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Factors Controlling Sludge Density During Acid Mine Drainage Neutralization

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SUMMARY OF MAJOR CONCLUSIONS

1. The formation of dense magnetic sludges through the controlled oxidation and neutralization of acid mine drainages, does not appear to be feasible under field conditions. This is due to the interference of aluminum with the formation of magnetic sludges, practical problems associated with maintaining the relatively high temperatures required for reasonably rapid reaction rates, and the extreme sensitivity of the overall oxidation reactions to physical conditions of aeration. A postulated mechanism of magnetic sludge formation is presented in Section II of this report, together with descriptions of successful attempts to utilize acidophilic iron oxidizing bacteria for $Fe^{3+}:Fe^{2+}$ ratio adjustment at low pH, and of an effective but impractical two-step procedure for removal of aluminum interference.

2. The density of sludge formed during the oxidation and calcium hydroxide neutralization of ferrous acid drainages depends generally on the concentrations of ferrous iron and aluminum in the drainages, and is strongly affected by pH and sludge recirculation. In general, dense sludges are associated with the formation of crystaline ferric hydroxy compounds, geothite (α-FeOOH) and/or lepidocrocite (γ-FeOOH). Sludge denisty generally increases with decreasing pH, and exposure of the sludge to high pH during the neutralization step enhances crystalline precipitate formation. Recycling of sludge can generally enhance sludge density, which is strongly dependent on sludge age, ferrous iron concentration, recycled 'seed' particle size and concentration, and oxidation rate. Care must be taken to avoid the formation of amorphous ferric hydroxide. The optimum pH for achieving good iron and aluminum removal is approximately 5.5. A detailed discussion of lime treatment, with and without sludge recirculation, is given in Section III of this report.

3. In the treatment of a ferrous acid mine drainage, the rate of oxidation is critical to process design for several basic reasons. It is readily apparent that the higher the rate of oxidation, the lower the necessary detention time in the aeration tank. However, the formation of the crystaline ferric hydroxy precipitates associated with dense sludges is favored by moderate rather than high oxidation rates, and a balance must be struck between oxidation rate, ferrous iron concentration, and the control of recycle sludge properties. Sludge recycle has a strong influence on the oxidation rate of ferrous iron, due to the chemical catalytic effect of the iron precipitates. This may be used to advantage in the attainment of realistically rapid rates of oxidation at the relatively low pH values most effective in the production of dense sludges (~ pH 5.5). At pH values above 4, the catalytic effect of acidophilic iron oxidizing bacteria is negligible, the catalysis being chemical in nature, and associated with recycled sludge solids. A detailed discussion of chemical and biological oxidation rates are given in Section III of this report.

4. The neutralization of mine drainages with calcium carbonate, as opposed to calcium hydroxide, appears to offer distinct advantages. The slower oxidation rate of ferrous iron all favor the formation of the crystaline precipitates, associated with dense sludges, and under carefully controlled conditions, higher density sludges can be obtained than when using calcium hydrate Carbon dioxide released can cause difficulties by interfering with the catalytic effect of sludge solids on iron oxidation, but a two step neutralization using limestone ($CaCO_3$) and Lime ($Ca(OH)_2$) appears to be a practical means of avoiding this difficulty.

INTRODUCTION

The term acid mine drainage (AMD) is used in this report to describe the water flowing from active or inactive surface or underground coal mines and gob piles. These waters are characterized by low pH and high concentration of sulfuric acid and sulfuric acid salts, particularly iron sulfates.

It has been estimated that AMD in the United States contributes more than four million tons of pollution per year to more than 11,000 miles of streams and receiving waters (1). Due to the widespread pollution of surface waters by AMD, many states have made chemical treatment a necessity by setting limits for pH and iron concentration in waters discharged from mines. The neutralization and iron removal processes currently used are handicapped by the formation of very voluminous sludges, making sludge handling and disposal both difficult and expensive. This project was directed toward finding means of obtaining higher density sludges from AMD treatment processes, with particular emphasis on the determination of the physical and chemical factors affecting the formation of dense sludges and the physical and chemical changes and processes associated with the sludge densification.

This project was started on July 1, 1970, with the specific objectives of developing procedures for obtaining denser settled sludges from synthetic acid mine drainage (SAMD) by lime precipitation. The formation, stability, and transition of "green rust II" to Fe_3O_4 and/or γ-FeOOH were studied and the results are reported in Section II. The results showed that the precipitation of iron from AMD in the form of high density magnetite is possible, but the problem of slow conversion of green rust II to magnetite at temperatures below 25°C, together with the severe interference of aluminum to the formation of magnetite, make the general application of magnetite sludge formation unlikely in the field at this time, and work on magnetic sludge formation was discontinued. Subsequently, the main efforts were directed toward work on dense sludge formation by oxidation and precipitation of iron from SAMD at pH below 7, using lime neutralization and sludge density enhancement by sludge recirculation.

Since the chemical oxidation rate of ferrous iron by oxygen decreases with decreasing pH and becomes too slow at low pH to be of interest for practical application, and since iron must be precipitated in the ferric form, studies of biological catalysis of ferrous iron oxidation by organisms of the Ferrobacillus-Thiobacillus group were incorporated in this phase of the project. The results of the low pH precipitation studies are presented in Section III.

Lastly, in Section IV, are reported exploratory studies on dense sludge formation using calcium carbonate for SAMD neutralization. Such studies were not anticipated in the original proposal, but chemical mechanisms elucidated during the course of the project indicated the advisability of the inclusion of this work. The preliminary results were promising, and more extended studies on the subject appear to be justified.

RELATED LITERATURE

Control of AMD is not a simple problem to solve. Treatment itself is a complex problem because of the wide chemical variation in AMD composition. Because positive control of AMD formation in active mines is not yet possible, and because forty percent of all AMD is estimated to come from active operations (1), most current abatement efforts take the form of AMD treatment processes.

Several types of AMD treatment processes have been tested. Ion exchange, reverse osmosis, distillation, electrodiolysis and crystallization are among the abatement processes that have met with limited success (1). The most conventional treatment is to neutralize the AMD with lime or limestone. In such a process, the sulfuric acid is neutralized and the iron is precipitated in form of insoluble ferric compounds, frequently using air to oxidize the ferrous iron. After settling, the supernatant is then satisfactory for discharge to the receiving stream and the settled sludge is disposed of in some manner. An undesirable side effect of the process, particularly when using lime for neutralization, is the formation of very voluminous sludges which are difficult and expensive to dispose of. Therefore, many recent studies in the AMD field have been directed toward formation of denser sludges. A number of routes have been pursued, some of which include:

1. Neutralization with lime or limestone, and oxidation of ferrous iron, under specific conditions, to produce denser sludges in the form of ferric hydroxides.

2. Modifications of processes mentioned in Item 1 above by using sludge recycle to enhance the dense sludge formation.

3. Removal of the iron as magnetite, Fe_3O_4, a dense ferromagnetic oxide of iron.

It should also be noted that work on precipitation of iron from AMD in the form of ferrous sulfide was done by Bituminous Coal Research, Inc. (BCR) (2), but the authors conclude that........"the process is less attractive than accepted methods of mine drainage treatment".

Major work on iron removal from AMD as magnetite was done by BCR (3). This work shows that predominantly ferrous iron AMD can be treated by a modified lime neutralization process to yield a ferromagnetic sludge. The magnetic sludges were obtained by precipitation of the ferrous iron with addition of hydrated lime to a pH of 8.5, and heating the sludge to at least 80°C, followed by mild aeration. A severe interference of aluminum on the magnetite formation was observed, and interference of magnesium was noted at pH above 9.6. The authors conclude that the magnetic sludge process appears to be technologically feasible in some instances.

The most frequently used AMD neutralization agent is lime, mainly because it is a relatively low-cost source of alkalinity. While lime may be added to AMD as a powder or as a slurry, in both cases the hydration of the lime is the first chemical reaction:

$$CaO + H_2O = Ca(OH)_2 \qquad \text{eq. (1)}$$

By the neutralization of the free sulfuric acid,

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O \qquad \text{eq. (2)}$$

and by the insolubilization of the ferric iron and aluminum,

$$3\ Ca(OH)_2 + Fe_2(SO_4)_3 = 3\ CaSO_4 + 2Fe(OH)_{3(s)} \qquad \text{eq. (3)}$$

$$3\ Ca(OH)_2 + Al_2(SO_4)_3 = 3CaSO_4 + 2Al(OH)_{3(s)} \qquad \text{eq. (4)}$$

the desired degree of treatment may be obtained.

The calcium sulfate formed may remain in solution, or precipitate in the form of gypsum, depending on the total sulfate concentration of the AMD. The symbols $Fe(OH)_{3(s)}$ and $Al(OH)_{3(s)}$ do not represent the composition of the actual compounds formed, but indicate only that ferric iron and aluminum are insolubilized. At pH of approximately 9 and higher, ferrous iron may also be precipitated.

$$Ca(OH)_2 + FeSO_4 = CaSO_4 + Fe(OH)_{2(s)} \qquad \text{eq. (5)}$$

To completely insolubilize iron, the ferrous iron is oxidized, usually by air oxygen, to ferric iron,

$$2FeSO_4 + 1/2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O \qquad \text{eq. (6)}$$

which then is insolubilized according to eq. (3). The neutralization rates of AMD with lime was observed by many investigators, and from the reported results, Hill (1) concludes that the reaction rate is fast. The utilization of lime is near 100 percent, which was also confirmed by Wilmoth and Scott in a test AMD plant (4). By fast neutralization of AMD with lime, the ferric iron is insolubilized in form of amorphous, gelatinous, hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$, which forms very voluminous sludge. Wilmoth and Scott state that lime treatment produces sludge that contains 1.5 to 1.7 percent solids. These researchers feel that this lime sludge will create major sludge disposal problems (4). Haines and Kostenbader indicate that using lime treatment, a sludge of only one percent solids is obtained (5).

Limestone is the cheapest neutralization agent known at present. The reactions of limestone with AMD may be summarized as follows:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2 \qquad \text{eq. (7)}$$

$$3CaCO_3 + Fe_2(SO_4)_3 + 3H_2O = 3CaSO_4 + 2Fe(OH)_{3(s)} + 3CO_2 \qquad \text{eq. (8)}$$

$$3CaCO_3 + Al_2(SO_4)_3 + 3H_2O = 3CaSO_4 + 2Al(OH)_{3(s)} + 3CO_2 \qquad \text{eq. (9)}$$

$$3CaCO_3 + 2FeSO_4 + H_2SO_4 + 0.5O_2 + 2H_2O \rightarrow 3CaSO_4 + 2Fe(OH)_{3(s)} + 3CO_2 \qquad \text{eq. (10)}$$

Limestone can remove the acidity of the AMD and precipitate the iron to acceptable levels. However, the use of limestone has several operating problems.

Limestone is a naturally occurring fossil rock composed primarily of calcium carbonate, and containing various amounts of magnesium carbonate, silica and other compounds. The chemical impurities in limestone can severely affect its neutralization properties. In general, Ford reports that the higher the calcite content and the smaller the particle size, the faster the neutralization rate of AMD with limestone (6). An exhaustive study on evaluation of limestone for AMD treatment is discussed in the report by BCR (7).

Another important factor affecting the neutralization rate of AMD with limestone is the coating of limestone with precipitated ferric hydroxide, and in high total sulfate AMD, calcium sulfate may also form on the surface of limestone (1). To overcome the coating problem, two techniques have been employed. One technique is to place limestone chips in a rotating drum. As the drum rotates, abrasive power is supplied to clean the surface of limestone, thus, continually exposing the fresh surface. This technique was used successfully by the Rochester and Pittsburgh Coal Company and the U. S. Bureau of Mines (8,9). To overcome the same problem, Glover (10) designed and experimented with an impeller attrition device with good results. A second technique is to use limestone that is finely ground. The coating problems are thus eliminated because of the large surface area of the limestone, and the powdered limestone tends to react more completely. This technique was used successfully by Wilmoth and Scott (4), BCR (7), Wilmoth, Scott and Hill (11) and others (12). It should be mentioned that the costs of AMD treatment with powdered limestone depends on the price and availability of finely divided limestone.

The maximum obtainable pH by treatment of AMD with limestone is limited. The carbonate ion, formed in the neutralization process, acts as a buffer and sets an upper limit on pH and also affects the rate and amount of limestone consumption. Hill reports that to attain a pH of 6.1, 1.5 times the theoretical amount of limestone is required, and that twice the amount of limestone has to be used to attain a pH of 7.0 as compared to the amount required to obtain a pH of 5.1. Hill used 1.52 times the stoichiometric quantity to treat to a pH of 5.1 with a reaction time of 7 minutes. By increasing reaction time to 20 minutes, the amount of limestone required was reduced to 1.29 times the stoichiometric amount (12). In a year-long test by Rochester and Pittsburgh Coal Company, in which AMD was treated to the pH range 6.2 to 7.3, the limestone efficiency was calculated at 65 percent (8). Wilmoth and Scott reported that a maximum pH of 6.5 was obtainable in the neutralizer with limestone treatment of AMD (4). Similar results are reported by BCR (7) and Wilmoth (11). The maximum attainable pH characteristic of limestone treatment has an advantage, as pointed out by Calhous, Wilmoth and Scott. They state that control of limestone treatment would be easy because of a maximum elimination of the danger of overtreatment (8,4). The disadvantage of pH limit is that ferrous iron removal may be difficult. The obtainable pH level is not sufficient to precipitate the ferrous ion, so oxidation to the ferric ion is necessary. Stumm reports a 100 fold increase in oxidation rate of ferrous iron for each unit pH increase in the neutral pH range (13). This accelerated reaction rate with increasing pH may determine the choice of alkaline reagent. It is obvious that to attain a pH of approximately 8, required for fast oxidation of ferrous iron, lime is a natural choice and may have an economic advantage over limestone. Another route of approach to the problem was followed by Wilmoth, Scott and Hill (11), using a combination limestone-lime treatment process. The treatment is accomplished in two separate stages. In the first step, AMD is treated with powdered limestone to pH near 4, and subsequently, treated with lime to any desired pH. Thus, the process is made amenable to treatment of ferric and ferrous iron AMD. The researchers claim that the "process has tremendous economic potential for cost reduction in acid mine drainage treatment". The advantage of the combination process depends on the cost ratio of lime to limestone and the lime required in the second stage. The researchers also state that the process should still be economically beneficial in ferrous iron situations.

The publications on sludge properties, obtained by AMD neutralization, are not abundant and frequently are presented in the form of comparison of sludge properties obtained from the same AMD but at different conditions and by different neutralization agents. Wilmoth and Scott treated an AMD with 4: 1 ferrous to ferric iron ratio and a large excess of limestone, and obtained a 3.5 to 5.0 percent sludge by volume and 9.5 percent sludge solids content on a dry weight basis (4). Calhoun states that a lime sludge has four times the volume of a limestone sludge (8). BCR reports the volume and solids content of sludges obtained by neutralization of several AMD with finely divided limestones and at different conditions in a batch neutralization experiment. The reported volume and solids content of sludges are from 0.1 to 2.2 percent and 4.2 to 13.4 percent, respectively, after 24 hours of settling. Some solids contents as high as 48.8 percent appear to be the result of excess settled limestone. In a continuous flow process, the sludge volume and solids content is reported 0.5 to 1.3 percent and from 6.0 to 9.9 percent, respectively, and in the runs obtained with sludge recirculation, the corresponding values are 0.2 to 1.2 and 5.9 to 13.0, all measurements taken after 24 hour settling (7). Wilmoth, Scott and Hill, in a combination limestone-lime treatment process, obtained sludge solids contents and compared them with the results of limestone treatment processes. At a flow rate of acid mine drainage of 5 gpm, the sludge percent solids was 10.7 in the limestone-lime process, 2.3 in the lime process, and 13.4 in the limestone process; the corresponding values at 10 gpm flow rate were 6.0, 1.4 and 15.6, respectively. They estimated the theoretical settling time for 5 gpm flow rate at 39 hours and at 10 gpm, 19.5 hours (11). From the results reported by the researchers cited above, it appears that lime treatment yields sludges in the range of less than one percent to 2.3 percent solid content, depending on ferrous to ferric iron ratio in the sludge, pH, and perhaps other conditions. The sludges formed by using limestone for neutralization contained solids from approximately 4 percent to 13.4 percent, also depending on ferrous to ferric iron ratio, pH of treated AMD, oxidation rate, and other conditions. The advantage of limestone treatment over lime treatment processes in obtaining denser sludges is obvious. The main disadvantages of the limestone treatment process is the formation of very finely divided precipitates which settle slowly, requiring larger settling tanks, and slow ferrous iron oxidation rates requiring prolonged aeration time associated with a large holding time of oxidation reservoirs. The combination limestone-lime treatment process is reported to eliminate some of the disadvantages of the limestone treatment process, but the solids content of the sludge is lower than in the limestone treatment process and requires two-stage treatment facilities.

Sludge solids content may be increased by sludge aging. Mihok and his co-workers have presented data that show lime treated sludge will compact from 12.0 percent volume to 6.6 percent after 42 days of aging, while a limestone treated sludge will settle from 2.6 percent to 1.9 percent over the same period (9). Birch reports that certain lime sludges will shrink from 10 volume percent to 5 percent in a period of several days (14). Other investigators have noted this shrinking of sludge volume with time (15,7). Mihok reported that limestone sludges settle to a rather dense mass (16), and Glover states that limestone sludges are much denser than lime sludges and attain higher densities when formed at lower pH (10). Attempts to thicken the sludge have met with limited success from a practical point of view (15). Another approach to sludge densification which should be mentioned is freeze-dewatering. BCR reports positive results on freeze-dewatering experiments on laboratory scale treatment of AMD sludges, achieving up to 90 percent reduction in sludge volumn (3).

