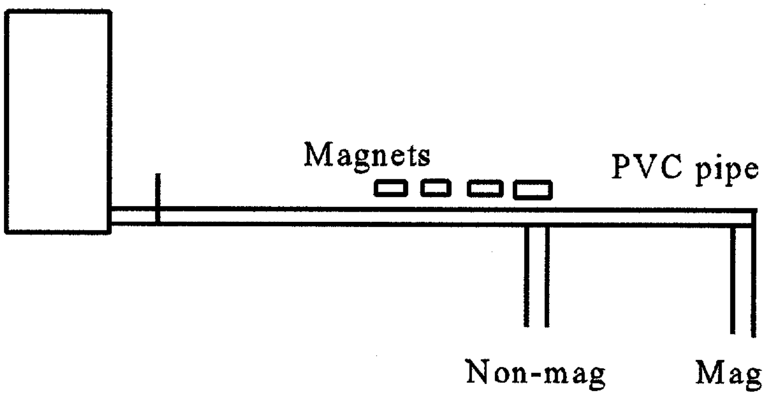
***Horizontal asymmetric T-tube*** **--** The magnets are placed ahead of the T-junction(Fig 14). The phosphoric acid suspension was passed through the magnetic field. It is assumed that paramagnetic materials were attracted by the magnets toward the upper PVC wall and flowed further along the PVC pipe . The diamagnetic material 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 the paramagnetic material. The acid used is 54% phosphoric acid with high solid content (table 52). Acid samples from both portions are centrifuged and the supernatant samples are treated for the iron and chromium measurement.

**Table 75**

**Magnetic treatment of 54% phosphoric acid by the asymmetric T-tube**

| | Magnet portion | Non-magnet portion | Difference* |
|---|---|---|---|
| Supernatant: | | | |
| Iron content (g/ 100 mL) | 0.647 ± 0.024 | 0.584 ± 0.032 | 10.8 % |
| Chromium content (ppm) | 110.3 ± 2.2 | 83.0 ± 0.3 | 32.9% |
| Student' t-test: | magnet *vs.* non-magnet for iron content | | |
| | t = 4.736, | Prob. = 0.000224. | |
| Solid : | | | |
| Iron content(%) | 10.72 ± 0.38 | 10.56 ± 0.14 | 1.5% |
| Student' t-test | t = 1.0904, | Prob. = 0.29695 | |

* Difference = (Iron, mag - Iron, non-mag) x 100% / (Iron, non-mag), density is 1.68 g/mL.



MAGNETIC TREATMENT OF ACID USING HORIZONTAL ASYMMETRIC T-PIPE

**FIGURE 14**

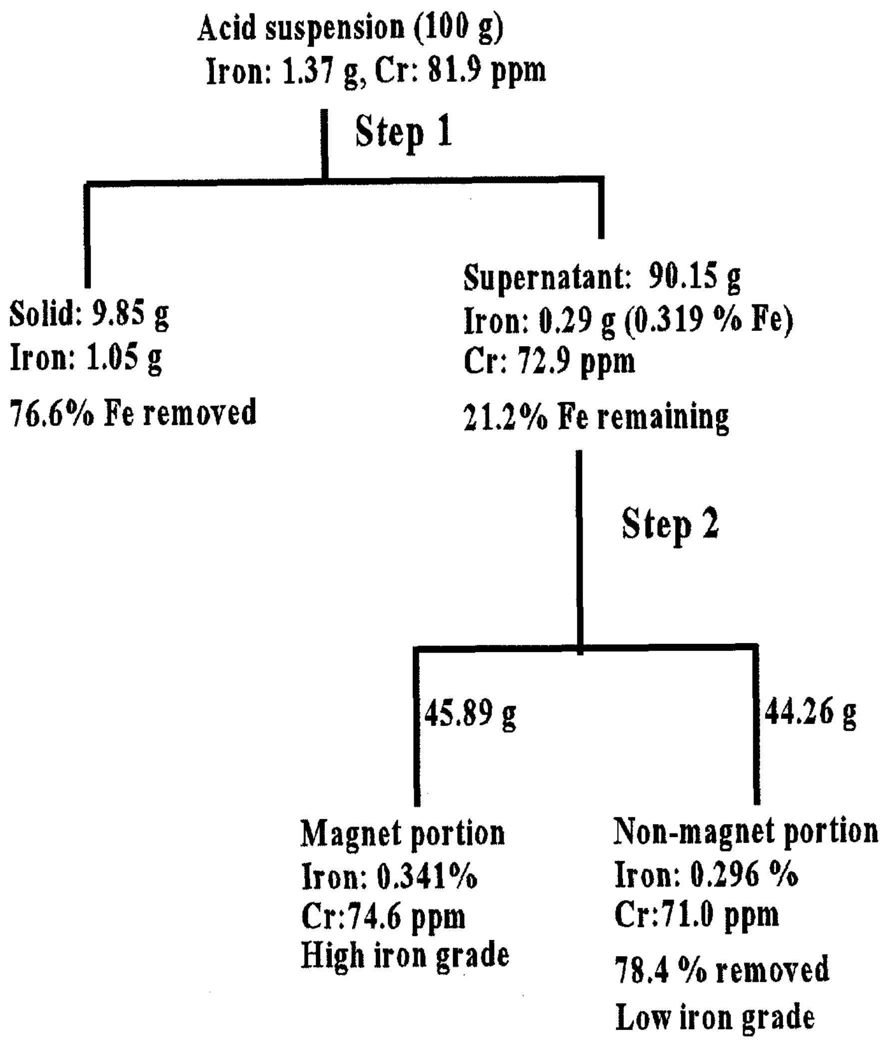
# Table 76

## Magnetic Treatment Of 54% Phosphoric Acid (Supernatant) By The Asymmetric T-Tube

| | Magnet portion | Non-magnet portion | Difference* |
|---|---|---|---|
| Supernatant: | | | |
| Acid volume (mL) | 2800 | 2700 | |
| Phosphate($P_2O_5$) | 49.73 | 50.37 | |
| Iron content (g/100 mL) | 0.573 ± 0.020 | 0.498 ± 0.009 | 15.1% |
| Student's t-test | magnet *vs.* non-magnet | | |
| | t = 10.666, | Prob. = $3.2829 \times 10^{-9}$ | |
| Chromium content (ppm) | 74.64 ± 1.80 | 71.03 ± 2.76 | 5.1 % |
| Student's t-test | magnet *vs.* non-magnet | | |
| | t = 3.283, | Prob. = 0.00468 | |

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

Results showed that there are significant iron differences between the two portions. Acid from the magnet side contains higher iron than acid from the non-magnet side. For the acid suspension treatment at an equal flow rate, a 10.8% iron difference and 32.9 % chromium difference has been achieved, respectively.These changes are statistically significant with the identity probability of <0.1%. However, the iron difference in solid is 1.5%, which is less than that in supernatant acid, and is not statistically significant with the identity probability of 30% (Table 75). For the acid supernatant magnetic treatment, 15.1% iron difference is observed (Table 76) and the phosphate values are unchanged. Chromium also is enriched in the magnetic side portion with a statistically significant difference of 5.1%.



IRON REMOVAL FROM 54 % PHOSPHORIC ACID BY MAGNETIC SEPARATION

**FIGURE 15**

## Table 77

## Magnetic Treatment Of 54% Phosphoric Acid Using An Asymmetric T-Tube*

| | Magnet side | Non-magnet side | Difference |
|---|---|---|---|
| Acid volume (mL) | 1650 | 6200 | |
| Iron content in acid (g/100mL) | 0.435 0.011 | 0.422 0.014 | 2.03% |

Student's t-test Magnet side *vs.* non-magnet side

t=1.9984, prob. = 0.06297

*Fig 14.

For the uneven flow rate, which was a 1 to 4 ratio of magnet side to non-magnet side, there is less significant difference (2%) (Table 77). This means that attracted materials have to be pushed ahead fast so that those materials can get to be separated from the bulk acid. Decreasing the flow rate on the magnet side portion, the paramagnetic materials are not efficiently pushed out and the iron difference is decreased. In this method, the flow rate and magnetic strength are attributed to the separation efficiency.

***Aeration of phosphoric acid suspension*** --The phosphoric acid suspension was obtained from CF Industries and contained 2-2.2 % solid. A 3-liter suspension was magnetically stirred and the gas (air or oxygen ) was passed through the suspension. The suspension was covered to minimize the loss of water. The suspension was centrifuged at 4000 rpm (Sorvall SS-3 model) for 30 minutes and the supernatant was measured for iron content by a thiocyanate colorimetric method. After a 24-hour oxygen treatment, the suspension was stirred for further precipitation of iron(III) compounds. More brown precipitate was found on the wall of the acid container. (Results are summarized in Table 78.)

## Table 78
### Treatment Of Phosphoric Acid* Suspension By Aeration

| Sample | Iron concentration ( g/100 mL) | t-test (vs. Initial) t | Prob. | Sig. Diff.** | Chromium ( $\mu$g/mL) |
|---|---|---|---|---|---|
| Initial | 1.116 ± 0.005 | | | | 65.2 ± 3.9 |
| Air treatment: | | | | | |
| 6 hours | 1.105 ± 0.002 | -3.979 | 0.01641 | Y | 66.0 ± 6.8 |
| 18 hours | 1.099 ± 0.003 | -5.451 | 0.00550 | Y | 61.4 ± 4.2 |
| Oxygen: | | | | | |
| 6 hours | 1.109 ± 0.012 | -1.0575 | 0.34990 | N | 62.8 ± 3.0 |
| 24 hours | 1.070 ± 0.050 | -1.525 | 0.20195 | N | 56.7 ± 2.8 |

* Density of phosphoric acid used was 1.33 g/mL.

** Student's t-test for statistically significant differences ("sig. diff.) between the initial sample and the treated one (Y, yes; N, no).