Recycling of settled sludge has been also tried to attempt to produce denser sludge. Birch noted that if precipitated sludge was recycled into the incoming AMD "(the) settling times were reduced about 50 percent and a larger and heavier flock was produced" (14). Bethlehem Steel researchers, Haines and Kostenbader, (5) have reported outstanding success in forming a dense sludge from AMD treatment with lime. These researchers noted that they could increase the sludge solids from 1 percent to 15-to-40 percent using a revised treatment process. A controlled amount of the settled sludge is recycled, mixed with the lime slurry that normally would be used in the neutralizer, and this sludge-lime slurry is then added to the neutralizer. Not only does this high density sludge (HDS) process improve the solids content in the sludge, but also reduces thickener requirements and final sludge volume. This improved process (HDS) is not an expensive revision of a typical AMD treatment plant. The HDS process works best when the AMD ferrous to ferric iron ratio is as high as possible. Previously, this high ferrous AMD was considered the most difficult to treat. The other process variables of major importance are recycle ratio, pH, and the point of lime slurry addition. The optimum recycle ratio, defined as the ratio of return sludge from the thickener to the wasted sludge, should be 25:1 to 30:1 and holds both for ferrous and ferric iron AMD. The best neutralization pH was found to be 7.2 to 7.7. At lower pH values, the oxidation rate of ferrous iron was too slow and at higher pH values, thickener operating problems were encountered. The point of lime slurry addition had a strong effect on process success or failure.

BCR reports the effect of sludge recirculation on the neutralization of AMD with limestone. The researchers state: "In general, recirculation of slurry improved the effectiveness of limestone treatment as shown by pH and percent ferrous iron removed from the raw coal mine water". A direct relationship between the volume of slurry recirculated and the effectiveness of ferrous iron removal and neutralization was also observed. The authors state, "as the amount of slurry mixed with the raw mine water is increased, there is a corresponding decrease in ferrous iron concentration and acidity in the effluent". Because of the experimental technique used, there is no way to distinguish the separate effects of pH and the mass of precipitated ferric compounds in the sludge on the rate of ferrous iron oxidation. The effect of sludge recirculation on the properties of the sludge are not pronounced. The recirculated sludge was defined as sludge plus the treated water rather than as settled sludge (7).

The oxidation rate of ferrous iron by air is a factor which affects the economic possibilities of a predominately ferrous AMD treatment process. Basic work on ferrous iron oxygenation was done by Stumm (13). The investigation results of Stumm show that the oxygenation rate of ferrous iron is strongly pH dependent. Above a pH of 4.5, the oxygenation rate increases a hundred fold for each pH unit increase, while below pH 4.5, the rate decreases less sharply and below pH 3 and less, the rate becomes constant and pH independent. The oxygenation rate is given by expression

$$\frac{d\,[Fe(II)]}{dt}^{-} = K\,[Fe(II)]\,[O_2]\,[OH^-]^{2}$$

and is valid at pH above 4.5. The results of other investigations on ferrous iron oxygenation are also discussed in the report of Stumm and Singer (13). Stumm (13) also reports the results of some work done on catalytic effects. In the presence of sulfate, the oxidation proceeds more rapidly than in perchlorate alone. This was also observed earlier by Huffman and Davidson (17) and George (18). Phosphate was found to catalyze the oxygenation of ferrous iron. Cupric ion has been reported to be an effective catalyst in phosphoric acid (19), sulfuric acid (17), hydrochloric acid (20), and in the neutral pH range (21), and up to a 400-fold oxygenation rate increase of ferrous iron in presence of cupric ion in sulfuric acid solution was observed when compared with oxygenation rates in perchloric acid alone and the absence of cupric ion.

Stumm (13) investigated the catalytic properties of clays, colloidal alumina, and colloidal silica. He found that colloidal alumina was the most effective catalyst, increasing the oxygenation rate 10 to 30-fold, and was followed in decreasing order of effectiveness by colloidal silica, bentonite, and kaolinite, the latter not showing any catalytic properties. Colloidal ferric hydroxide was found to have no catalytic properties.

The catalytic properties of activated carbon were investigated by Lamb and Elder (22), Mihok (23), Stumm (13), and BCR (24). The activated carbons used by Lamb and Elder, Mihok, and BCR showed pronounced catalytic properties, but Stumm reports that activated carbon used in his work had no catalytic properties in the range of the pH of experiments.

Stauffer and Lovell (25) investigated the reaction rates of ferrous iron oxidation in the pH range of 4.5 to 5.7. The reaction rate constant ($\min^{-1} \times 10^{-5}$) increased from 1.5 at pH of 4.5 to 3030 at pH of 5.35 and continued to increase to pH 5.7. The oxygenation rate was first order with respect to ferrous iron concentration. Aluminum interference was observed and was found to increase proportionally with increasing Al:Fe(II) mole ratio. The oxygenation rate increased with increasing amount of Fe(II) precipitated as $Fe(OH)_2$.

Many investigators report the results of ferrous iron oxygenation in AMD on pilot plant scale and full scale plant experiments. The results are reported on the basis of holding time, time required to oxidize a definite percentage of total ferrous iron in a particular installation, and in terms of initial and final pH of the oxygenation tanks, and of a particular AMD. The many variables involved in a treatment of a particular AMD prevent, at this time, the generalization of the reported results in terms of a fundamental mechanistic model, and, therefore, the review of these investigation results, although significant, will be omitted in this report.

A unique ferrous iron oxidation process used at the Yanahara Mine (Japan) is reported by Ikegami (26,27). Nitrogen oxide is used as a catalist in a quantity of 1/30 to 1/40 part of ferrous iron present in the water, the reaction sequence being given by the author as:

$NO + 1/2O_2 \rightleftharpoons NO_2$ eq. (1)

$Fe^{2+} + NO_2 \rightleftharpoons Fe(NO)^{2+} + 1/2O_2$ eq. (2)

$Fe(NO)^{2+} + H^{+} + 1/2O_2 \rightarrow Fe(NO)^{3+} + H_2O$ eq. (3)

$Fe(NO)^{3+} + Fe^{2+} \rightarrow Fe(NO)^{2+} + Fe^{3+}$ eq. (4)

The nitrogen oxide is obtained by catalytic oxidation of ammonia;

$4NH_3 + 5O_2 \rightarrow NO + 6H_2O$. eq. (5)

After oxydation, the iron is removed from the water in a process referred to as an iron-aluminum replacement process. The aluminum precipitate formed in a later stage of the process is recirculated to the oxidized acid mine drainage and the iron is precipitated according to the reaction.

$Fe^{3+} + Al(SO_4)_m(OH)_n \rightarrow Fe_2(SO_4)_m(OH)_n + Al^{3+}$ eq. (6)

The iron is precipitated as dense sludge and is of high purity (60% Fe_2O_3). It may be mentioned that the process is particularly suitable for very high ferrous iron and sulfuric acid concentration AMD treatment.

It was already mentioned that the oxidation rate of ferrous iron with air in acid solutions is too slow for practical application. Efforts have been directed toward finding means to accelerate the oxidation rate of ferrous iron in acid solutions and promising results have been reported on the utilization of biochemical catalysis exerted by microorganisms.

Since Winogradsky first postulated that the energy yield from the oxidation of ferrous iron might serve as the sole support for the growth of a CO_2-assimilating microorganism, a variety of species of iron oxidizing bacteria have been described in the literature. Silverman and Lundgreen (28) concluded that only a few species are obligate chemoautotrophs; namely, Gallionella sp., Thiobacillus ferrooxidans, and Ferrobacillus ferrooxidans.

Gallionella is nonacidophylic (29,30) and is, thus, not generally found in AMD. Although the acidophilic iron oxidizing chemoautotrophs have been differentiated as separate species, with T. ferrooxidans and F. ferrooxidans being most prominent in the literature, there is increasing opinion that these strains may, in fact, be variants of a single species, and the iron oxidizing bacteria associated with acid mine drainage are often classified generally as the Thiobacillus - Ferrobacillus group (31).

Bacteria in the Thiobacillus-Ferrobacillus group are Gram negative bacilli measuring from 0.6 to 1.0 in width and from 1.0 to 1.6 μ in length. They are often actively motile, darting with a whiplike motion across the microscope field before becoming attached. The cells can best be shown by using Congo red in a negative staining procedure (32) or by phase contrast microscopy.

The bacteria are able to oxidize iron in an acidic environment according to the reaction

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad \text{eq. (7)}$$

The energy yield from the reaction is 11.3 Kcal/g atom of iron, but it has been estimated that only approximately 20% of this is utilized to fix carbon dioxide, which requires about 20 Kcal per g atom of carbon (33). Dugan and Lundgren (34) proposed a model mechanism to describe the oxidation of iron by the organism. Polarographic assays of the culture medium demonstrated an iron "complex" involving oxygen. The "complex" was formed by ferrous iron with phosphate and/or sulfate and oxygen, but the ferrous iron was not oxidized. The "complex" became bound to the cell wall or cell membrane, or both, where the iron was oxidized by either iron oxidase or oxygenase enzymes. The ferric ions then diffused away from the cell and reacted with water or sulfate ions to produce ferric hydroxide or sulfate.

These microorganisms oxidize iron in the pH range of 2.0 to 4.5 (32). Different workers obtained different optimum growth conditions as shown in Table I, and no growth has been reported at temperatures above 37°C (28).

These microorganisms have an obligatory requirement for carbon dioxide (33). It was shown by MacDonald, et al. (35) that the specific growth rate is independent of carbon dioxide concentrations greater than 0.01% in the gas phase and growth under these conditions (including normal air) is not carbon dioxide limiting. Whitesell, et al. (36) showed that a level of 17% carbon dioxide in the gas phase is inhibitory both for cell growth and iron oxidation.

TABLE I

OPTIMUM GROWTH CONDITION OF THE IRON BACTERIA

Workers	Optimum pH	Optimum Temperature(°C)
Leathen, et al. (33)	3.5	20 ~ 25
Silverman, et al. (29)	2.5	28
MacDonald, et al. (36)	2.5	33
Dugan, et al. (35)	3.0	
Whitsell, et al. (37)		25 ~ 30 varied with different strains

There have been numerous efforts toward biological treatment of acid mine drainage. Glover (37,38) developed an activated sludge process by using bacteria of the type described above. During the startup, the acid mine drainage was seeded with an ocherous deposit from a mine to an aeration chamber. From this chamber, the waste went to a settling tank. The sludge was collected, recirculated, and mixed with the incoming acid mine drainage.

Once the process was started, the seed was no longer necessary. The rate of iron oxidation was much greater in this process than in an aeration system alone, and was, in general, first order with respect to the ferrous iron concentration. The activated sludge process was followed by limestone neutralization to remove the ferric iron. Data were given, however, only for pilot scale operation (0.5-5 l/min.).

Whitsell, et al. (36) developed a biological ferrous iron oxidation scheme for the treatment of acid mine drainage which did not feature sludge recycle as such, but did provide for modest split flow through an inoculum generation tank with effluent from the inoculum tank flowing into the main oxidation tank. The intention was to aid start-up of the unit, and perhaps aid in continuous operation of the system. The main oxidation tank was split into two complete mix compartments, in series. While biological iron oxidation at low pH in this type of system was quite promising in bench-top scale units, scale up to a 2000 gallon oxidation tank volume with detention times on the order of 14-18 hours gave very disappointing results.

The one instance in which a biological ferrous iron oxidation process is known to give satisfactory performance in full scale operation is that of the process developed by Mitsubishi Metal Mining Co., Ltd. for application at the Hosokura Zinc Mine in Japan (39,40). This process features split flow of the feed, with 20% of the flow diverted continuously through an inoculum generation tank, the inoculum tank effluent and the remaining flow then being fed into a six-compartment-in-series oxidation tank, with a twenty-four hour detention time. Flow through the unit is about 80 gallons per minute, and the conversion of ferrous to ferric iron is in excess of 98%. In this particular instance, following iron oxidation, the flow is subjected to two stage neutralization using limestone and lime, with iron removal following neutralization with limestone to about pH5, and zinc recovery following lime treatment.

The literature sources cited this far include reports on the volumes and solids content of sludges formed in the treatment of actual and synthetic AMD and of ferrous or ferric iron solutions, but it appears that investigation of the basic chemical and physical processes affecting the dense sludge formation was generally neglected. Because the work presented below was oriented toward the investigation of the basic phenomena of dense sludge formation, the following short literature review is concerned with publications closely related to it.

Much research has been directed toward finding the conditions of formation and the identification of various hydroxides, oxyhydroxides, and oxides of iron. Most of the work was designed to study the corrosive oxidation of metallic iron, but it is also applicable to the investigation of dense sludge formation. A rather extensive literature survey on many of these iron compounds has been conducted by Feitknecht (41), and many of the comments in the following paragraphs may be attributed to him.

By oxidation of ferrous hydroxide or of buffered ferrous salt solutions at pH greater than 6, principally dark-green compounds, which are frequently called ferroso ferrites, are formed (42,43,44,45,46). According to Feitknecht and Keller (44), one has to distinguish between two series of these Fe(II) Fe(III) compounds. In one series, the lattice structure is the same as $Fe(OH)_2$. However, a maximum of about ten percent of the Fe^{2+} ions are replaced by O^{2-} ions. The second type is the hydroxy salts of Fe(II) Fe(III) formed from oxidation of ferrous salt solutions. These are often called green rust compounds (47) and have a lattice structure the same as Cobalt(II) (III) hydroxy salts (48). The structure is double layered as it is in many two and three valence metal compounds (49).

By further oxidation, black, brown, or yellow compounds are formed. However, the specific conditions at which each is formed has not yet fully been established. The x-ray diffraction diagrams of the black products obtained are identical with those of magnetite, but analysis of the black products has shown that Fe(II) is present in smaller proportions than predicted by the formula Fe_3O_4 (50,51,52). Also, 2 or 3 percent water is always present (53). Furthermore, Starke (52) has assumed that when magnetite is formed in water solutions hydroxyl groups are included in the lattice, and, therefore, the compound may be called hydroxymagnetite, but since this is still unproven, we will ignore it and call the black product simply magnetite. The exact conditions of magnetite formation are not reported, but most workers agree that its formation is favored by the slow oxidation of Fe(II) compounds (54).

The following hydroxides and oxyhydroxides of Fe(III) are described in the literature:

1. Amorphous Fe(III) iron hydroxides with water content varying between $Fe(OH)_3$ and FeOOH.
2. α-FeOOH, which has the same structure as goethite. When prepared in the laboratory, it is yellow.
3. β-FeOOOH, a yellow compound.
4. γ-FeOOH, an orange-brown compound with the same crystal structure as lepidocrocite.

The following ferric oxides are known:

1. Hexagonal α-Fe_2O_3, which is identical to hematite.
2. Cubic ferromagnetic γ-Fe_2O_3, which is identical to the mineral maghemite.

3. δ - Fe_2O_3, which does not occur naturally, and which, according to more recent research, is better called δ - FeOOH.

The amorphous Fe(III) hydroxides are formed by rapid precipitation of ferric salt solutions, but are never formed by oxidation reactions. The structure of the "amorphous" ferric hydroxide is not defined at present. Schwertmann (55) states that other researchers show that the ferric hydroxide gel shows microcrystals of hematite. However, Schellmann (56) felt that the gel was $Fe(OH)_3$ because infrared analysis showed a high number of combined hydroxyl ion stretches.

Stumm and his co-workers (13) have done research on the hydrolysis of ferric iron. In aqueous solution the ferric ion behaves as a multiprotic Bronsted acid. The protons from the coordinated water molecules of the Fe(III) are transferred to the solvent water:

$$Fe(H_2O)_6^{3+} + H_2O = Fe\ (H_2O)_5(OH)^{2+} + H_3O^+ \qquad \text{eq. (8)}$$

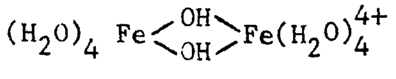
$$Fe(H_2O)_5(OH)^{2+} + H_2O = Fe_2(H_2O)_4(OH)_2^{+}+ + H_3O^+ \qquad \text{eq. (9)}$$

etc.

Such reactions can proceed until all of the coordinated water molecules have been deprotonated, resulting in the formation of anionic hydroxo-ferric species. These simple hydroxo-ferric complexes tend to polymerize by a condensation process

$$2Fe(H_2O)_5(OH)^{2+} = Fe_2(H_2O)_8(OH)_2^{4+} + 2H_2O \qquad \text{eq. (10)}$$

and the dimer has the structural configuration



$$(H_2O)_4\ Fe\begin{smallmatrix}\diagup OH \diagdown \\ \diagdown OH \diagup\end{smallmatrix}Fe(H_2O)_4^{4+} \qquad \text{eq. (11)}$$

The dimer may react hydrolytically, involving a proton-transfer

$$Fe_2(H_2O)_8(OH)_2^{4+} + H_2O = Fe_2(OH)_7(OH)_3^{3+} + H_3O^+$$

and by additional condensation reaction

$$2Fe_2(H_2O)_7(OH)_3^{3+} = Fe_4(H_2O)_{12}(OH)_6^{6+} + 2H_2O \qquad \text{eq. (12)}$$

one molecule is further dehydrated. In systems oversaturated with respect to insoluble ferric hydroxide, a series of such hydrolytic and condensation reactions, takes place, the multimeric and polymeric hydroxo-species serving as kinetic intermediates in the formation of the solid ferric hydroxide precipitate. On conclusion of the review of the mechanism of ferrous hydroxide formation, Stumm (13) mentions that the freshly-precipitated ferric hydroxide continues to react and generally converts to α - FeOOH. Feitknecht and Schindler (57) report that under specific conditions, α - Fe_2O_3, β - FeOOH and γ - FeOOH may be formed. In addition to these crystalline products, an amorphous material is always present, even after a prolonged period of aging.

Stumm (13) also discussed the effect of the presence of inorganic ligands other than OH^-, particularly SO_4^{2-}, and concludes that the influence of other inorganic anionic ligands is insignificant except in the acidic pH range, and when present in a relatively high concentration and when the ligands have a strong affinity for complexing with ferric iron. Wendt (58) observed that the dimerization, eq. (10), is considerably slower than the simple proton-transfer reaction and that the former is accelerated in the presence of simple anions, X^-, via a reaction of the form

$$FeX^{(3-n)} + FeOH^{2+} = Fe\begin{smallmatrix}\diagup OH \diagdown \\ \diagdown X \diagup\end{smallmatrix}Fe^{(5-n)}$$

Thus, it is apparent that the ferric iron is precipitated from acid solutions with a relatively high sulfate concentration as $Fe(OH)_n(SO_4)_m$, the sulfate content of the precipitate increasing with decreasing pH and increasing SO_4^{2-} concentration. Generally, the ferric hydroxosulfates (Yellow Boy) form denser precipitates when compared with the precipitates of amorphous ferric hydroxides.