## Conclusion

Magnetic field did remove paramagnetic impurities from wet-processed phosphoric acid by different types of apparatus in this research. The phosphate content was not changed.The percentage of iron removal from acid varied with the treatment method, in which the fluid transportation and magnetic field were different. The highest efficiency of iron separation achieved so far was 15.1% (Table 76) with a horizontal asymmetric T-tube method. The chromium separation was achieved up to 32.9% (Table 75). Figure 15 showed the 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 t-tube method further removed another 15% of iron from supernatant acid. In the horizontal PVC Y-tube (Figure 13), percentage of iron removal from acid was up to 4.12% (Table 71).The magnetic field with alternate magnet positions worked much better than random magnet positions (Table 74), because the former was strongly keeping the paramagnetic particles along the magnetic side wall of the tube. In the horizontal asymmetrical Y-tube, iron concentration in magnetic side portion of acid was higher than that of the non-magnetic side (Table 62). However, this method was not as significant as the method previously mentioned. When the combination of hydrocyclone and magnetic field was used, the underflow portion contained a higher iron amount than the overflow portion of acid (Table 54- Table 55). The magnetic field, which was place on the underflow area, attracted the paramagnetic materials from hydrocycloned fluid and the remained fluid was pumped out of the overflow. Oxidation (aeration) had no notable effect. This suggests to us that the iron is in the maximum oxidation state.

## DISCUSSION

Excessive metallic impurities in phosphoric acid have imposed both economic and operating penalties on the industry. Removal of these unwanted metals would reduce post precipitation in the acid, reduce or eliminate scaling in the system, and make it possible to achieve DAP grades of 18-46-0 without the addition of supplemental nitrogen. This project was proposed for two years and was concerned with the application of principles of magnetic separation to separate unwanted metals and materials from phosphoric acid.

Specifically, we proposed separation of iron compounds and scale from phosphoric acid. Based upon recommendations of the Technical Advisory Committee, and with permission of the Project Manager, we reversed the plan of attack, and focused the first year on the problems of scale separation.

The separation was based upon use of diamagnetism (being repelled by a magnetic field) to separate ordinary substances, like scale, and paramagnetism (being drawn into a magnetic field) to separate iron from phosphoric acid.

Previous studies had demonstrated the effect of diamagnetism was effective with carbonate scale, and we had developed a theory to help explain these observations.

In the second year, we are using paramagnetism to try and reduce the concentration of iron in phosphoric acid.

Scale refers to coating or crustations, typically inside kettles, boilers, and pipes. Most commonly this is associated with water deposits , but in fact other processes can be associated with scale deposits. Table 79 indicates that some deposits are associated with the precipitation of sparingly soluble salts, associated with water supplies. Other processes, including atherosclerosis , represent examples of scale deposits. Costs are associated with removal of scale deposits. With raw water, scale deposits lead to cleaning costs (descaling), as well as heat loss because of their insulating properties. Other scales can have other costs, including disease. Anti-scale magnetic treatment has had a long history, as well as a controversial one, but the applications seem promising and worth reviewing (Baker and Judd, 1996).

Prevention of scale formation in pipes by means of magnetic fields was summarized in the 1996 issues of a noted news magazine for chemists (Reece, 1996 a,b), but it was noted that leading experts were unable to provide a satisfactory explanation of the phenomenon. It seems appropriate to review the problem, which is of considerable interest because of the prevalence of hard water and because of implications for solving problems in the phosphate industry.

Typically, magnetic behavior of materials falls in one of four magnetic categories (Table 1, Table 79). The main categories for our purposes are paramagnetism (substance is drawn into a magnetic field, or appears to be heavier in a magnetic field than it really is), typical of iron, and diamagnetism (substance is repelled by a magnetic field and appears to be lighter than it actually is), typical of sulfates and carbonates of magnesium and calcium.

## Table 79
### Scale Forming Substances

| Substance | Location |
|---|---|
| Calcium carbonate | Water pipes and cooling towers, oil well pipes |
| Calcium sulfate | Water pipes and cooling towers |
| Barium sulfate | " |
| Calcium phosphate | " |
| Magnesium hydroxide | " |
| Silica | " |
| Zinc phosphate | " |
| Sodium fluorosilicate | Wet process phosphoric acid plants |
| Paraffins | Petroleum pipe and pipelines, car engines |
| Cholesterol | Plaque in arteries resulting in atherosclerosis |

### Diamagnetic treatment of substances

***Diamagnetism as applied to water treatment*** -- Diamagnetism has been used for water treatment for over 100 years. The first known patent on this subject was issued in 1890 (France and Cabell, 1890). The method has grown world- wide since the pioneering work of a Belgian engineer T. I. S. Vermeiren, who founded a company (EPURO) in the early 1940s. Commercial units using magnets to treat water and other fluids were introduced in the early 1950s.

The initial US reaction was not altogether favorable. A company that was producing magnetic units for water treatment was the subject of a complaint submitted to the Federal Trade Commission (FTC) ( Elvis, 1961) . The FTC investigated the firm selling the units in 1954 and placed an administrative order. The affected company brought the FTC to federal court, and in 1961, the court ruled against the FTC. The basis of the FTC action was an allegation of misrepresentation, that the units did not in fact work. Court records revealed that 3,000 units malfunctioned, or about three percent of the 100,000 units sold at that time.

Subsequently, the use of magnetism, actually diamagnetism for water treatment has spread, and it is used in over 30 nations. Units were developed by Moody in the late 1950s and early 1960s. His significant patent (Moody, 1966) was purchased in 1978 by AquaMagnetics® International, and additional applications have been devised and patented by this firm.

Anti-scale magnetic treatment (AMT) thus has a controversial history, but it also has a history of effectiveness (Baker and Judd, 1996) in being able to reduce calcium carbonate and other in-place scale or to produce a softer and less tenacious scale (e.g., aragonite instead of calcite form of calcium carbonate). We believe that the basis of the effectiveness of magnetic treatment will become evident from the following treatment.

***Mathematical treatment*** -- Magnetic-based separations can be understood on the basis of Faraday's Law (Eqn 1).

$$\mathbf{E} = -\boldsymbol{N}\,\mathbf{d}\boldsymbol{\phi}\,/\mathbf{dt} \qquad \mathbf{(1)}$$

Here, E is the electromotive force of mutual induction, ***N*** is the number of ampere turns per meter and $\mathbf{d}\boldsymbol{\phi}$ /dt is the rate of change of magnetic flux with time.

The application is seen in the following thought experiment. Presume a uniform magnetic field, i.e., one that has the same webers/$cm^2$ at every point, has been established perpendicular to the fluid flow in a pipe. Next presume that two conductors , one on each side of the pipe, are placed on the walls of this pipe, and are connected by a galvanometer. Next presume that the fluid is an ionic medium. The fluid is a moving conductor through the magnetic field, and there occurs a change in the flux linkages created by this conductor, and an electromotive force is generated. For this experiment, certain consequences follow. The magnitude of the force can be calculated from Faraday's Law (Eqn. 1). When the current produced by the induced electromagnetic field (EMF) reaches its Ohm's Law value, the flux ceases to change and the induced EMF becomes zero.

The direction of the induced EMF is described by Lenz's law, i.e., the EMF induced in a circuit caused by a change in magnetic flux will be in the direction current could flow in order to oppose this change in flux. Because the conductor (moving fluid) is passing through a magnetic field, the EMF generated is termed " motional" or " generated" EMF

(Eqn. 2).

$$\mathbf{E = -}\boldsymbol{N}\mathbf{\,d\phi /dt = BLV} \qquad (2)$$

Here B is the magnetic flux density perpendicular to the fluid flow, L is the diameter of the pipe containing the conducting fluid, and ($d\phi /dt$) is the change of flux with the change of distance (time).

When the mean velocity of the conductor (moving fluid) is V meters per second, time required to move a distance, (ds), is given (Eqn 3)

$$dt = ds /V \qquad (3)$$

Combining Eqn 3 and Faraday' s Law (Eqn. 1), one obtains (Eqn 4) Faraday's Law, as modified for motional electromotive force and in the form applicable to conducting fluid treatment

$$E = - N\, d\phi /dt = BL\,(ds)/\,(ds)/\,V = BLV \qquad (4)$$

For example, assume a pipe has a diameter of 10 cm and contains a fluid moving at the rate of $2 \times 10^{-4}$ cm/s through a flux density perpendicular to the fluid of 10 Wb/ $m^{2}$. The calculated EMF ($EMF_{calc}$) for these conditions is $2 \times 10^{-5}$ volts because (Eqn 5a, 5b)

$$\text{EMF calc} = -\ \text{gauss} \cdot \text{magnetic susceptibility} \cdot \text{conductivity} \cdot \text{diameter} \cdot \text{f(length)} \cdot d\phi /ds \cdot ds/dt \qquad (5a)$$

and

$$\text{EMF calc} = -\text{Wb/cm}^2 \cdot \Omega/\text{cm} \cdot \text{cm/cm} \cdot \text{Wb/cm} \cdot \text{cm/s} \qquad (5b)$$

***Basis for success*** -- Benson and co-workers (1994) suggested an explanation of the useful effects of a magnetic field to minimize scale formation. The explanation is given in terms of the change of spin-orbital system entropy arising from the orientation of the atom magnetic moment within an applied magnetic field. The relationship of the entropy to the available spin states is given by the Boltzmann definition of entropy, $S_B$, (Eqn. 6). Here, $S_B$ is the entropy,

$$S_B = k_B \cdot \ln W \qquad (6)$$

$k_B$ is the Boltzmann constant, and W is the number of permutations based on the spin-orbit coupling and the orbital angular momentum. The loss of the spin state degeneracy leads to more permutations to distribute the spin populations.