Schellmann (56) studied the formation of crystalline ferric compounds by aging ferric hydroxide gels in solutions that contained various ions. α - FeOOH, goethite, was formed at high pH values and α - Fe_2O_3, hematite, was formed at low pH values.

In the neutral range, both hematite and geothite were formed. The adsorption of ions by the ferric iron gel has an effect on the particular compound formed. The ion adsorbed by ferric gel has a greater effect than does the pH. If ferric gel adsorbs negative ions, particularly SO_4^{2-} and HCO_3^- , the crystallization tends toward goethite formation. If the $Fe(OH)_3$-gel adsorbs such positive ions as Mg^{2+} or Ca^{2+}, the crystallization is toward hematite. Schellmann (56) also stated that the ions of Na^+, K^+, Ba^{++}, Cl^- and NO_3^- had no effect on the transformation of ferric gel to hematite or goethite. Schwertmann (55) found that at a pH of about 12, geothite was formed from a gel formed by the reaction of $FeCl_3$ with NH_4OH and washed to remove NH_4^+ and Cl^- ions. At a pH below 12, hematite was formed. However, Schwertmann also found some α - FeOOH, goethite, at pH as low as 6.5 even after long aging. The largest crystals were formed at room temperatures, where at high temperatures, poorer crystals were formed due to faster crystal formation. Similar results were obtained earlier by Bohn (59) and Krause (60). γ - FeOOH, lepidocrocite, apparently is not formed from amorphous $Fe(OH)_3$.

It should be mentioned that on aging of the $Fe(OH)_3$-gel, the formation of α - FeOOH and α - Fe_2O_3 is associated with the formation of dense precipitates.

By oxidation of solid ferrous hydroxide or ferrous salt solutions at pH of 3.5 and higher, the following products may be formed: magnetite, Fe_3O_4, α - , γ - , or δ - FeOOH.

According to Krause and coworkers, (61) high hydroxyl ion concentration is favorable for the formation of α - FeOOH. However, it may be formed by oxidation of ferrous bicarbonate solutions (62) or in ferrous salt solutions when the oxidation is conducted directly to the formation of ferric compounds (63). Sulfates and fluorides also enhance its formation. The formation of

γ- FeOOH is favored by the presence of chlorides, bromides and iodides (64).

γ - FeOOH as a thermodynamically unstable modification may be converted to α- FeOOH. The conversion is accelerated by the presence of OH^- or Fe^{2+} (60,64). The conditions at which γ- FeOOH is formed have been reported (65,64,66,67), and the products often contained small amounts of α - FeOOH. Some suggestions for the mechanisms and causes of formation can be found in the work of Nitschmann (68). Schwertmann (55) also studied the effects of iron oxidation on the final crystalline products formed. He concluded that frequently, γ - FeOOH, lepidocrocite, is formed, but the results are sensitive to pH, oxidation rate, and presence of other ions. During his studies, Schwertmann kept pH constant within ± 0.25 units. When oxidation was conducted with a carbon dioxide and oxygen mixture, and when the ratio of carbon dioxide to oxygen was greater than one (by volume), goethite was formed. When a carbon dioxide free oxygen was used or the ratio of carbon dioxide to oxygen was less than one, lepidocrocite was formed. Schwertmann stated that in presence of a high concentration of carbon dioxide, ferrous carbonate is formed, and the oxidation of ferrous carbonate leads to formation of goethite. At a pH of 4 to 5, he obtained lepidocrocite, with some goethite present. As the pH was increased, better crystals were formed. Schwertmann concluded that pH 7.0 was the best for lepidocrocite formation by air oxidation of ferrous iron solutions. Schwertmann performed some oxidation experiments using a three percent solution of hydrogen peroxide. He concluded that even though the oxidation occurs at a much higher rate, the products formed are the same. However, he noted that in the high pH range, the fraction of magnetite formed was higher than with air oxidation. Schwertmann (55) also mentioned that in the high pH region, oxidation was incomplete, due to the formation of magnetite, Fe_3O_4, which is not a completely oxidized iron compound. Interesting observations were reported by Nitschmann (68). Nitschmann performed oxidation of dilute $FeSO_4$- solutions in the presence of metallic iron with air at elevated temperature, and observed the effect of addition of crystallization nuclei, consisting mainly of γ - FeOOH. Depending on the number of nuclei added, per volume of the ferrous sulfate solution, he obtained γ - or α - FeOOH or a mixture of both. The mechanism of the process was explained by the observation that γ - FeOOH is affected by the presence of Fe^{2+} and OH^- ions and undergoes topochemical and pseudomorph transitions by forming α - FeOOH. The final product composition depends on the rate of growth of γ - FeOOH crystals and on the rate of transition of γ - FeOOH to α - FeOOH, which starts at the surface of the γ - FeOOH crystals. Thus, by varying the amount of added nuclei, it is possible to affect the kinetics of the two competing processes and consequently, the composition of final product. When a comparatively small amount of nuclei is present, the γ - FeOOH crystals grow so fast that the transition to α - FeOOH is practically negligible, but when the quantity of nuclei is large, the transition to α- FeOOH, which starts at the surface of the crystals, is faster than the γ - FeOOH crystal growth and the final product is α - FeOOH.

The β - FeOOH is formed by hydrolysis of FeOCl (69) or $FeCl_3$ (70,71) solutions or by oxidation in moist air of $Fe_2(OH)_3Cl$ (46), but it is never formed by oxidation of ferrous compounds in water solutions.

All work done on the formation of ferromagnetic δ - FeOOH has indicated one common tendency. It can be formed by very rapid oxidation of ferrous compounds with an excess of oxidants like H_2O_2 and O_2. According to Schikorr (45), Baudisch and Welv (72), and Glemser and Gwinner (73), it was found that these preparations contained from 7.7 to 16 percent bound water. Glemser and Gwinner had originally proposed to call the compound δ - Fe_2O_3, but due to the high water content and investigation of the crystal structure, it is more reasonable to call the compound δ - FeOOH.

α - Fe_2O_3 is formed by aging amorphous ferric hydroxide in water or alkaline solution (59,60). Frequently, α - FeOOH is also present. However, no evidence was found in the literature that α- Fe_2O_3 could be formed by oxidation of solid ferrous hydroxy compounds at room temperature.

The ferromagnetic cubic γ - Fe_2O_3 is formed by heating magnetite precipitate in air (74), by fusing magnetite with KNO_3 or by heating it with persulfate solution. It is also formed by dehydration of γ - FeOOH in air at 300°C, and has a structure very similar to that of magnetite (75,76,77,78). If magnetite is heated to 150°C, no change in the X-ray patterns can be observed, but by heating to higher temperatures, superstructure lines appear (79). If the γ - Fe_2O_3 is formed from water-containing magnetite, the γ - Fe_2O_3 still contains water. If water-free magnetite is oxidized, a water-free γ - Fe_2O_3 is obtained, which also shows superstructure lines (80). The structure of γ - Fe_2O_3 and γ - FeOOH have been compared by Bernal and coworkers (81). Magnetic properties have been investigated by Simon and coworkers (82).

There is still little knowledge of the kinetics and mechanisms of the discussed oxidations, but generally, three types of the transformations are believed to be involved:

1. Transformations through the free solution.
2. Two-phase topochemical transformations.
3. One-phase topochemical transformations.

Furthermore, Feitknecht and his coworkers (41) have shown that when a suspension of Fe(II) compounds is oxidized by an oxygen-containing gas mixture, the overall oxidation rate is determined by three important steps:

1. The rate of dissolution of the oxygen.
2. The rate of diffusion of the oxygen to the particle surface.
3. The reaction rate of the adsorbed oxygen with the particle.

The first two steps are dependent on the gas flow rate and the intensity of mixing in the solution, while the third step is independent of these factors. Feitknecht (41) found the oxidation rate of $Fe(OH)_2$ to be linear with gas flow rates up to 1.5 liters per minute for 40 ml solution. This implies that in this range, step 1 and 2 are controlling.

According to Miyamoto (83), the rate of oxidation is mainly affected by the oxygen dissolution step. For the first stage of oxidation, formation of the green $Fe(O,OH)_2$, a one-phase topochemical reaction was assumed. The mechanism proposed was that in the structure of ferrous hydroxide, ferrous ions release electrons, hydroxide sites release protons, and then protons and electrons migrate to the surface and react there with adsorbed oxygen to form water (44,84,85).

Feitknecht (41) has also investigated the formation and subsequent oxidation of magnetite. His results show that the rate at which oxygen can reach the $Fe(OH)_2$ particle and the pH of the solution are of greatest importance. α -, γ -, and δ - FeOOH are formed at high oxidation rates.

Magnetite can be formed by slow admission of oxygen to either ferrous chloride solution at pH 13 or to ferrous sulfate solution at pH 8.5. The oxygen flow rate, at which magnetite is formed, instead of FeOOH, is not narrowly defined. However, of all the magnetite precipitates produced in this manner, none contained the theoretical 66.7 percent ferric iron of the total iron. The X-ray diagrams of precipitate with Fe(III), less than 70 percent showed, besides magnetite, also peaks of δ - FeOOH. This δ - FeOOH was probably formed during preparation of X-ray specimens by oxidation of $Fe(O,OH)_2$ in air. The conclusions drawn from this were that the preparations containing more than 66.7 percent Fe(III) are mixtures of magnetite and either $Fe(O,OH)_2$ or Fe(II)-Fe(III) hydroxy salts.

In the above preparations of magnetite, when ferrous hydroxide was oxidized with a mixture of 0.5 percent oxygen and 99.5 percent nitrogen, the ferric iron content of the product increased uniformly with time up to 66.7 percent, then the increase of Fe(III) content was slow. When this oxidation was continued with a gas mixture of higher oxygen concentration, the oxidation rate increased temporarily and then slowed down again. Furthermore, if air was used as the oxidant, precipitates with high ferric content were formed in a short time. When the oxidation was fast, small magnetite crystals which could be easily oxidized were formed, but by slow oxidation in strongly alkaline solutions, coarse crystals of magnetite with lower ferric content were formed.

Feitknecht further investigated magnetite formation in strongly alkaline solutions. His work and Keller's (46) X-ray diffraction diagrams both substantiated the transformation from $Fe(O,OH)_2$ into magnetite. Electron microscope pictures showed that when the oxidation was carried out slowly, hexagonal flakes of $Fe(O,OH)_2$ first formed and that with further oxidation, the flakes disappeared and well-shaped cubes of magnetite were formed. It was deduced from this evidence that the mechanism was through the solution. Feitknecht proposed that in strongly alkaline solutions, a high concentration of hydroxyl complexes exist, and that the magnetite nuclei spontaneously form according to the reaction:

$$2\ Fe(OH)_4^- + Fe(OH)_3^- = Fe_3O_4 + 4H_2O + 3OH^-$$

In a ferrous chloride solution buffered at pH 8.5, the primary product of oxidation is Fe(II) Fe(III) hydroxychloride. Feitknecht's electron microscope pictures showed that the ferrous hydroxide and Fe(II)Fe(III) hydroxysalts both formed flake-like crystals, but the hydroxychloride flakes were much smaller and thicker. The pictures showed that after oxidation to magnetite, the precipitate consisted almost entirely of these small thick flakes, pseudomorphous with the hydroxysalt. Therefore, magnetite has the same crystal outer shape as the Fe(II)Fe(III) hydroxychloride. The formation of magnetite under these conditions can thus be deduced to be a two-phase topochemical reaction.

The thermodynamic stability of magnetite can be best described by use of a Pourbaix diagram. These diagrams represent the stability of solids and dissolved species as a function of pH and Eh. A description of the construction and use of the diagrams is given by Garrels and Christ (86). Pourbaix diagrams of relation among iron minerals show that at 25°C and 1 atm., magnetite is stable only above pH 7.5 (86).

As has been discussed in previous pages, mixtures of ferrous and ferric hydroxides can be treated to produce magnetite. However, certain ions, especially aluminum, magnesium, and silicate may interfere with the formation, and voluminous sludges are the result. The interference is confined to pH ranges in which these ions exist in sparingly soluble form.

Aluminum interference is confined to a pH between 4.1 and 10.8 (87). At pH below 4.1, Al^{3+} is in solution, and for pH above 10.8, the aluminate ion is soluble. However, at pH's between these two limits, aluminum hydroxide is quite insoluble. It is unfortunate also that the pH at which magnetite is most easily formed lies within this range.

Kakabadse and Whinfrey (87) have found that magnesium interference exists in solutions at 25°C only above pH 9.6. Similar results were reported by BCR (3). Silica on the other hand exhibits interference effects at pH below 10.7.

Kakabadse and coworkers (87,88) have investigated the mode of interference by use of adsorption and redox experiments. The studies have shown that aluminum favors adsorption on ferric hydroxide, and the ferric and aluminum hydroxides are co-precipitated leaving ferrous hydroxide unaffected.

A complex mode of interference was suggested for magnesium. The interference above pH 9.6 is most pronounced when the ratio of magnesium to ferrous iron is unity, and can be attributed to a "magnesio-wustite" (MgO, FeO) type sublattice within the magnetite phase (88).

Adsorption studies showed that silica is very strongly adsorbed on ferrous hydroxide. Whether the bond between the silica and the ferrous hydroxide is strong enough to be called chemical is uncertain, but redox experiments suggest that it is (87).

The literature survey suggests that by neutralization and oxidation of AMD denser sludge formation is expected when the sludge formation is conducted at conditions which favor formation of dense crystalline compounds, particularly ferric hydroxy sulfates, α - FeOOH, goethite, γ - FeOOH, lepidocrocite, δ - FeOOH and Fe_3O_4, magnetite, or the combination of these compounds even in the presence of the amorphous insoluble ferric hydroxy compounds. The research reported in the following sections was conducted along the established guidelines based on the literature survey.

SECTION I.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The neutralization and oxidation operations of ferrous sulfate-sulfuric acid solutions, ferric sulfate-sulfuric acid solutions, aluminum sulfate-sulfuric acid solutions and synthetic acid mine drainage (SAMD) were performed by using 800 ml solution in 1000 ml beakers. The solutions were stirred on a Phipps and Bird six gang paddle stirrer with 1 inch x 3 inch paddles at definite RPM. In experiments where oxidation with air or nitrogen-air mixture was performed, the gases were introduced through 8mm gas dispersion tubes with 12mm diameter coarse fritted glass cylinders, close to the bottom and to one side of the stirrer paddle. The base was added to the solution by graduated pipettes, when sodium hydroxide solutions or calcium hydroxide suspensions were used, or in fine powder form when calcium carbonate was used.

The pH of the solutions was measured with Sargent pH Meter Model DR S-30000, Beckman Zeromatic pH Meter or Beckman Model H2 Glass Electrode pH Meter and Sargent S-30072-15 Combination Electrode or Sargent S-30070-10 Miniature Combination Electrode or Beckman Standard Calomel and Glass pH electrodes. The choice of a pH meter and electrodes depended on the desired accuracy of measurements and convenience.

In experiments where dissolved oxygen concentration or concentration change was measured, the Yellow Spring Instrument Company Oxygen Meter Model 51 or 54 were used.

The precipitate sludge volume was measured, after settling for definite time, in 1000 ml graduated cylinders or one liter Imhoff cones, depending on the sludge volume and accuracy desired.

The sludge content was determined by transferring the sludge or a fraction of the sludge volume to a weighing bottle, evaporating on a steam bath and drying the solids at 110°C until constant weight was achieved.

Deviations from the above outlined procedure are indicated in the text and when more elaborate or specialized apparatus was used, a short description and/or schematic drawing of the equipment is presented.

For the preparation of the required solutions, reagent grade chemicals were dissolved in distilled water, generally by preparing stock solutions of higher concentration and diluting aliquots of the stock solutions to required volume and concentration. The composition and concentration of the solutions used in experiments are given in the description of the particular experiments in the text. A formulation for synthetic acid mine drainage (SAMD) was obtained from Ronald D. Hill of EPA in Cincinnati. The formulation corresponds to the following concentrations:

Ca^{2+}	80.0 mg/l
Mn^{2+}	7.8 mg/l
Al^{3+}	15.0 mg/l
Fe^{2+}	200.0 mg/l
Mg^{2+}	24.0 mg/l
SO_4^{2-} (total)	1200.0 mg/l
pH	2.1

Variations of this formulation were used and are mentioned at the appropriate place in the text.

The total iron in solutions was determined by the o-phenanthroline method, following the procedure: Phenanthroline Photometric Method adapted for water analysis <u>Standard</u> <u>Methods</u> (twelfth edition, 1965, prepared and published by the American Public Health Association), using Beckman DU Spectrophotometer and 1 cm or 5 cm cells. The total iron was also determined by atomic absorption techniques using a Perkin-Elmer Atomic Absorption Spectrophotometer Model 303. The choice of method depended on the concentration of total iron and accuracy desired.

The determination of ferrous iron was done by titrating the sample solution with 0.1 or 0.01 N $K_2Cr_2O_7$- solution, depending on ferrous iron concentration, using sodium diphenylamine sulfonate indicator. In a few cases, the orthophenanthroline method was also used.

The determination of aluminum in solutions was done by using an Alizarin Red-S Photometric Method adapted for water analysis (Analysis of Coal and Coke Ash, pp. 407, 1971 Annual Book of ASTM Standards, Part 19, American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103), and Beckman DU Spectrophotometer.

Total sulfate was determined gravimetrically by precipitation as barium sulfate.

Total iron in sludge was determined by dissolving the sludge in conc. HCl, oxidation, followed by titration with $TiCl_3$- solution (Applied Inorganic Analysis, W. F. Hildebrand, John Wiley and Sons, Inc., New York). Calcium, manganese and magnesium in sludge was determined by Atomic Absorption techniques and aluminum and sulfate by methods already mentioned above.

More detailed descriptions of the specialized equipment, procedures and analysis are found in the master thesis of Klingensmith (90), Swartz (91), and Chao (92).

X-ray diffraction analysis was done in the Minerology Department of Ohio State University by Sylvia Chen, under supervision of Dr. Rodney Tettenhorst.

SECTION II.