In absence of a magnetic field, the ground-state spin level would be degenerate (Fig. 16). However, in the presence of a magnetic field of magnitude $\mathbf{B}_o$, a splitting of the energy level occurs, and for S = 1/2, two terms result from m = +1/2 and m = -1/2( where m is the magnetic spin quantum number). More specifically, the two energy levels are ± 1/2( $\gamma h/2\pi$ ) $\mathbf{B}_o$, and the difference in energy between the two energy levels is a function of the applied field, and is given below (Eqn. 7).

$$E = \pm (\gamma h/2\pi)\, B_o \qquad (7)$$

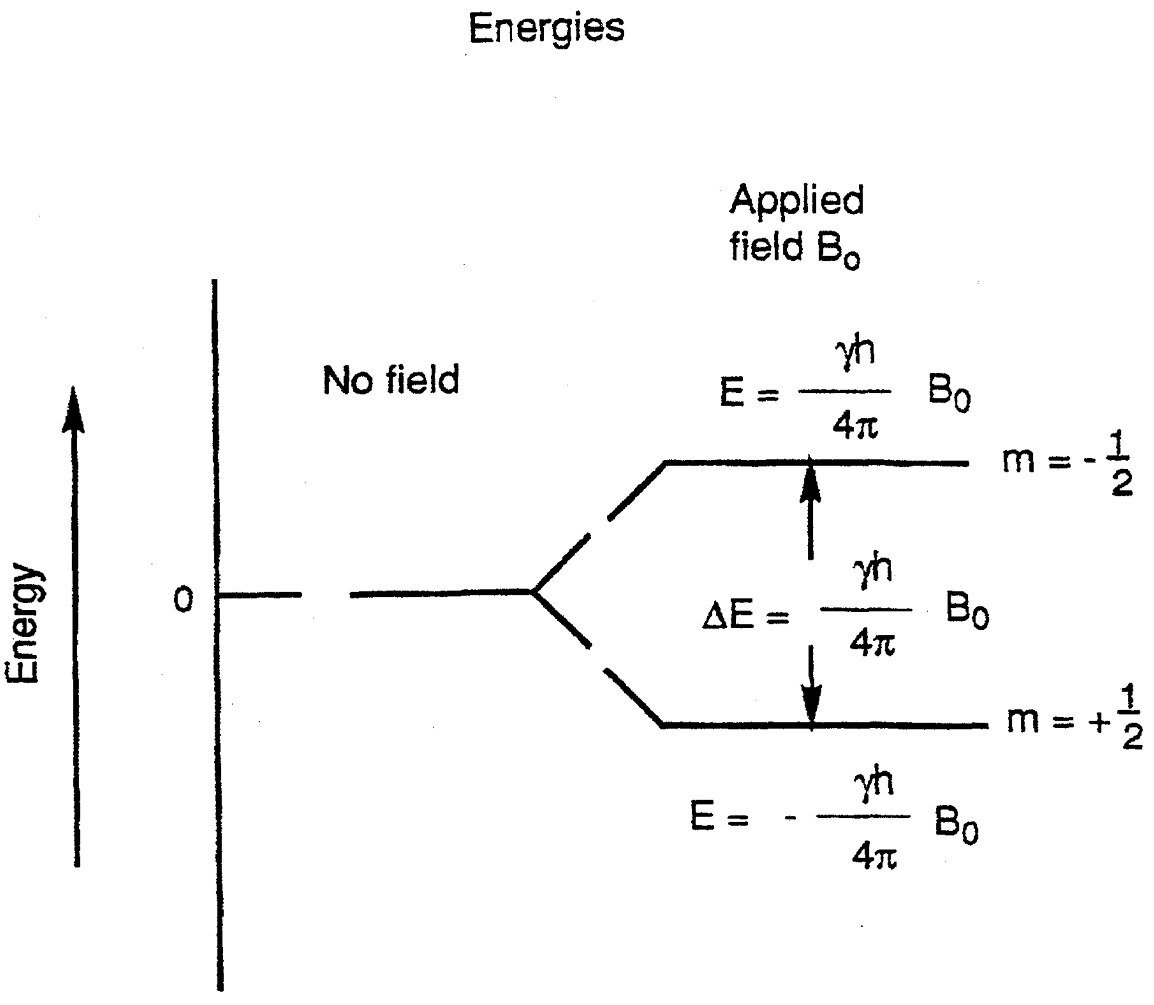
Here, E is the energy of the system, $\gamma$ is the gyromagnetic ratio, ***h*** is Planck's constant, and $\mathbf{B}_o$ is the applied magnetic field.

Thus, in the presence of a magnetic field, there is an increase in the permutations, and two energy levels result for each one that existed before, and as a result, there is a change in entropy between the spin system and the lattice surrounding as the spins are distributed within the new levels. For paramagnetic substances at low temperatures, the presence of a magnetic field would simply result in the alignment of the magnetic field and lead to a reduced entropy. Diamagnetic substances, however, do not have the alignment because the opposing electron spins cancel the orientation, but the effect on the lattice remains the same.

An increase in entropy is reflected in an increase in the solubility for aqueous saturated magnesium hydroxide, as indicated by the equilibrium equation (Eqn. 8).

$$\mathrm{Mg(OH)} \quad = \mathrm{Mg_{aq}}^{++} + 2\ \mathrm{OH_{aq}}^{-} \qquad (8)$$

Using magnesium hydroxide as a model system, one would predict the effect of a magnetic field should increase the entropy of the system, as reflected in an increased solubility, an increased concentration of hydroxide ion, and an increased pH. The results (Benson et al., 1994), indicated in Table 80, are consistent with the predictions of the model.



VARIATION IN ENERGY FOR A DIAMAGNETIC SUBSTANCE IN THE PRESENCE OF A MAGNETIC FIELD

**FIGURE 16**

## Table 80

### Properties Calculated From Observed Effect Of Applied Magnetic Field On A Model System, Solubility Of Magnesium Hydroxide In Water*

| Property | No field | Magnetic field |
|---|---|---|
| pH | 10.2 | 10.8 |
| $K_{sp} \times 10^{12}$ | 1.99 | 7.85 |
| $\Delta G^o$, kJ/mol | - 83.7 | - 63.2 |

*Benson et al., 1994

The effective splitting of the magnetic spin-state degeneracy in the presence of a magnetic field appears to be canceled when spins are paired. The resultant magnetic moment is shielded from the applied magnetic field. However, a molecule in a solid lattice has many magnetic moment contributions, which do not completely shield the resultant magnetic moment. As a result, the number of available permutations of the resultant magnetic moment increases due to the applied magnetic field.

A detailed discussion of diamagnetism is presented by Kittel (l971). An important point to note is that the total molar magnetic susceptibility is predicted by the Van Vleck equation. The equation is useful for showing the magnitude of both contributions, and a triumph of Van Vleck's theory was the close agreement between the calculated and experimentally observed magnetic moments for the lanthanide ions. According to this equation, the number of permutations available increases in a magnetic field, regardless of the prevailing diamagnetic or paramagnetic properties, and, thus, the entropy of the system is increased.

In terms of the solubility product equilibrium involved in scale formation, the shift in equilibrium can be interpreted in terms of a magnetic perturbation of the system. As is seen from the Gibbs equation (Eqn. 9), which describes the free energy change of the solubility equilibrium (Table 80), the response of the system would arise from changes in the entropy term

$$\Delta G^{o}\,(\text{solubility}) = -RT \ln K_{sp} = \Delta H^{o}_{soln} - T\,\Delta S^{o}_{soln} \qquad (9)$$

***Criteria for successful application*** (Carpenter, 1991) -- The successful application of magnetism to scale prevention depends upon water composition. Calcium carbonate with a magnetic susceptibility of -0.381 cgs units can be controlled, and deposits removed, as can deposits of calcium sulfate ( - 36.4) or sodium fluorosilicate . Paramagnetic species, such as the hydrous oxides of iron and manganese, however, are troublesome, and may need to be removed. An empirical iron treatment table has been developed (Table 81) , which can be used as a guide. Roughly, a maximum of 1 ppm of iron and/or manganese can be tolerated for each 200 ppm of total dissolved solids (TDS).

## Table 81

**Iron Treatment Decision Table (Carpenter, 1991)***

| Iron, ppm | Hardness, grains/gal | | | | |
|---|---|---|---|---|---|
| | 0-5 | 5-10 | 10-20 | 20-40 | >40 |
| 0.3 | B* | A | A | A | A |
| 0.3-1.0 | C | B | A | A | A |
| 1.0-2.0 | C | C | B | B | A |
| 2.0-3.0 | C | C | C | C | B |
| >3.0 | C | C | C | C | C |

*A, No iron treatment suggested; B, iron treatment optional; C, iron treatment needed.

Corning (1988) suggested that two physical properties are sometimes neglected in evaluating water-conditioning processes. First, Langelier's Index (Sisson, 1973) can be used to determine the tendency of water (knowing the pH, temperature and calcium hardness) to corrode or form a lime coating ; a negative index means that the water in question will dissolve existing calcium carbonate deposits. Second, solubility tables for calcium carbonate are also important because at normal pH for natural water, the solubility of this substance decreases with increasing temperature.

***Some examples of the application to scale prevention*** --- Scaling can add to the cost and danger of processing . Operating costs increase due to costs of makeup water, the costs of replacing control chemicals (corrosion inhibitors, dispersants, pH control chemicals). Scaling adds to energy costs and operating concerns. For example a thin scale (0.61 mm, 0.024 in) of calcium sulfate scale on boiler tubes results in 183 °C temperature drop across the scale, as well as higher skin temperatures, increase in energy inefficiency, and perhaps may contribute to metallurgical problems with the tubes (Grutsch and McClintock, 1984).

Fryer (1995) provided some examples of cost savings for successful installations. The use of magnetic fields was tested for an 8,000 - ton cooling tower system at Eli Lilly in Indianapolis. The treatment system was considered successful and resulted in a simple payback of 3.3 years ( installation costs for the system and its monitoring equipment.) The cost for magnetic treatment was $1.85 per thousand- ton hours (water, biocides, maintenance, and electricity for the pump motor), as compared with $10.51 per thousand-ton hours for a chemical treatment system (included water, maintenance and chemical costs plus electricity). In addition, it was possible to increase the number of cycles of concentration which results in water savings. The Eli Lilly installation typically has 1.5 cycles using municipal water and chemical treatment, but with in-line magnets, the number of cycles increased to nine. Chemical biocides are still needed with magnetic treatment, though the amount needed may decrease, relative to chemical treatment.