FORMATION OF MAGNETIC SLUDGES

Results and Discussion

In the early-stage exploratory studies, 800 ml of pure ferrous sulfate-sulfuric acid solution (200 mg/l Fe^{2+} and 1000 mg/l total $SO_{4-}{}^{2-}$) at pH 1.9 and saturated with air at room temperature, (25° to 28°C), were placed in a 1000 ml beaker, provided with a paddle stirrer and an air inlet tube. The solution was neutralized with an approximately 1N calcium hydroxide suspension to the desired pH and air was passed through the solution at specified rate for a specified time.

Generally, dark blue precipitates, green-rust II, were formed, which in shorter or longer time period, turned to black magnetic, $Fe_3O_4 \cdot nH_2O$, or dark brown magnetic or non-magnetic or reddish brown non-magnetic precipitates, depending on the pH of the solution, the air flow rate, and time of aeration. The most dense black, magnetic precipitates were formed at pH 8.5 to 9.0. At very slow air flow rates, dense black, magnetic precipitates were usually formed during the aeration period. At fast air flow rates and prolonged aeration times, the dark-blue precipitates were oxidized to dark-brown or reddish-brown non-magnetic voluminous precipitates. It was also observed that the geometry of the oxidation equipment and the efficiency of the air dispersion device had a pronounced effect on the formation of magnetic precipitates. These observations indicated that the controlling factor was the oxidation rate of the ferrous iron. Further experiments were performed using an air-nitrogen mixture. Good conversion of ferrous hydroxide, or the dark blue precipitates, with an excess of ferrous iron, was observed when the oxygen concentration in the solution did not exceed 2 mg/l and the nitrogen air mixture contained from

2 to 5 percent oxygen, depending on the flow rate. These observations were in accord with the observations made by Feitknecht (41) and others.

Feitknecht (41) observed that conversion of green rust may be explained by a two-phase topochemical reaction. Feitknecht's observations suggested that the conversion of green rust II to magnetite occurs at enhanced rate when the ratio of ferric to ferrous iron in the dark blue precipitate is 2: 1. A series of runs were made using a solution of 96.5 mg/l of Fe^{2+}, 23.5 mg/l Fe^{3+}, 800 mg/l total SO_4^{2-} and 8 mg/l of dissolved oxygen at temperature of 27°C, solution saturated with air. 8 mg/l O_2 will oxidize one mg-mole of ferrous iron or 55.85 mg. When all the oxygen is consumed in the reaction the precipitate should contain 40.7 mg ferrous iron and 79.3 mg ferric iron, corresponding to a mole ratio of 1: 2. The experiments were performed similarly to those described above, omitting only the aeration of solution, and the concentration of oxygen was measured with respect to time. At pH 8.5 to 10.0 and 27°C, the conversion of green rust II to magnetite was fast, in some cases forming immediately, and the oxygen concentration decreased to near zero in two to four minutes. The highest conversion rates were observed when the pH of the solution was raised abruptly to 8.5 to 9.5 and the concentration of $Ca(OH)_2$- suspension was decreased to approximately 0.2N. Non-magnetic precipitates were formed when the pH of the ferric-ferrous iron solution was raised slowly. At lower pH, ferric iron was the primary precipitate, and at higher pH, ferrous iron precipitated. A two-phase topochemical reaction, conversion of green rust II to magnetite, should proceed at a faster rate when two ferric iron atoms and one ferrous iron atom are closely spaced; by slowly raising the pH of the solution, the favorable conditions were not attained and, consequently, the formation of magnetite was inhibited. Using concentrated $Ca(OH)_2$ - suspension, localized high pH developed which inhibited the formation of magnetic precipitates. Also, $Ca(OH)_2$ particles occluded in the green rust II flocs settled on the bottom of the reaction container and the high pH observed in the settled precipitate retarded the formation of magnetite.

Table II shows some results of the experiments. The figures in the column marked "Magnetic Response" indicate on a relative semiquantitative scale the magnetic response of the settled precipitates. A small magnet was slowly moved up the outside wall of the glass settling container starting at the bottom of the container. The figures indicate the height in milimeters the precipitate was pulled up by the magnet along the inside wall of the glass container. This procedure was acceptable considering the exploratory nature of the study.

The volume of the settled sludge formed at the most favorable conditions and 24 hours settling time was from 0.9 to 1.1 percent with a solids content from 2.5 to 2.7 percent. The sludge volume obtained by precipitation of a solution of 120 mg/l Fe^{3+} and 800 mg/l total SO_4^{2-} with $Ca(OH)_2$- suspension at pH 8.5 was from 6.8 to 7.0 percent with a solids content of 0.38 to 0.41 percent after 24 hours settling time. The volume and solids content of the magnetic sludge was only approximately 15 percent of the sludge volume and solids content of a sludge obtained at similar conditions from a solution of ferric iron.

During the course of the work, it also was observed that a small quantity of reddish-brown flocs formed in the supernatant solution after the magnetic precipitates settled. When the magnetic precipitate settled, the supernatant solution was practically oxygen-free, but soon oxygen slowly dissolved from the ambient air and oxidized the ferrous iron left in the supernatant solution to less soluble ferric iron, which precipitated in form of reddish-brown floc. The oxidation of ferrous iron and the subsequent hydrolysis of the ferric iron to less soluble ferric hydroxide was associated with

TABLE II

Effect of pH, concentration and rate of addition of $Ca(OH)_2$-suspension on magnetic precipitate formation.

Run No.	pH after $Ca(OH)_2$ addition	Normality of $Ca(OH)_2$	Addition* of $Ca(OH)_2$	Precipitate Color	After Settling			
					hours	Supernatant pH	Precipitate color**	Magnetic response***
11	11.0	1.0	F.S.	D.Br.	16	10.5	D.Br.	0
12	11.0	1.0	F.S.	D.Br.	16	10.5	D.Br.	0
14	10.0	1.0	F.S.	Gr.Br.	3	9.8	D.Br.	0
					6	9.6	B.	15
13	9.9	1.0	F.S.	D.Br.	16	8.8	B.	40
15	9.7	1.0	F.S.	D.Br.	2.5	9.0	B.	5
					6	8.9	B.	35
16	9.0	1.0	V.F.	Gr.Br.	.25	8.4	D.Br.	0
					2	6.6	B.	20
					5.5	6.5	D.Br.	35
10	8.5	.2	V.F.	D.Br.	16	6.3	D.Br.	15
17	8.6	.2	V.F.	D.Br.	1	6.5	D.Br.	20
					5	6.9	D.Br.	30
18	9.5	.2	V.F.	D.Br.	1.6	9.0	B.	30
					5	8.9	B.	50
19	10.5	.2	V.F.	D.Br.	4.5	10.3	D.Br.	0

Initial solution: 96.5 mg/l Fe^{2+}, 23.5 mg/l Fe^{3+}, 800 mg/l total So_4^{2-}, 8.0 mg/l O_2,
pH 1.95, temp. 27°C.
After O_2 consumed for oxidation: 40 mg/l FeII and 80 mg/l FeIII.

*) F.S. - fast stream, V.F. - at once in one batch

**) D.Br. - dark brown, Gr.Br. - greenish brown, B. - black a decrease of pH, which was observed experimentally. To determine the extent of iron removal, samples of the supernatant solution were taken immediately after the sludge settled and were analyzed for total soluble iron. The results are shown in Table III. It is interesting to note that the total iron found in the supernatant is close to the solubility of ferrous iron at specified pH as determined by Stumm (13), and shown in the last column of the Table III.

Similar runs were made using a solution of 200 mg/l total iron and 800 mg/l total sulfate. The results (Table IV) were similar with those obtained with the solution of 120 mg/l total iron. The exploratory studies showed that at a temperature of 25° to 28°C, magnetic precipitates may be obtained from pure ferrous sulfate-sulfuric acid solutions by neutralization of the solution with calcium hydroxide suspension to pH 8.5 to 9.5. Initially formed voluminous ferrous hydroxide precipitates were converted, through an intermediate dark-blue phase - green rust II, to dense black magnetic precipitates, $Fe_3O_4 \cdot n H_2O$, by slow oxidation with air. The favorable oxidation conditions were achieved when the oxygen concentration in the solution did not exceed 2 mg/l and depended on the solution-air contacting device. The best conditions were achieved when an air-nitrogen mixture with oxygen concentration not exceeding 5 percent by volume was used. The drawback of this procedure was that by oxidation of ferrous iron with air at room temperature, it was very easy to inadvertently form voluminous non-magnetic ferric hydroxide precipitates.

An alternative procedure was to precipitate the iron from a solution with a pH of two or less and containing ferric and ferrous iron at a mole ratio of 2: 1, by neutralization with calcium hydroxide suspension to a pH 8.5 to 9.5. The voluminous dark blue precipitates formed green rust II and were converted by aging to dense magnetic precipitates, $Fe_3O_4 \cdot H_2O$, the observed

TABLE III

Concentration of Total Iron in the Supernatant Solution

Sample Number	pH of Supernatant	Total Iron in Supernatant mg/l	Solubility* of Ferrous Iron mg/l
1	8.5	6.2	7.0
2	9.5	.52	.5
3	10.0	.24	.2
14	9.3	1.18	1.0
15	9.0	2.00	2.2
16	9.0	2.40	2.2
17	9.1	1.56	1.6
18	9.5	.80	.6
19	9.6	.52	.4

*) Dr. Werner Stum, "Oxygenation of Ferrous Iron: The rate-Determining Step In the Formation of Acie Mine Drainage" pp 2-5. Water Pollution Control Research Series. DAST-28, 14010-06/69. U.S. Department of the Interior. Federal Water Pollution Control Administration.

TABLE IV

Effect of pH and Settling Time on Formation of Magnetic Precipitate

Run No.	pH on addition of $Ca(OH)_2$	Normality of $Ca(OH)_2$	Precipitate Color*	After Settling			
				hours	Supernatant pH	Precipitate Color*	Magnetic responce**
3	10.5	1.0	D.Gr.	.5	10.5	D.Gr.	0
				3.5	10.4	D.Gr.	0
				15.5	9.6	Br.	5
5	10.5	1.0	Gr.B.	1.5	10.4	B.	0
				6.5	10.1	D.Br.	5
				10.0	9.3	Br.	35
2	9.7	1.0	D.Bl.	.5	9.7	D.Gr.	0
				3.5	9.3	D.Br.	10
				16.0	8.0	D.Br.	30
4	9.5	1.0	Bl.B.	.25	9.4	Bl.B.	0
				2.0	9.0	B.	25
				6.5	8.1	D.Br.	30
				20.0	7.2	D.Br.	35
1	8.5	1.0	D.Br.	.5	6.5	D.Gr.	0
				1.2	6.3	Gr.B.	0
				4.5	5.6	D.Br.	5
				16.5	4.9	D.Br.	6
6	8.5	1.0	Bl.B.	.3	7.6	Br.	6
				5.3	6.8	D.Br.	6
				19.0	6.75	D.Br.	7
9	10.6	.2	Bl.B.	3.2	10.5	D.Br.	0
				72	7.9	D.Br.	10
8	9.5	.2	D.Br.	3.7	8.3	D.Br.	15
				72	6.7	D.Br.	25
7	8.8	.2	Gr.B.	.2	8.4	D.Br.	--
				4.0	5.9	D.Br.	9
				72	5.0	D.Br.	10

Initial Solution: 122.5 mg/l Fe^{2+}, 77.5 mg/l Fe^{3+}, 800 mg/l total SO_4^{2-}
8.0 mg/l O_2, pH 2.2, temperature 25 to 27°C.
After O_2 consumed for oxidation: 66.5 mg/l FeII and 133.5 mg/l FeIII.

*) B. - black, Br. - brown, Bl.B. - bluish black, Gr.B. - greenish black, D.Bl. - dark blue, D.Br. - dark brown, D.Gr. - dark green.

*) 0 - nonmagnetic, figures represent magnetic response on arbitraty semiquantitative scale.

transition period was from near zero to 24 hours at room temperature. This latter procedure required a solution with an initial pH of two or less, and the total soluble iron with a mole ratio of ferric to ferrous iron of 2: 1. The low pH was necessary to prevent the hydrolysis and precipitation of ferric iron before the neutralization step. Keeping in mind the purpose of this study, the applicability of the second procedure would be limited to treatment of acid mine drainage with pH not exceeding two, and a mole ratio of ferric to ferrous iron less than two. The probability of finding an acid mine drainage with the required mole ratio of ferric to ferrous iron is practically nil, and, therefore, an oxidation step would be required to adjust the ferric to ferrous iron ratio. The oxygenation rate of ferrous iron in solution at low pH proceeds too slowly to be considered practical under field conditions. However, the oxidation rate of ferrous iron at low pH may be increased utilizing the acidophilic iron oxidizing autotrophs of the Ferrobacillus-Thiobacillus group.

A continuous bacteria culture was used to study the effect of the Ferrobacillus-Thiobacillus on the formation of magnetite. The requirements of this micro-organism are carbon dioxide, oxygen, ferrous iron, low pH, and other trace nutrients. A synthetic mine water which was formulated by Bailey (93) was used to feed the bacteria. The feed contained 1000 mg Fe^{2+} and 0.5 ml H_2SO_4 per liter, which kept the pH at 1.98. It should be noted that the bacteria are present in the natural environment, and if introduced into a favorable environment, will begin reproducing and oxidizing iron. The growth of bacteria in the feed tank was undesirable since a constant feed composition was essential to the experimental procedure. Rather than sterilize the equipment, oxygen was excluded from the feed. To accomplish this, nitrogen was bubbled through the feed solution for twenty minutes after preparation and the feed was stored under 2 psi nitrogen pressure. These precautions helped maintain the dissolved oxygen near zero.

The continous culture apparatus is illustrated in Figure 1. The feed tank was a five-gallon glass bottle equipped with glass tubes for admission of nitrogen and withdrawal of the feed. The oxygen-free synthetic mine water was pumped from the feed tank by a solid state Veristaltic Pump manufactured by Manostat Corporation. A 6 ml/min flow rate was maintained by use of a General Electric Type TSA-14 Repeat Cycle Timer. The feed was pumped directly into a small calibrated surge tank which permitted flow measurements and maintained more uniform flow into the reaction vessel. The reaction tank was an 8400 ml Polyethylene bottle which operated essentially as a continuous stirred tank reactor. Feed entered the bottom of the tank while effluent overflowed at the top. Air was bubbled into the reactor to achieve stirring and to supply bacteria with oxygen.

Two kinds of analysis were made on the culture. The bacteria were counted to verify constant growth. The counting was done using a calibrated counting chamber and a phase contrast microscope. Samples of the feed were periodically analyzed to verify no growth in the feed tank. Another measure of the bacterial activity in the reactor was the ferrous iron content of the effluent, determined by titration with 0.1N $K_2Cr_2O_7$.

The main purpose of bio-oxidation experiments, at this particular point in the course of this study, was to determine the possible interference of products generated in the bio-oxidation process on the formation of magnetic precipitates. The experiments with the bio-chemically oxidized solutions were performed similarly to the experiments performed with pure ferrous-ferric sulfate-sulfuric acid solutions. No interference on the formation of magnetic precipitates was observed. To obtain more accurate information on the conditions at which dense sludges are formed, a series of experiments were performed

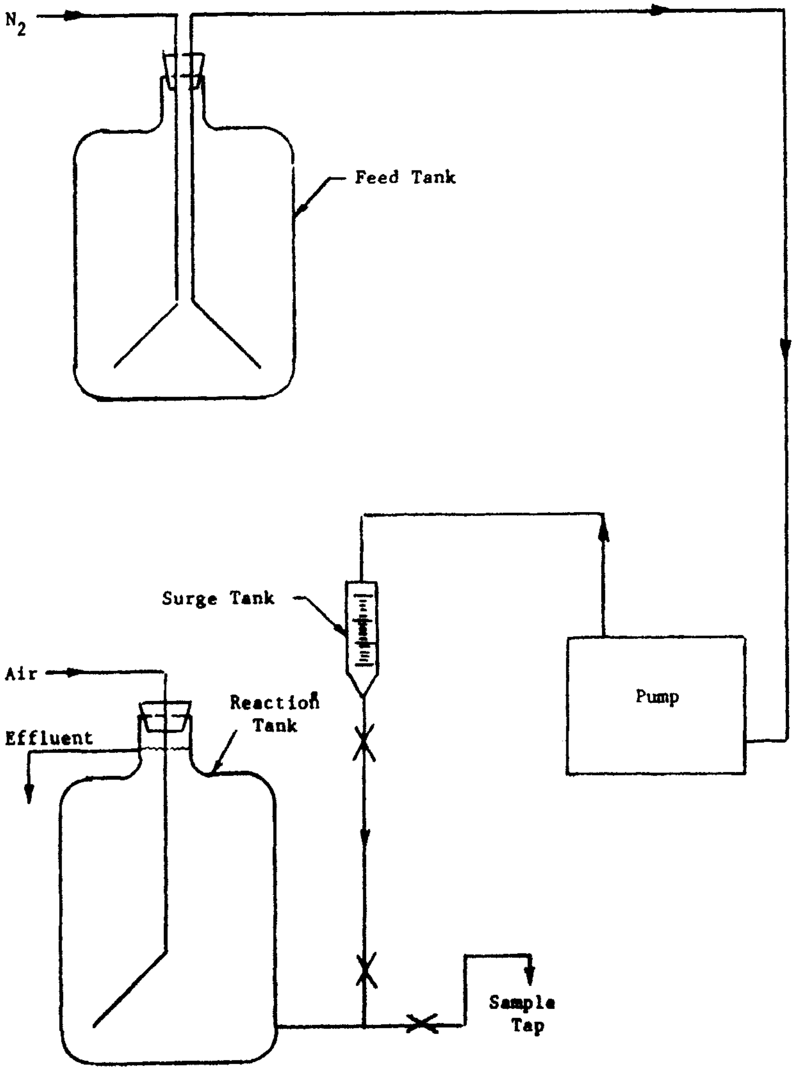


Figure 1

Continuous Culture Apparatus

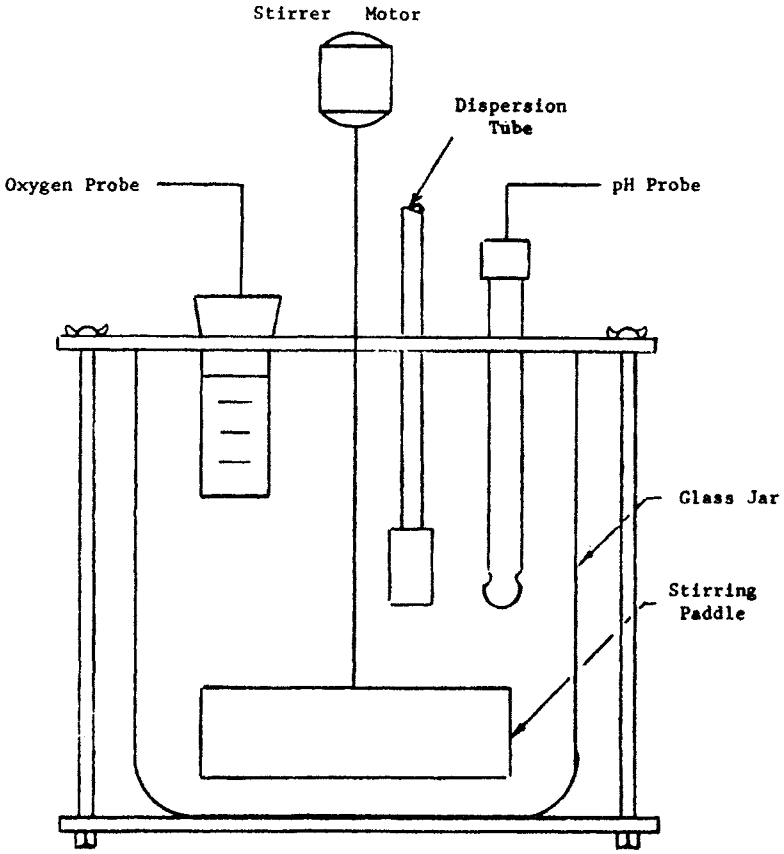


Figure 2

Experimental Neutralization Cell

by excluding the effect of oxidation on the magnetic sludge formation. Solutions of pure ferrous-ferric sulfate and sulfuric acid were purged with nitrogen to remove any dissolved oxygen, in the reaction cell shown in Figure 2, and treated with calcium or sodium hydroxide. The suspension from the reaction cell was transferred to a graduated cylinder with a nitrogen atmosphere and allowed to settle at quiescent conditions. The sludge volume and the magnetic response was measured at specified time intervals.

More detailed information on the work reported on bio-oxidation and on the following part of this section is found in the M.S. thesis of Klingensmith (90).

Figure 3 shows the effect of pH on the sludge density. The optimal pH was 8.3 to 9.5. After one hour aging, the sludge was dark blue and non-magnetic, but after 24 hours, the sludge was black and magnetic.

Figure 4 shows the effect of mole ratio of ferric-to-ferrous iron. As was expected, at a mole ratio of 2: 1, the most dense and magnetic sludge was formed. The sludge volumes were measured after 24 hours aging.

Figure 5 shows the effect of total iron concentration on the sludge volume. After one hour aging and 1500 mg/l total SO_4^{2-}, the sludge was dark blue, non-magnetic, and the volume was directly proportional to the total iron concentration. After 24 hours aging, the sludge was black, magnetic, and the volume was relatively independent of the total iron concentration in the range from 100 to 400 mg/l total iron.

Figure 6 shows the effect of total sulfate concentration on the sludge volume, using calcium hydroxide or sodium hydroxide for the adjustment of pH. In a range of 600 mg/l to 1500 mg/l total sulfate concentration, and with 48 hours aging, there is no significant difference between sludges formed with calcium hydroxide or sodium hydroxide, but calcium hydroxide shows a

Total Iron	200 ppm
Ferric:Ferrous Ratio	2.0
Solution Volume	500 ml.
Base	1.0 N $Ca(OH)_2$
Air	Excluded
Sulfate Concentration	1100 ppm
Time	○ 1 hr.
	▭ 24 hr.

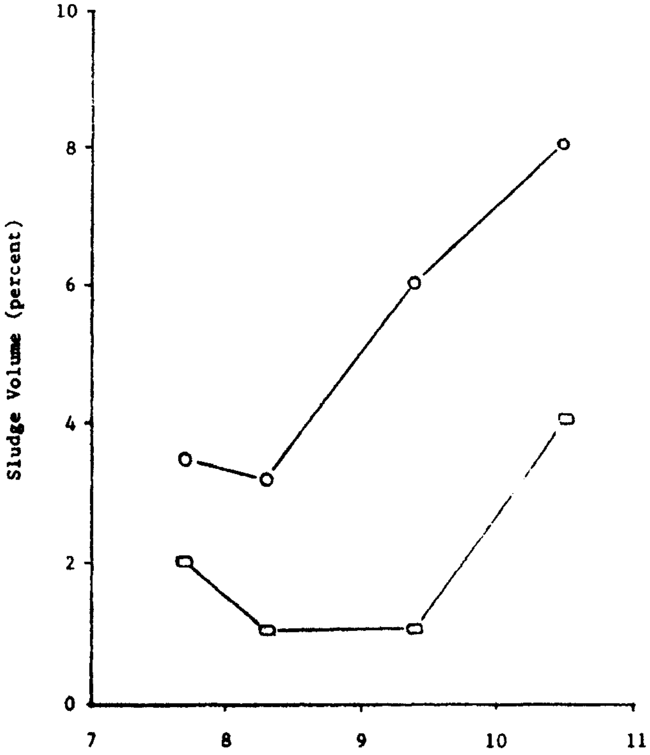


Figure 3

Final pH vs. Sludge Volume

Total Iron	200 ppm
Solution Volume	500 ml.
Final pH	9.2
Total Sulfate	1100 ppm
Base	0.5 N NaOH
Air	Excluded
Time	24 hr.

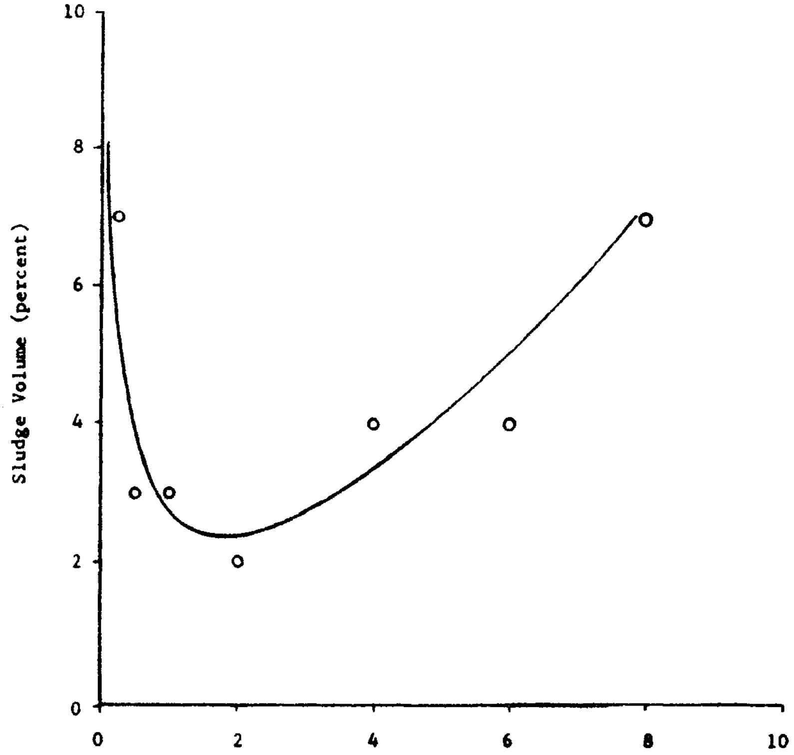


Figure 4

Ferric:Ferrous Ratio vs. Sludge Volume

Ferric:Ferrous Ratio		2.0
Solution Volume		500 ml.
Final pH		9.0
Base		1.0 N $Ca(OH)_2$
Air		Excluded
Sulfate Concentration	○	800 mg/l - 1 hr.
	▭	1500 mg/l - 1 hr.
	×	1500 mg/l - 24 hr.

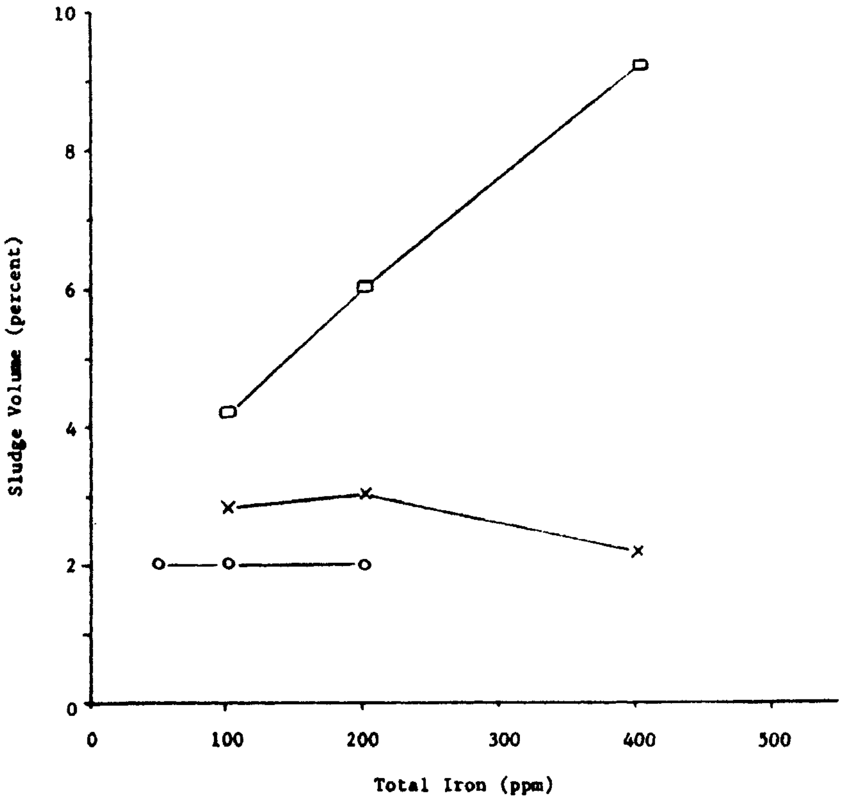


Figure 5

Total Iron Concentration vs. Sludge Volume

Total Iron		200 ppm	
Ferric:Ferrous Ratio		2.0	
Solution Volume		500 ml.	
Final pH		9.1	
Base	○	1.0 N $Ca(OH)_2$	- 1 hr.
	▭	1.0 N $Ca(OH)_2$	- 48 hr.
	△	1.0 N NaOH	- 1 hr.
	×	1.0 N NaOH	- 48 hr.
Air		Excluded	

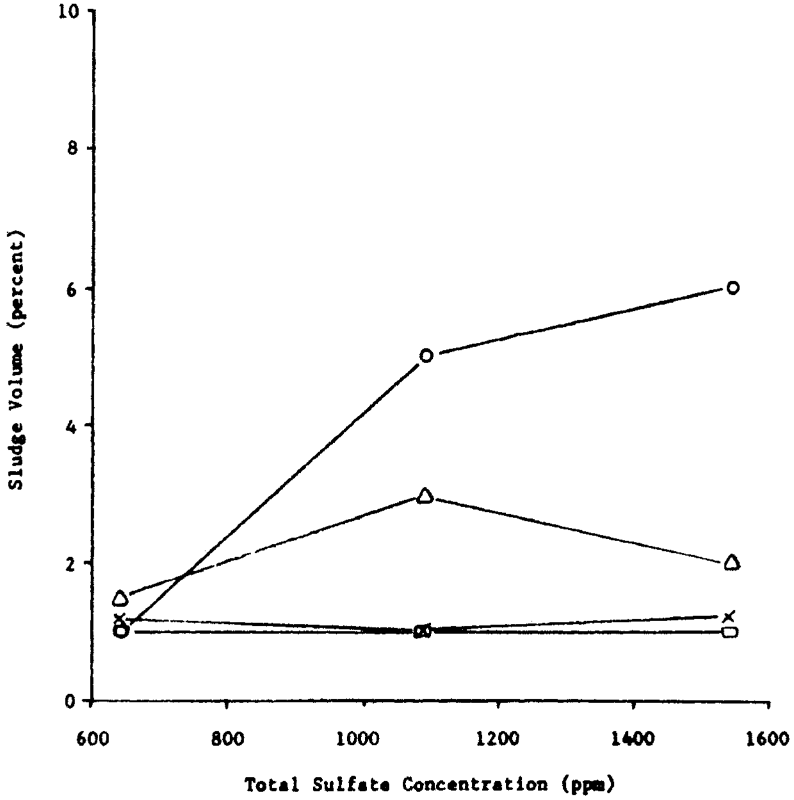


Figure 6

Total Sulfate Concentration vs. Sludge Volume retarding effect on the rate of dense sludge formation during the initial period of aging at higher total sulfate concentrations. The retarding effect of calcium was attributed to the co-precipitation of calcium sulfate at the higher total sulfate concentration.

Figure 7 shows the effect of base concentration on the sludge volume. Calcium hydroxide of 0.04 N was a true solution and the sludge volumes obtained using 0.04 N calcium hydroxide solution or 0.04 N sodium hydroxide were identical after one hour and 24 hours aging. At higher concentration than 0.04 N, the calcium hydroxide was in suspension, and the sludge volumes obtained with $Ca(OH)_2$- suspension were considerably larger after one hour aging when compared with sludges formed with sodium hydroxide. After 24 hours aging, the sludge volumes obtained with $Ca(OH)_2$- suspension and NaOH solution were identical. Using $Ca(OH)_2$- suspension calcium hydroxide particles were "emmeshed" in the green rust II flocs, forming localized high pH and retarded the formation of magnetic sludge. The "emmeshed" calcium hydroxide particles slowly dissolved, and the pH of the sludge increased. With time, the dissolved calcium hydroxide diffused out of the sludge and the pH decreased. The pH change was confirmed experimentally by measuring the pH of the sludge with respect to time. Also, the possible effect of co-precipitation of calcium sulfate at high sulfate concentration may not be overlooked.

The sludge volume obtained at the most favorable conditions was 1 percent, with solids content of 5 percent on the average. X-ray diffraction analysis of the black magnetic precipitates showed the characteristic peaks of magnetite. The peaks were relatively wide, indicating small crystals of magnetite.

The effect of temperature was striking. At a temperature of 15°C, the dark blue precipitates, after 48 hours aging, were still non-magnetic,

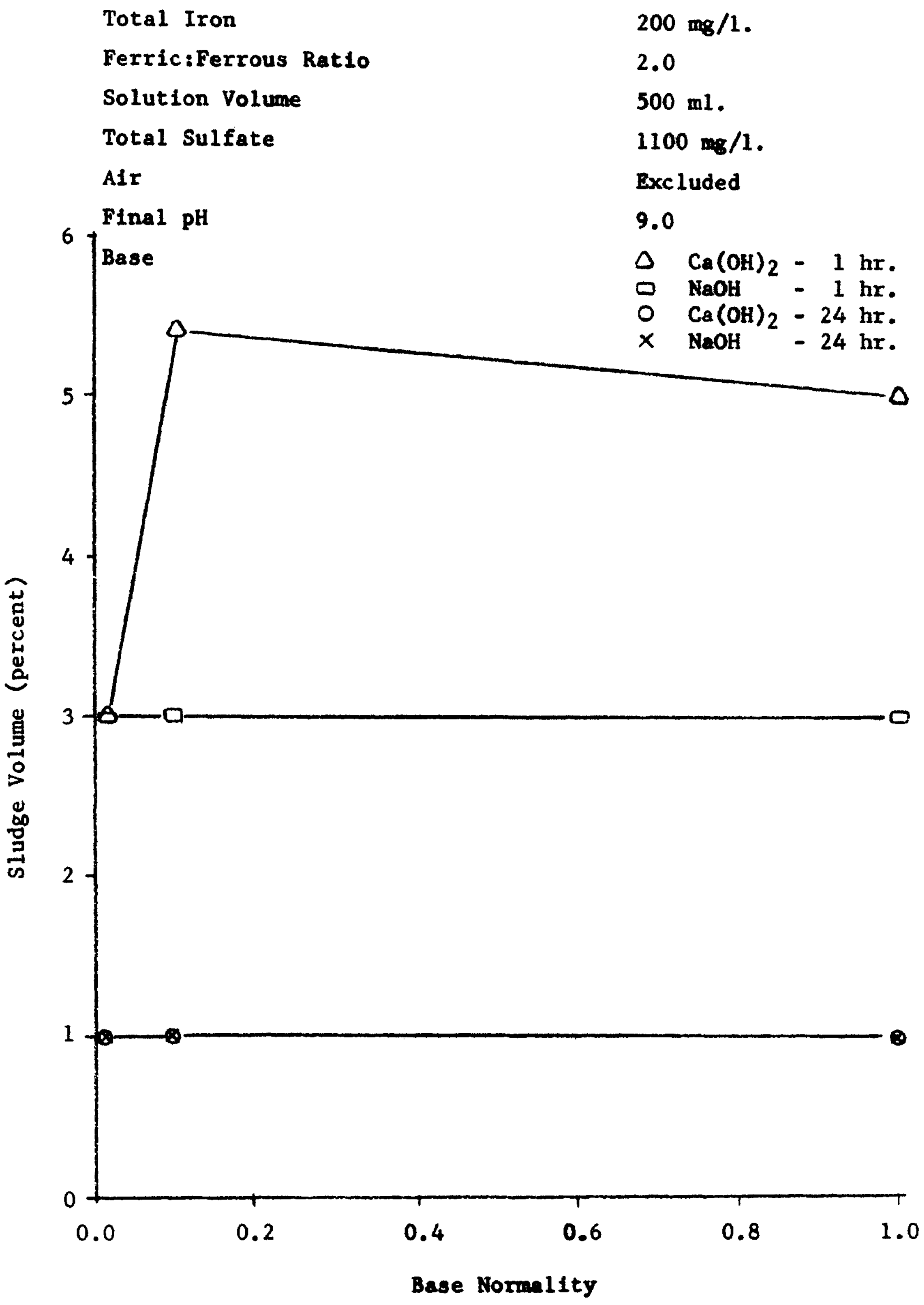


Figure 7

Base Normality vs. Sludge Volume

indicating the strong effect of temperature on the rate of magnetite formation.