***Other applications of diamagnetism*** **--** Diamagnetism can be usefully applied to systems other than scale treatment . Carbon scale can be a problem, and magnetic units have been developed that remove hydrocarbon deposits. These can form in pipes in petroleum refineries, when crude oil is passed through the pipes. The use of magnets mounted on the outside of pipes has prevented paraffin buildup in Venezuela refineries. Magnets were mounted on short sections of stainless steel (300, 304, 316, 316L series) pipe inserts about 0.5 m long. Under ordinary conditions build up could occur within 24 hours in 10- to 12-in. pipes; with 2,000-gauss magnets (one per each inch of pipe diameter), the buildup was not a problem during a six-month test.

These applications show the range of usefulness of diamagnetism in managing nuisance scale and other deposits, and should suggest other applications.

Magnetic treatment of water certainly has controversial aspects. Fryer (1995) wrote, “Over two hundred articles have been written about magnetic treatment of water and no clean conclusion emerges from the literature.” It is hardly surprising that there could be confusion where there is not a clear understanding of the principles involved and in a field when there has been an understandable tendency to rely upon pragmatic solutions to an important problem. On the other hand, it is our hope that having presented what we think are the appropriate equations and development of the theory, there is a rational explanation, as well as a model that could be tested, and results that are consistent with those predicted by the theory (Benson et al., 1994). Diamagnetism has useful applications to management of scale of various kinds, and it also has other applications that are a consequence of the theoretical treatment considered here.

## Magnetic treatment of scale

***Effect of magnetic treatment on scale solubility --*** In the production of phosphoric acid, scale is a nuisance material that must be cleaned out of pipes. We used diamagnetism to enhance the solubility of sodium fluorosilicate scale from a phosphoric acid plant. The problem of trying to prevent scale formation is more challenging for sodium fluorosilicate scale than for certain carbonate scale because of the magnitude of the magnetic susceptibilities. The observed value for sodium fluorosilicate was $\chi_g = -0.31 \times 10^{-6}$ c.g.s. units, whereas the reported value for calcium carbonate is only slightly greater ($\chi_g = -0.382 \times 10^{-6}$ c.g.s.). In all treatments the solubility of sodium fluorosilicate scale in water was increased in the presence of magnetic field, compared with the control. The same was true of the solubility of scale in 28% phosphoric acid. Analysis of variance (ANOVA) showed a significant difference in scale solubility. The stronger magnetic field increases the scale solubility in phosphoric acid significantly (2000 gauss vs 1200 gauss). For small particles, e.g. -230 mesh scale, change in scale solubility in water with five-cycle run in a magnetic field was more significant than one-cycle treatment. The change in solubility of scale in phosphoric acid(28%) is presumably due to the increase of scale entropy, S, and destabilization of the sodium fluorosilicate lattice under the magnetic field. Magnetic effects on solubility were also investigated at higher temperatures, e.g., 50°C and 100°C. These results show the effect of a magnetic field on scale solubility at high temperature is more significant than at room temperature. At room temperature, the solubility of fluorosilicate scale was 1.70g/100 mL of 28% phosphoric acid, and at 50 °C, in the presence of a magnetic field, the solubility increased by 25-28% (Table 21).

The presence of a magnetic field enhances the solubility of sodium fluorosilicate, and one may expect that in practical terms, these would reduce the tendency for this material to condense on, pipes, particularly curved or rounded pipes. Another implication of our observation is that one may expect that given enhanced solubility of the fluorosilicate scale, the material would precipitate at a more convenient stage, i.e., in a large holding tank that would be more accessible than a 4-6 inch pipe.

The process we have used, thus, would not eliminate scale, but it would mitigate against its obvious inconvenience of formation in pipes. The effect persists for some period of time (so-called “memory effect” before equilibrium is restored). Magnetic treatment would shift scale formation to an open area where it could be filtered off more conveniently and more economically.

We believe that these experiments form a sound theoretical and practical basis for future efforts to manage scale in phosphoric acid plants. This could be achieved through the judicious placement of suitable magnets so that scale instead of forming in inconvenient

convenient location for separation.

***Iron separation from scale by magnetic field*** **--** After magnetic treatment, iron was enriched in the smaller particles of scale, and iron was removed from the larger particles. Iron distribution with the particle size showed that the magnetic field shifted the iron concentration to smaller particles, even in solution (Fig. 5. - Fig.7. ). The scale solubility change and iron removal followed the same trend with the magnetic treatment. We assume that iron species tend to coexist with smaller scale particle and they are located at a interstitial position in $Na_2SiF_6$ lattice. When $Na_2SiF_6$ scale is dissolved, the iron species in scale go into suspension whether they are dissolved or not. Under magnetic field treatment, more small particles were observed because of higher entropy and less stable lattice, and those small particles are easily dissolved in solution because of their higher specific surface area. It is consistent that the scale shifts to smaller particles under a magnetic field. A more significant effect would be observed if the stronger magnetic field were applied too. These treatment schemes have implication for converting the scale to a useful, and saleable product by removing iron.