BCR (3) studies showed the retarding effect of aluminum and magnesium on the formation of magnetic sludges from ferrous sulfate-sulfuric acid solutions by precipitating with calcium hydroxide and "mild" oxidation of the formed ferrous hydroxide with air. Our experiments also showed that the interference of aluminum on magnetite formation was not eliminated when the ratio of ferric to ferrous iron in solution was 2: 1. Also, SAMD with the ratio of ferric to ferrous iron, adjusted to 2: 1 did not yield magnetic sludge. The formation of magnetic sludges by lime treatment of AMD without eliminating the severe interference of aluminum limits the applicability of the process to AMD with low aluminum concentration.

Only one possibility to eliminate aluminum interference, a two-step procedure, appeared to be feasible for treatment of AMD with the formation of dense magnetic sludge. This procedure, discussed below, would further be limited to treatment of an all-ferrous AMD with a pH of 4 or less. It should be mentioned that in treatment of a raw AMD with a pH higher than four, no interference on formation magnetic sludge is expected because of the low inherent aluminum content. In the two-step procedure investigated, the insolubility of aluminum in the pH range of 4 to 10 is utilized (1). Ferrous iron solubility, although decreasing with increasing pH, is relatively high up to a pH of approximately six, thus allowing a pre-precipitation of aluminum.

Exploratory experiments were made to determine the solubility of aluminum in the presence of ferrous sulfate. A solution of 15 mg/l aluminum, 200 mg/l ferrous iron, as the sulfate, 1200 mg/l total SO_4^{2-}, and pH 1.9 was stripped of oxygen by nitrogen in the reaction cell shown in Figure 2, neutralized with calcium hydroxide suspension ($\sim$ 1 N) to the desired pH, and allowed to settle, excluding air, for 24 hours. Samples of the clear supernatant solution were analyzed for aluminum and iron. The results are shown on Table V.

Ferrous iron co-precipitated with aluminum was so small that the variations of total iron in the supernatant solution were within accuracy of the analytical procedure. The exploratory studies showed that it is possible to separate aluminum by precipitation with calcium hydroxide at pH-5 and eliminate its interference on formation of magnetic sludge.

The two-step procedure was carried out as follows:

SAMD was stripped of oxygen by purging with nitrogen in the reaction cell, as indicated by an oxygen meter, and the pH was adjusted to 5 with a suspension of $Ca(OH)_2$. The resulting suspension was transferred to an Imhoff cone, under a nitrogen atmosphere, and allowed to settle for 24 hours. The supernatant solution was transferred to a 1000 ml beaker, the ferrous iron was precipitated with 1 N $Ca(OH)_2$- suspension at pH 8.5 to 9.0 and oxidized with air. The dark blue-green precipitate and the solution were transferred to an Imhoff cone and allowed to settle for 24 hours. For the most part, black magnetic sludge was formed within 24 hours aging, at room temperature. Frequently, voluminous dark brown magnetic sludges were formed, indicating the presence of δ - FeOOH (46) (73) (74) due to high oxidation rates. Consistent results were obtained when the oxidation rate was slow, using an air-nitrogen mixture and heating the solution to 80-90°C. Typical experimental results are shown in Table VI.

The sludges obtained by the "one-step procedure", Items 1-3, were voluminous dark brown and non-magnetic as a result of aluminum interference. The magnetic dark brown sludges formed by oxidation of the ferrous iron precipitate with air at room temperature, Items 4-6, indicate an excessive oxidation rate, Fe Column. Partly due to the voluminous aluminum sludge,

pH of supernatant	1.	3.0	5.0	6.0
mg/l in supernatant	15.0	15.0	.17	.1

TABLE V

Effect of pH on Solubility of Aluminum in
200 mg/l FeII-sulfate solution at room temperature

TABLE VI

ONE STEP PROCEDURE

SOLUTION		SLUDGE VOLUME	TOTAL SOLIDS
ITEM	COMP.	PERCENT	g/100 ml
1	Fe + AL	5.7	.92
2	Fe+Al+Mg	5.8	.89
3	SAMD	6.1	.85

TWO STEP PROCEDURE

SOLUTION		SLUDGE VOLUME PERCENT			TOTAL SOLIDS g/100 ml		
No.	COMP.	Al	Fe	TOTAL	Al	Fe	TOTAL
4	Fe + Al	1.9	2.0	3.9	.6	1.6	1.2
5	Fe+Al+Mg	2.1	2.4	4.5	.7	1.5	1.0
6	SAMD	1.9	2.1	4.0	.7	1.6	1.2
7	SAMD	1.3	.3*	2.1	.3	3.9	1.7
8	SAMD	.15**	.65***	.6	1.6	4.8	4.3

Item 1: 200 mg/l total Fe(Fe^{3+}:Fe^{2+}=2:1), 15 mg/l Al^{3+}, 1200 mg/l total So$_4^{2-}$.

2: 200 mg/l total Fe(Fe^{3+}:Fe^{2+}=2:1), 15 mg/l Al^{3+}, 24 mg^{2+}, 1200 total So$_4^{2-}$.

3: SAMD 200 mg/l total Fe(Fe^{3+}:Fe^{2+}=2:1.

4: 200 mg/l Fe^{2+}, 15 mg/l Al^{3+}, 1200 mg/l total So$_4^{2-}$, Fe-precipitate oxidized with air at room temperature.

5: 200 mg/l Fe^{2+}, 15 mg/l Al^{3+}, 24 mg/l Mg^{2+}, 1200 mg/l total So$_4^{2}$, Fe-precipitate oxidized with air at room temperature.

6. SAMD 200 mg/l Fe^{2+}, Fe-precipitate oxidized with air at room temperature

7: SAMD 200 mg/l Fe^{2+}, *) Fe-precipitate oxidized with air at 90°C.

8: SAMD 200 mg/l Fe^{2+}, **) Al precipitated with CaCo$_3$, ***), Fe-precipitated with CaCo$_3$, ***), Fe-precipitate (with CaCo$_3$) oxidized with air nitrogen mixture (5 v/o O$_2$) at 90°C.

Al Column, and the voluminous ferromagnetic brown sludges the gain in sludge volume decrease is relatively small when compared with the "one-step procedure", Items 1-3. Item 7 shows that with "slow" oxidation rates with air and heating the solution to 90°C, the total volume of sludge is approximately one-third of the volume of sludges formed in the "one-step" procedure.

It was observed, in the course of a related work reported below, that dense aluminum sludges were formed by neutralization of acid aluminum sulfate solutions with calcium carbonate, $CaCO_3$, to pH of 5.5 to 6.0. Item 8 represents the average results by precipitating aluminum with $CaCO_3$ at pH 5 and the formation of black strongly magnetic sludges by oxidizing the ferrous iron precipitate with air-nitrogen mixture at a temperature of 90°C.

The efforts to obtain magnetic sludges without separation of the aluminum sludge failed. The work so far reported may be considered of more or less exploratory nature and considerable more work should be required to determine the exact extent of various interfering effects on dense magnetic sludge formation in AMD treatment. Considering the temperature effect, the severe aluminum interference, and the sensitivity to the oxidation conditions, development of a satisfactory process applicable under field conditions appeared problematic and the work on formation of dense magnetic sludges was discontinued.

Conclusions

1. When pure ferric-ferrous sulfate-sulfuric acid solutions, with a ratio of ferric to ferrous iron of 2: 1, are quickly neutralized with calcium hydroxide-suspension to a pH of 8.5 to 9.5, an initially formed dark blue-green precipitate, apparently "green rust II", is converted by aging to a dense black ferromagnetic precipitate - hydrated magnetite, $Fe_3O_4 \cdot n\, H_2O$. The rate of conversion is strongly temperature dependent and increases with

temperature increase. At lower-than-room temperature, the conversion is too slow to be considered for practical application.

2. No interference on magnetic sludge formation is observed when pure ferrous sulfate-sulfuric acid solutions are oxidized utilizing the acidophilic iron oxidizing autotrophs of the Ferrobacillus-Thiobacillus group to arrive at the desired ferric-ferrous mole ratio of two.

3. The oxidation process of predominantly ferrous iron precipitates with air, in order to convert them to magnetic precipitates, is very sensitive to the physical conditions of aeration, and difficulties may be encountered in application of the process under field conditions.

4. The severe interference of aluminum on the formation of ferromagnetic sludges limits the applicability of the process to predominantly ferrous iron acid mine drainage at very low aluminum concentration (AMD with a pH above four).

5. On laboratory bench scale it was shown that it is possible to eliminate interference of aluminum by a procedure outlined as follows:

A ferrous AMD of a pH lower than four is treated with a calcium hydroxide or calcium carbonate suspension to adjust the pH to five, preferably under exclusion of air, and the aluminum sludge removed by settling. The supernatant is treated with calcium hydroxide suspension at pH 8.5 to 9.0 and the precipitated ferrous hydroxide oxidized with air at elevated temperature. The smallest sludge volumes of aluminum are attained when using calcium carbonate in the first neutralization step.

6. Considering the temperature effect, the severe aluminum interference, the sensitivity of the oxidation process on the conditions employed, and the involved process for the elimination of aluminum interference, it is strongly suggested that the dense magnetite sludge process is not feasible under field conditions at present.

SECTION III.

FORMATION OF DENSE SETTLED SLUDGE BY NEUTRALIZATION OF SYNTHETIC ACID MINE DRAINAGE WITH CALCIUM HYDROXIDE AND SLUDGE "RECIRCULATION"

The main objective of this work was to determine the effect of process variables on the sludge volume and the chemical and physical properties of solids formed by neutralization of synthetic acid mine drainage (SAMD) with calcium hydroxide. Particular emphasis is given to the effect of sludge "recirculation."

The concentration of ferrous iron and aluminum in the SAMD used in this work, co-jointly with other factors, obviously were the quantities which primarily determined the sludge volume.

The total concentration of calcium in solution after neutralization of the SAMD with calcium hydroxide, as estimated and experimentally verified, did not exceed the solubility of calcium sulfate. The effect of final calcium sulfate concentration, as long as its solubility was not exceeded, on the formed sludge volume and solids content and composition was assumed to be minimal and the validity of the assumption was verified later experimentally.

To gain insight on the processes associated with the dense sludge formation, some work was done using pure ferrous sulfate-sulfuric acid and aluminum sulfate-sulfuric acid solutions. Ferrous iron was oxidized with hydrogen peroxide or air. The main purpose of using hydrogen peroxide for oxidation of ferrous iron in the process of neutralization of pure ferrous sulfate-sulfuric acid solutions and the SAMD was to evaluate the effects of selected variables over a wide range of conditions on the chemical and physical properties of formed solids and, consequently, the sludge volume and its solids content. Use of hydrogen peroxide for ferrous iron oxidation in an acid mine drainage (AMD) treatment process under field conditions at present appears economically unfeasible and later efforts were mainly directed toward utilization of air in the oxidation process.

1. Neutralization of pure $FeSO_4$ - H_2SO_4 Solutions

a) Oxidation with H_2O_2.

800 ml of solution (200 mg/l Fe^{2+} and 1000 mg/l total SO_4^{2-}) were neutralized with 1 N $Ca(OH)_2$- suspention to the desired pH and oxidized with one percent hydrogen peroxide solution at constant pH, then transferred to a 1000 ml graduate cylinder and allowed to settle at quiescent conditions for 24 hours. The sludge volume was measured and the supernatant solution analyzed for total iron and calcium. The suldge was filtered, washed with three 10 ml portions of distilled water, dried at 105°C, weighed and analyzed for iron, sulfate and calcium. The results are shown on Table VII.

Similar experiments were conducted to determine the effect of pH and aging on sludge volume. The total sulfate concentration was increased to 1200 mg/l and the ferrous iron was oxidized with H_2O_2 before pH adjustment with $Ca(OH)_2$. The results are shown on Figure 8. The precipitates formed at pH 3.0 were of yellow color and of fine particle size which settled slowly. The precipitates formed in the pH range of 3.5 to 4.5 were red-brown and flocculent and, on aging, the color changed to yellow. The precipitates formed at pH above 4.5 were voluminous, flocculent, reddish brown, and retained the reddish brown color on aging. The reddish brown precipitates were typical of the appearance of amorphous ferric hydroxide gel. The volume of sludge formed at pH 4.1 decreased to 1.2 percent after 30 days aging. The sludges formed at pH 3.6 and pH 6.0 were X-ray amorphous after one week aging. A sludge formed at pH 4.1 and 75 days aging, accompanied with a color change to light yellow, showed the presence of poorly developed goethite (α- FeOOH)

TABLE VII

Effect of pH on Sludge Composition and Volume of Sludges Formed by Oxidation of $FeSo_4+H_2SO_4$-Solution with H_20_2.

	Solution* neutralized to and oxidized at			
	pH 3.0		pH 4.0	
Sludge volume percent	3.3		5.0	
Sludge solids g/100 ml	1.14		.85	
Supernatant Solution:	Determined	Estimated	Determined	Estimated
mg/l Ca	365	371	416	396
mg/l total Fe	7.2	-	1.4	-
Sludge Solids:				
percent Fe_20_3	75.07	-	78.37	-
percent FeOOH		68.1		74.8
percent So_3	13.92		11.14	
percent $Fe(OH)SO_4$		29.4		23.6
percent CaO	.1		.1	
Not determined	11.01	2.5	10.49	1.6
percent Total	100.0	100.0	100.0	100.0
X-ray diffraction analysis	amorphous		amorphous	

*) 200 mg/l Fe^{2+} and 1000 mg/l total So_4^{2-}

Solution: 200 ppm Fe^{2+}, 1200 ppm total SO_4^{2-}
oxidized with 1% H_2O_2-sol. before pH adjustment
pH adjusted with 1N $Ca(OH)_2$-suspension

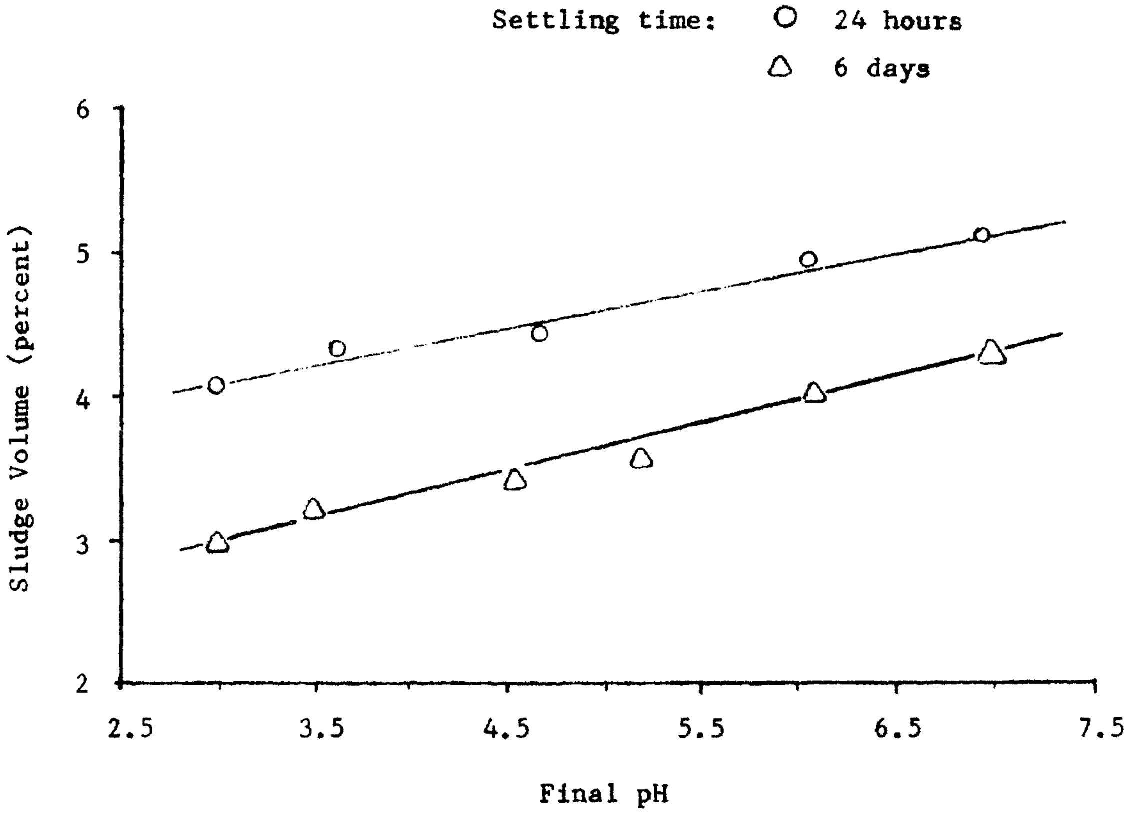


Figure 8

Effect of pH and Aging on Sludge Volume

crystals. The formation of goethite was expected because Schellmann (56) showed that by aging of amorphous ferric hydroxide goethite and lepiderocite are formed. The presence of sulfate, however, favors the formation of goethite. The light yellow color of the sludge also indicates the presence of goethite even when the goethite crystals are so tiny that they are not detected by X-ray diffraction analysis.

The residual concentration of ferric iron in the supernatant solution after 24 hours settling was less than one mg/l at pH 4.0 and above, decreasing with increasing pH. It should be mentioned that erratic residual ferric iron concentrations were observed in the vicinity of pH 3, explained by the sharp change of ferric iron solubility in this range as was shown by Stumm (13) and Hill and Wilmoth (11). Thus, to attain satisfactory ferric iron removal in the treatment of AMD, the final pH should be above 3.

Generally, the preliminary work showed that the sludge volume increased with increasing pH, but decreased on aging. The sulfate content of sludge solids increased with decreasing pH, and the calcium content was negligible when compared with the calcium concentration in the supernatant solution, 416 mg/l. The preliminary work also showed that the physical and chemical properties of the sludge solids, particularly the formation of goethite, strongly affected the sludge volume.

Similar results were obtained by neutralization of the ferrous sulfate solution with sodium hydroxide, suggesting a relatively small effect of calcium on the physical and chemical properties of the sludge solids (91).

b) Oxidation with Air.

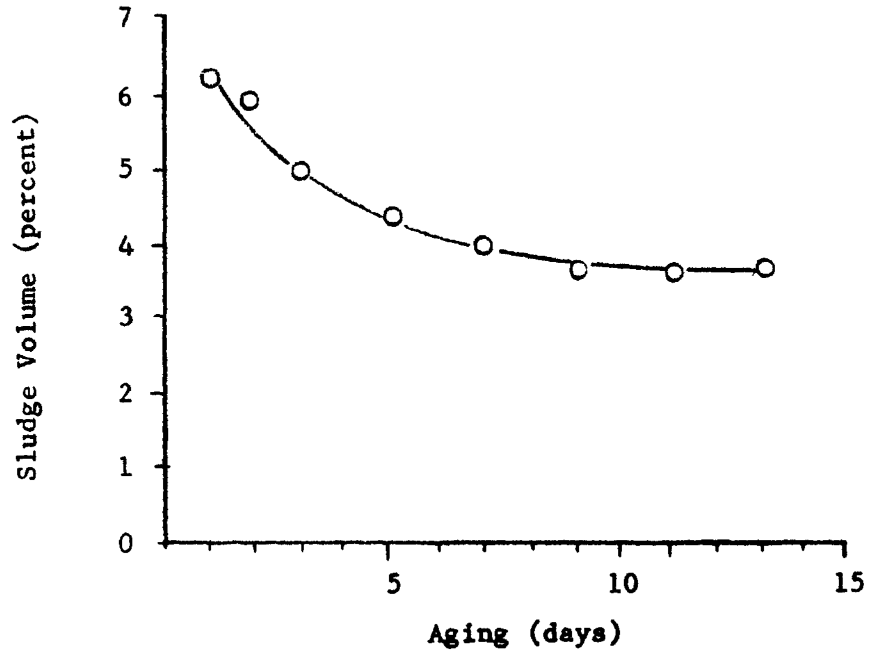
800 ml of solution (200 mg/l Fe^{2+} and 1200 mg/l total SO_4^{2-}) were neutralized with 1 N $Ca(OH)_2$ to the desired pH and oxidized with dispersed air, maintaining the pH constant. After a specified settling time in 1000 ml

graduate cylinders, the sludge volumes formed at pH 5.5 and 6.0 were 4.4 and 6.2 percent, respectively, after 24 hour settling time, indicating again a sludge volume decrease with pH decrease.

Figure 9 shows the sludge volume decrease on aging of sludge formed at pH 6.0. After 13 days, the sludge volume decreased to 60 percent of the sludge volume after 24 hours settling with a corresponding solids increase from 0.69 to 1.14 percent.

The X-ray diffraction analysis of the 13 days aged sludge solids showed an X-ray amorphous structure.

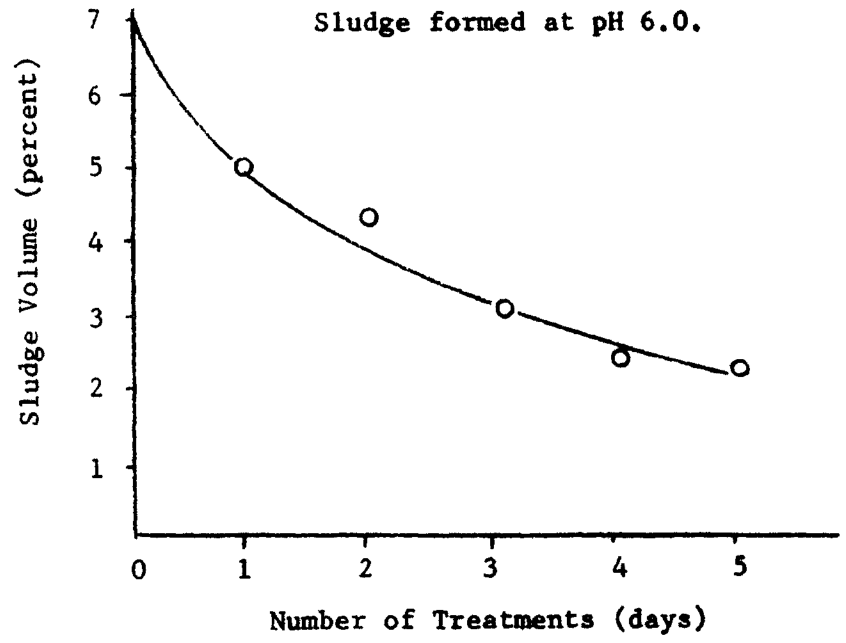
Several experiments were performed by exposing the sludge to high pH followed by a return to the pH of oxidation and precipitation. The ferrous sulfate-sulfuric acid solution (200 mg/l Fe^{2+}) was neutralized to pH 6.0 with 1 N $Ca(OH)_2$- suspension and oxidized with dispersed air, maintaining the pH constant. After 24 hours settling, the sludge volume was recorded, the supernatant solution was siphoned off, and approximately 15 ml of 1 N $Ca(OH)_2$- suspension, was added to the sludge. The resultant pH of the mixture was 12.4 and the mixture was allowed to remain undisturbed for 15 minutes. The mixture was then added to 800 ml of sulfuric acid solution (1200 mg/l SO_4^{2-}) and stirred. The final pH of the sludge-sulfuric acid solution was adjusted to 6.0, the sludge was allowed to settle for 24 hours, and the sludge volume was recorded, The procedure was then repeated for several more times, with the results shown in Figure 10. The sludge, after first precipitation, was voluminous, of reddish brown color, and settled rapidly. After each subsequent treatment, the color of sludge became lighter and very fine particles were observed which settled more slowly than at the first precipitation. After the fifth treatment the sludge, light yellow, was filtered and samples were prepared for X-ray diffraction analysis. The analysis showed the presence of



Solution: 200 ppm Fe^{2+}, 1200 ppm total SO_4^{2-}. Neutralized with 1N $Ca(OH)_2$ - suspension to pH 6.0.

Figure 9

Effect of Aging on Sludge Volume



Sludge formed at pH 6.0.

Figure 10

The Effect of Exposure of Sludge to High and Low pH on Sludge Volume poorly developed goethite crystals (α - FeOOH). The original sludge volume of 7 percent decreased to 2.5 percent with a corresponding solids content of 0.62 percent and 1.7 percent. The sludge volume, after 5 treatments in 6 days, was only 35.7 percent of the original sludge volume, but the untreated sludge, after 13 days aging, Figure 9, was 60 percent of the original sludge volume. Again, the formation of dense sludge was associated with a physical and chemical change of the sludge solids: at the conditions of the experiments, the transition of ferric hydroxides of an amorphous gel-like structure (probably $Fe(OH)_3$) by loss of water to ferric oxihydroxide compounds, α- FeOOH, and the growth of goethite crystals were the main factors affecting the sludge volume. Apparently, the formation of goethite was associated with exposure of the sludge to high pH, as was pointed out by Schellmann (56) and Feitknecht (57), who indicated that the formation of goethite is accelerated by high pH and presence of sulfate ions.

c) Sludge Recirculation.

The results of preliminary work were used as guide lines for adapting the procedure and conditions for series of experiments with sludge "recirculation". Two series of experiments were conducted, at pH 5.5 and 6.0. Nevertheless, the preliminary work showed that denser sludges were formed at lower pH, the lowest pH of 5.5 was selected due to the rapid decrease of oxidation rates of ferrous iron with decreasing pH. The preliminary work also showed that exposure of the sludge to high pH accelerated the formation of crystalline α- FeOOH and, consequently, the formation of denser sludge; therefore, the logical point of calcium hydroxide addition was to the recirculated sludge before its addition to the fresh ferrous sulfate-sulfuric acid solution.

The following procedure was adopted: A solution of ferrous sulfate-sulfuric acid, (800 ml of 200 or 400 mg/l Fe^{2+} and 1200 mg/l total SO_4^{2-}) was neutralized with 1 N $Ca(OH)_2$ suspension to pH 5.5 or 6.0 and oxidized with dispersed air, maintaining the pH constant. The completeness of ferrous iron oxidation and the hydrolysis of ferric iron was indicated by the pH remaining constant for at least 15 minutes. The sludge was transferred to a 1000 ml graduated cylinder and allowed to settle for 24 hours, when the sludge volume was recorded, the supernatant solution was siphoned off, $Ca(OH)_2$- suspension was added to the sludge, and the mixture was allowed to remain undisturbed for 15 minutes. The sludge - $Ca(OH)_2$- slurry was then added to a fresh $FeSO_4$ - H_2SO_4 - solution, the pH of the mixture was adjusted to 5.5 or 6.0, oxidized with air, etc. The procedure was repeated as many times as desired. The $Ca(OH)_2$- suspension was added to the sludge in such a quantity, 14 to 15 ml, that when the sludge - $Ca(OH)_2$- mixture (pH approximately 14.2) was added to the fresh $FeSO_4$ - H_2SO_4 - solution, the resulting pH was slightly lower than 5.5 or 6.0.

The results shown on Figure 11 up to 40 days were obtained from experiments with a solution of 200 mg/l Fe^{2+} and 1200 mg/l total SO_4^{2-}. At pH 5.5, the sludge volume increased from 3.7 percent (initial sludge volume) to 10 percent after four recycles and remained fairly constant up to 17 recycles. The solids content of the sludge increased from 0.81 percent (initial sludge) to 1.5 percent after four recycles and to 5.4 percent after 17 recycles. From 17 recycles to 33 recycles, the sludge volume decreased from 10 percent to 7.5 percent with a solids content of 13 percent.

At pH 6.0, the sludge volume increased from 6.2 percent, initial volume, to 17.5 percent after 11 recycles, then decreased to approximately 16 percent and remained approximately constant up to 21 recycles and then decreased to 12.5 percent after 39 recycles. The solids content of the sludge increased from 0.48 percent, initial sludge volume, to 1.9 percent after 11

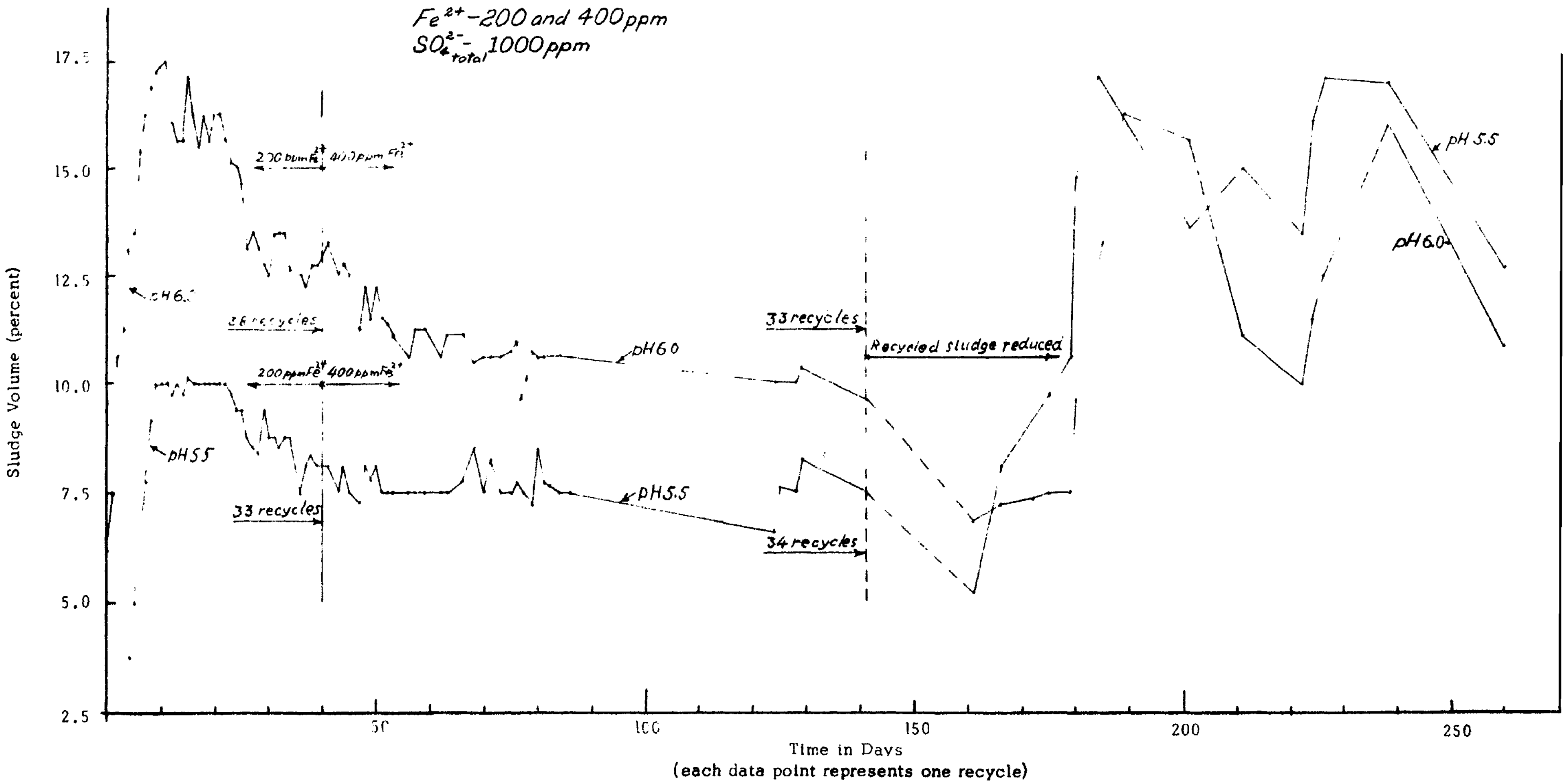


Figure 11

Pure FeSO$_4$ · **Solution Sludge Volume vs. Recycle Number and Time;**
pH .5 and 6.0

recycles, then increased to 3.9 percent after 21 recycles and finally increased to 9.4 percent after 39 recycles. The sludge solids content was estimated using an average value obtained from parallel runs at similar conditions.

When comparing the sludge volumes at pH 5.5 and 6.0, it is obvious that the sludge volume is strongly affected by the pH of solution, the sludge volume being smaller at lower pH of the oxidation step.

The volume of sludge formed at pH 6.0, after five recycles in five days, was 13.5 percent, as shown on Figure 11. The sum of sludge volumes shown on Figure 10, also formed at pH 6.0 and exposed to high and low pH from zero to 5 times in five days, amounts to 23.8 percent, indicating that there is no simple aging - cyclic pH variation sludge volume relationship.

The maximum sludge volume was observed after 11 recycles at pH 6.0, and after only 4 recycles at pH 5.5.

The color of the initially formed sludges was reddish brown, but with an increasing number of recycles, the color changed to yellow. The rate of color change was approximately proportional to the number of recycles required to attain the maximum sludge volume.

The X-ray diffraction pattern of the sludge formed at pH 5.5 showed narrower and higher peaks of goethite when compared with the X-ray diffraction pattern of sludge formed at pH 6.0, indicating the presence of a larger fraction of better developed crystals of goethite in sludge solids formed at pH 5.5. The X-ray diffraction analysis was made on sludge formed at pH 5.5 after 33 recycles. Again, the X-ray diffraction analysis showed that the formation of goethite was associated with the color change of sludge from reddish brown to light yellow.

The formation of dense sludge by sludge recirculation is associated with many effects which favor the formation of crystalline ferric oxihydroxicompounds, particularly goethite (α - FeOOH), at the conditions of the experiments.

At lower pH, the solubility of ferric iron is increased and, consequently, the growth of the large number of tiny goethite crystals, introduced into the mixture with the recycled sludge, is favored. The same effect is attained by slower oxidation rates of ferrous iron with air. The oxidation rate with air decreases rapidly with decreasing pH, according to Stumm (13). The ferric iron in solution is maintained at supersaturated conditions for prolonged times, and the growth of goethite crystals is prolonged.

The temporary exposure of sludge to high pH favors the formation of goethite from the amorphous ferric hydroxide and the growth of goethite crystals, probably through the solution, because of the high solubility of $Fe(OH)_4$- ions and because of the presence of sulfate. The conversion of amorphous ferric hydroxide to crystalline α - FeOOH is a relatively slow process and the effect of aging on sludge volume is obvious.

Analyses of sludge solids showed an increase of sulfate with decreasing pH; an average of approximately one percent SO_4 was found in sludge solids formed at pH 6.0 and up to 5 percent in sludge solids formed at pH 5.5. The sulfate in sludge solids is present mainly in the form of ferric hydroxisulfate, which hydrolize very slowly at lower pH and forms α - FeOOH. Exposure of the sludge to high pH aids the hydrolysis of ferric hydroxisulfates and, consequently, the formation of goethite.

The mechanical effect of stirring on the formation of dense sludge may not be overlooked. The mechanical strength of ferric hydroxide flocs is weakened by the transition to tiny crystals and the flocs are easily disintegrated by stirring. Upon settling, denser sludge is formed due to closer packing of crystals, but it has an undesired side effect; the very tiny crystal aggregates settle slowly, and longer settling times are required to obtain a clear supernatant with low iron concentration.

The total iron concentration of the supernatant solution after 24 hours settling at pH 6.0 was 0.09 mg/l, and after filtration on Whatman 42 paper, was 0.04 mg/l; at pH 5.5, the total iron in the supernatant solution was 0.24 mg/l, dropping to 0.17 mg/l after filtration.

Figure 11 shows that the sludge volume formed at pH 6.0 and up to 38 recycles, and the sludge volume formed at pH 5.5 and up to 33 recycles did not show any tendency to increase. It is obvious that this phenomenon cannot proceed indefinitely, and after some number of recycles, the sludge volume should increase. Apparently, the quantity and the chemical and physical properties of the recirculated sludge were such that in the process of insolubilization of iron from the fresh ferrous iron solution of 200 mg/l Fe^{2+}, the recirculated sludge could accumulate the insolubilized iron without a total sludge volume increase.

To observe the effect of increasing iron concentration in the solution on the sludge volume and to accelerate the rate of solids accumulation in the sludge, a solution of 400 mg/l Fe^{2+} and 1200 mg/l total SO_4^{2-} were used in the rest of the experiments shown on Figure 11. The sludge volume formed at pH 6.0 continued to decrease for an additional 12 recycles and remained approximately constant for another 17 recycles at a volume of approximately 10.6 percent. There was no apparent tendency to increase. The sludge after this number of recycles, 38 recycles with 200 mg/l Fe^{2+} solution plus 29 recycles with 400 mg/l Fe^{2+} solution, was allowed to age for 38 days. The sludge volume decreased from 10.6 percent to 10.0 percent, showing still more the effect of aging. After a period of 38 days aging, the sludge was recirculated for four more times and still had the capacity to accumulate precipitated iron without a total volume increase.