## Paramagnetic treatment of substances

***Iron removal from phosphoric acid*** **--**There are some unwanted paramagnetic impurities in wet-processed phosphoric acid (WPA)(Hein 1968).These materials have caused economic and operating penalties on the industry. Removal of these unwanted metal ions would reduce post precipitation in the acid. The solubilization or precipitation of ferric iron can be controlled at various $P_2O_5$ concentrations. Above 60% $P_2O_5$, the pyrophosphate content controls the solubility of ferric iron. Although the iron is relatively soluble at 60% $P_2O_5$ (~3%$Fe_2O_3$), the presence of other impurities oxides ($Al_2O_3$, $MgO$, etc) reduces the free water to a low concentration where the composition is more like the pure system at 67-70% $P_2O_5$. Since ferric iron does not form strong soluble complexes with the impurity components such as F or $SO_3^-$, the ferric iron complex with orthophosphate reaches saturation at about 1.0% $Fe_2O_3$, and precipitates. At higher impurity concentrations the free- water content approaches zero, and as pyrophosphate ions form, iron is again complexed to very soluble complexes, up to 7% $Fe_2O_3$ (Hein 1968).

Below 60% $P_2O_5$, alkali metals (or ammonia) (K’, $NH_4^+$, and $Na^+$) control the precipitation. When the alkali-metal content is above 0.01%, iron alkali-metal phosphates precipitate until the iron is reduced to 0.2% $Fe_2O_3$. When the alkali-metals (or ammonia) content is below 0.01%,The highly-soluble acid ferric phosphates will remain in solution until the iron content reaches about 7-9% $Fe_2O_3$.

Two major iron forms in the 28% acid at 25 °C are $FeH_3(PO_4)_2\ 4H_2O$ and $Fe_3H_9(PO_4)_6\ H_2O$. If the temperature is increased to 75 °C, only $FePO_4\ 2H_2O$ is observed in 28.5% acid suspension (Frazier, 1992). Like the temperature effect, we assumed that the magnetic field may change the iron composition in the $Fe_2O_3$-$Al_2O_3$-$P_2O_5$-$H_2O$, affect the solubility of iron compounds, and then affect the sludge precipitation. The magnetic field could break iron- and aluminum-fluorine complexes and precipitate freed iron and aluminum. During the concentration process of 28% acid, many different impurities precipitate. Ferric iron, alone and in conjunction with potassium, precipitates readily at $P_2O_5$ concentration above 35%. This ferric iron is identified as the major sludge-forming impurity in shipping grades of WPA.

For the phosphoric acid made in Central Florida, iron content in solution is much lower than reported. 28% acid contains 0.75-0.83% iron in solution and ~5% solid which has high iron content (5.4 -9.3%). (Table 51). In 54% phosphoric acid, iron in solution is reduced (0.3%) and solid content is as high as 10% of acid. Most of the iron went to the solid and this solid contained high iron (10.64%) (Table 52). Alkali-metals reduce the iron in acid solution.

Magnetic separation for removal of paramagnetic materials is well-known. Paramagnetism techniques are used in magnetic filtration of suspended ferro-,ferri, and para-magnetic particles, removal of colored impurities from Kaolin clay, water purification, etc.

We used a magnetic field to remove sludge-forming impurities, iron and chromium, from phosphoric acid. Magnetic treatment of phosphoric acid helps the fast impurity precipitation and removal of solid as well as solvated paramagnetic species from acid.

The solid can be separated by a hydrocyclone, and a magnetic field improved the efficiency of this solid-liquid separation. In the presence of a magnetic field, more iron was transferred to the underflow by the hydrocyclone. The mechanism is presumably a combination of paramagnetism and the fluid dynamics of iron. Under a magnetic field, the soluble iron complex is broken, then freed iron is precipitated and attracted by the field, and then is transferred to the underflow portion of the hydrocyclone. Solid content in phosphoric acid suspension is increased after the magnetic treatment (Table 61).

Attraction method works for paramagnetic material removal from both acid supernatant and acid suspension. Among these methods we investigated, horizontal Y- tube reached the most significant iron separation. Some factors, such as magnetic field strength, time the suspension spent in the field, fluid flow rate, and the junction which separates fluid into two portions, affect the attraction of the particles to the field. When acid fluid is slowly passed through the magnetic field, paramagnetic species are attracted on the side where the magnets are placed. The diamagnetic species are repelled to the other side of the tube. When the fluid is moved horizontally to the Y-junction, two portions are separated. Iron and chromium are removed by this attraction method and efficiency is dependent on the apparatus and magnetic field. There is an optimum flow rate for the paramagnetic separation. If the flow rate is too slow, the attracted portion and the repelled portion are mixed before reaching the Y-junction. If the flow rate is too fast, paramagnetic materials are not attracted before reaching the Y- junction. Under 7 x 3 000 gauss field, 15.1 % iron separation (Table 76) and 32.95% chromium separation (Table 75) occurs.

Magnet orientation affects the separation efficiency (Table 74). To get better separation, magnets are placed alternately so that paramagnetic species moves through the pole when the fluid moves along the magnet place.

In summary, the magnetic attraction method works for paramagnetic material removal from wet-processed phosphoric acid. It is easily designed and the magnetic field is applied at any position of the apparatus. Under the optimum condition, more than 15% iron separation could be achieved.

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