Similar results were obtained with sludge recirculation at an oxidation pH of 5.5, except that the sludge volume was smaller. After 33 recycles using 200 mg/l Fe^{2+} solution plus 34 recycles using 400 mg/l Fe^{2+} solution, the sludge volume was 7.5 percent. After 38 days of aging, the sludge volume decreased to 6.6 percent, but after five additional recycles, showed a volume increase.

The runs were terminated after a total of 71 recycles at pH 6.0, and after a total of 67 recycles at pH 5.5, the solids content of the sludges were determined, and X-ray diffraction analyses performed.

The final sludge volume at the termination of the pH 6.0 run was 9.5 percent with a solids content of 22.5 percent. The sludge solids content of the sludge, at a volume of 10.6 percent, before aging for 38 days, was 20.8 percent, estimated value.

The sludge at the termination of the pH 5.5 run was 6.5 percent with a solids content of 33.5 percent. The sludge solids content of the sludge, at a volume of 7.5 percent before aging for 38 days, was 30.2 percent, estimated. X-ray analysis of both sludges showed a clear goethite crystal structure, but again indicated better crystal development in the sludge solids formed at pH 5.5.

Shortly before termination of the run at pH 5.5, an increase of sludge volume during the last recycles was observed, indicating that the capacity of recycled sludge to accumulate insolubilized iron without total sludge volume increase was exhausted, thus, setting a limit of sludge volume at 7.5 percent with a solids content of 30 percent, under the conditions of the experiment. At the termination of the run at pH 6.0, however, this limit had not yet been reached.

It should be mentioned here that the time required for complete oxidation of ferrous iron in solution decreased with increasing number of recycles, and with the change of color to light yellow. At the time of these experiments, it was assumed that the increase of the oxidation rate was associated with the presence of microorganisms which multiplied during the experiments and biologically catalized the oxidation process. It will be shown later that the increase of the oxidation rate of ferrous iron was mainly associated with the recirculated sludge, and was not the result of bio-oxidation.

From the results shown on Figure 11, the conditions may be estimated at which the first experiments with 400 mg/l Fe^{2+} solution were performed. After addition of the sludge, $Ca(OH)_2$ suspension, to the fresh ferrous iron solution and adjustment of the pH to 6.0, the resultant mixture had the following composition: 400 mg/l total iron, 1200 mg/l total sulfate, and 540 mg/l Ca^{2+} (determined) and 9.2 g/l recycled sludge solids of ages from zero to 40 days and 38 recycles. The mixture adjusted to pH 5.5 had the same composition, except that the concentration of Ca^{2+} was 500 mg/l and the recycled sludge solids content was 7.0 g/l, of ages from zero to 36 days and 33 recycles.

To determine the effect of recycled sludge age and recycle number on the sludge, the total volumes of the sludges from the terminated runs were used in the recycle runs shown on the right side of Figure 11, starting at the abscissa value of 161 days. The sludge was added to the 400 mg/l ferrous sulfate-sulfuric acid solution in such a quantity as to obtain a sludge solids concentration equal to the sludge solids concentration in the first runs with 400 mg/l Fe^{2+} concentration, or 9.2 g/l at pH 6.0 and 7.0 g/l at pH 5.5. It should be emphasized that the recirculated sludges at pH 6.0 contained sludges of ages from 20 to 161 days and total of 71 recycles, and at pH 5.5 contained sludges of ages from 20 to 157 days and total of 67 recycles. The procedure was similar to that described above except that varying aging time was allowed between recycles. A total of 15 recycles were accomplished in a period of 100 days, this time period being approximately equal to the runs made with 400 mg/l Fe^{2+} solution, at which point these experiments were terminated. The sludge volumes were recorded before each recycling step and are shown on Figure 11 as dots; the horizontal distance between the dots represent the number of days of sludge aging between recycles.

The runs at pH 6.0 show a fairly constant sludge volume for 5 recycles in 18 days, indicating that the capacity of recycled sludge to accumulate more insolubilized iron without volume increase was not completely exhausted. At this point in time, the volume of sludge increased sharply and, thereafter, showed a very strong dependence on sludge aging between the recycles. The runs at pH 5.5 showed a large volume increase from the first recycle, indicating that the capacity of the recycled sludge to accumulate more insolubilized iron without sludge volume increase was already exhausted. This sludge showed a very strong dependence of sludge volume on the aging period between the recycles. The color of the sludge formed after each recycle was reddish brown, after 24 hours settling, indicating the presence of amorphous ferric hydroxide, but on aging, the color became lighter, approaching the yellow color of goethite. The x-ray diffraction analysis of the sludges formed both at pH 6.0 and 5.5 showed, besides goethite, the presence of fairly well-developed crystals of lepidocrocite (γ - FeOOH). X-ray diffraction analysis also indicated that a larger fraction of lepidocrocite was present in the sludge formed at pH 5.5.

Nitschmann (68) showed that the tendency toward formation of goethite or lepidocrocite depends on the concentration of nucleation centers in the solution of ferrous sulfate. Predominantly, goethite was formed when relatively large concentrations of ferric oxihydroxide nuclei are present, but lepidocrocite will form when the concentration of nuclei is restricted. Remembering also that the size of crystals formed of relatively insoluble compounds is limited, depending on the degree of supersaturation, the results of the last series of runs are not unexpected. The sludge solids used had undergone so many recycles and were aged for so long a time that a relatively large fraction of the goethite crystals had reached the limiting size and only a relatively small fraction of crystallization centers were available for crystal growth and, consequently, in accordance with Nitschmann (68), the formation of lepidocrocite was favored. The rate of formation of ferric iron, by oxidation with air, was relatively higher than the rate of lepidocrocite crystal growth, and, consequently, the excess of ferric iron was insolubilized in the form of amorphous ferric hydroxide.

The last series of experiments indicate the required properties of recirculated sludge for the development of dense sludge from pure ferrous iron solutions. Depending on the ferrous iron concentration in the solution to be treated and on the oxidation rate of ferrous iron, the recirculated sludge must contain a certain amount of nucleation centers and/or minute crystals of ferric oxihydroxide so that when the recycled sludge is added to the ferrous iron solution, there is present a quantity of nucleation centers and/or minute crystals per unit volume sufficient to accumulate the insolubilized iron by a process of crystal growth. If these conditions are not satisfied, the insolubilized iron will form amorphous ferric hydroxide, a process associated with formation of voluminous sludges. Under these conditions, prolonged aging is required to increase the sludge density.

2. Neutralization of Pure Aluminum Sulfate - Sulfuric Acid solutions

The purpose of the following work was to obtain some information on the volume, solids content, and the physical and chemical properties of sludges solids formed from pure aluminum sulfate - sulfuric acid solutions by neutralization with calcium hydroxide, under conditions similar to those of the work on pure ferrous sulfate - sulfuric acid solutions, with emphasis on sludge "recirculation".

Preliminary experiments showed that aluminum was not precipitated from acid solutions by addition of calcium hydroxide until a pH of approximately 4 was reached. The concentration of aluminum in the supernatant solution decreased with increasing pH and the total aluminum concentration in the supernatant solution after 24 hours settling at pH 4 was close to 3 mg/l, at pH 5, it was 0.2 mg/l, and at pH 6, it was less than 0.1 mg/l. To achieve good aluminum removal from acid solutions, the final pH of the solution may not be below approximately 4.5. Also, preliminary experiments showed that the sludge volume was very strongly affected by the final pH of the solution. Close to pH 7, the sludge volumes formed fluctuated erratically with minor changes in conditions, indicating a transition region of the physical properties of sludge solids. Considering the results of preliminary experiments, and in order to obtain results comparable with the results obtained from runs with pure ferrous sulfate-sulfuric acid solutions, two series of runs were conducted at pH 5.5 and pH 6.0. The work was done following the procedure outlined in the section on neutralization of pure ferrous sulfate-sulfuric acid solutions with sludge recirculation except that the oxidation step was omitted. After neutralization with calcium hydroxide, the suspension was stirred until the pH of 5.5 or 6.0 remained constant for at least 30 minutes. An aluminum sulfate-sulfuric acid solution of 30 mg/l Al^{3+} and 1200 mg/l total SO_4^{2-} was used in this part of the work, with the results shown in Figure 12. The dots show the sludge volume in percent, and the horizontal distance between the dots represent the aging in days between the recycles.

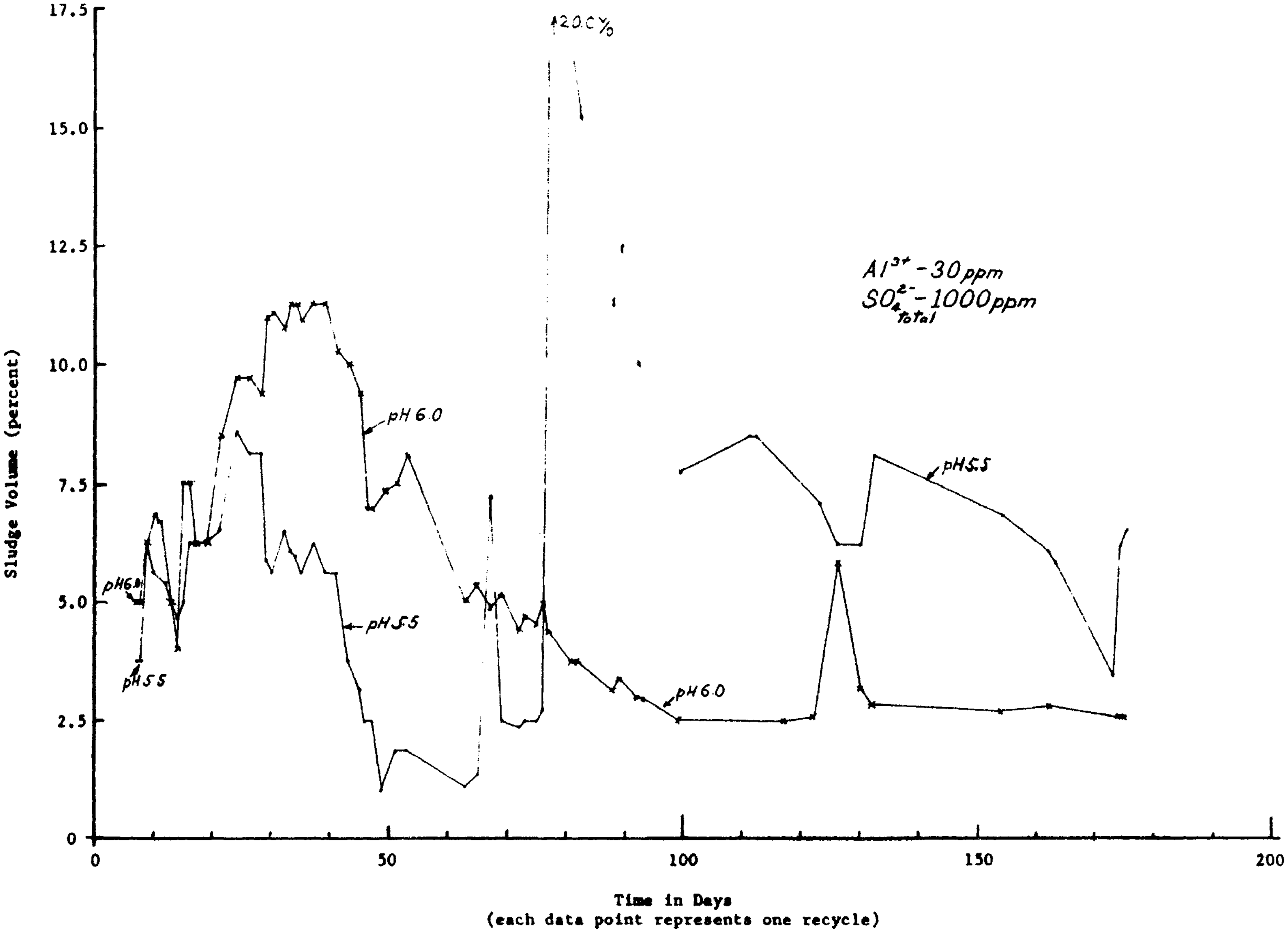


Figure 12

Pure $Al_2(SO_4)_3 \cdot 18H_2O$ - Solution Sludge Volume vs. Recycle Number and Time; pH 5.5 and 6.0

The sludge initially formed at pH 6.0 had a volume of 5.0 percent with a solids content of 0.2 percent. The sludge volume increased up to 11.2 percent after 15 recycles and then remained fairly constant up to 22 recycles at a volume of 11.2 percent with a solids content of 2.0 percent. It should be mentioned here that the observed fluctuation of the sludge volume was mainly associated with the speed of addition of sludge and calcium hydroxide mixture to the fresh aluminum sulfate-sulfuric acid solution when the stirring speed was kept constant. More consistent results were achieved when the addition was performed as rapidly as possible. The effect of aging on the sludge between runs was less pronounced than the effect of the deviation of pH from the specified value. From the 22nd recycle up to the 44th recycle, the sludge volume decreased from 11.2 percent to 2.5 percent and then remained fairly constant (except at recycle 47) until the termination of the run at total 53 recycles in 170 days. The sludge volume at the termination of run was 2.7 percent with a solids content of 14.9 percent. The sudden increase of the sludge volume observed at the 47th recycle was due to the higher pH (approximately 8) of the solution during the precipitation, indicating the sensitivity of the sludge volume formed to pH in the range of approximately 7. The x-ray diffraction analysis of the sludge solids distinctly showed the pattern of gibbsite (γ - $Al(OH)_3$).

Results of the run at pH 5.5 up to 23 recycles followed closely the pattern of the results of the run at pH 6.0, except that the sludge volumes were considerably smaller. The initial sludge volume was 2.7 percent with a solids content of 0.26 percent. The volume then increased to 8.2 percent with solids content of 1.6 percent after 14 recycles. After 15 recycles, the sludge volume decreased to 5.6 percent and remained fairly constant up to 23 recycles, with a solids content of 3.7 percent. After the 23rd recycle, the volume decreased during the remaining 5 recycles to 1.3 percent (average) and remained approximately constant for four consecutive recycles at 1.3 percent with a solids content of 19.0 percent after the 32nd recycle. The sudden volume increase to 7.2 percent at the 33rd cycle was due to an inadvertent overshoot to pH 8.5. After the 34th recycle, the sludge volume decreased to 2.5 percent and during the next six recycles, remained constant, but did not decrease to 1.3 percent, the volume observed at 28th and 32nd recycles, indicating that the damage done by the pH overshoot was not overcome. To observe the effect of high pH during the recycle process, the pH of the 38th recycle was intentionally overshot to 10.5. The sludge volume increased to 20 percent and during the next 15 recycles, with relatively long aging periods between recycles, did not quite decrease to the volume of 2.5 percent observed at the 37th recycle. The last experiments showed that the pH of insolubilization of aluminum from acid solutions strongly affects the sludge volume. Near neutral pH, and higher, the aluminum is precipitated in the form of an amorphous aluminum hydroxide which is associated with the formation of very voluminous sludges. Its conversion to gibbsite (γ- $Al(OH)_3$) occurs very slowly. From preliminary studies and the results shown in Figure 12, the optimum pH appears to be in the range from 5 to 6.

In the pH 5.5 and pH 6.0 studies, the increase of the aluminum sludge volume to a maximum, followed by a subsequent decrease, at pH 5.5 and 6.0, together with the relatively small effect of aging on sludge volume, clearly suggests the process of dense sludge formation by sludge recirculation. During the recycles associated with the sludge volume increase, the formation of seed crystals and nucleation centers is in progress, but less of the insolubilized aluminum is accumulated on the seed crystals and nucleation centers by crystal growth. When the concentration of tiny crystals, seed crystals, and nucleation centers introduced by sludge recirculation reaches some optimal value per unit volume of solution, most of the insolubilized aluminum is accumulated on the particles by crystal growth. The larger crystals, on settling, pack closer than odd shaped aglomerates of tiny particles, and consequently, lead to denser sludge formation. Samples from two parallel runs at pH 5.5 performed under similar conditions but terminated at a specified number of recycles were analyzed by x-ray diffraction. The sample from the run terminated before the sludge reached maximum volume (6 recycles in 7 days) showed x-ray amorphous structure, but the sample taken from the run terminated after the sludge passed the maximum volume, 15 recycles in 16 days, showed the presence of gibbsite (γ- $Al(OH)_3$). The results show that the formation of dense sludge is associated with the formation of gibbsite, with the major factors affecting the formation of gibbsite being pH and seeding. The possible formation of very voluminous aluminum sludges may affect the sludge volume significantly in an AMD treatment process, and should always be considered.

3. Neutralization of Synthetic Acid Mine Drainage with Calcium Hydroxide

The synthetic acid mine drainage (SAMD) used throughout this work was of the following composition:

Al^{3+}	15.1 mg/l
Ca^{2+}	80.0 mg/l
Fe^{2+}	200.0 mg/l
Mg^{2+}	24.0 mg/l
Mn^{2+}	7.8 mg/l
SO_4^{2-} total	1200.0 mg/l
pH	2.1

This formulation for the SAMD was obtained from Ronald D. Hill of the Environmental Protection Agency in Cincinnati. SAMD of the above composition has also been used by other researchers and, thus, serves as a convenient means for comparison of data obtained by different workers.

Hydrogen peroxide and air were used for the oxidation of ferrous iron, depending on the pH. Since chemical oxidation rates with air are very slow at low pH, hydrogen peroxide was used to observe the effect of pH on sludge volume at low pH, to compare the effect of very fast oxidation with the slower oxidation by air, and to simulate a process of treatment of SAMD containing only ferric iron by oxidizing the ferrous iron completely before the neutralization step.

a) Oxidation with H_2O_2.

The experimental work on SAMD treatment with calcium hydroxide and hydrogen peroxide oxidation was done primarily by Paul Swartz (91). The procedure was the same as described previously for the treatment of pure ferrous sulfate-sulfuric acid solutions, except 0.52 percent hydrogen peroxide solution was used for ferrous iron oxidation instead of air.

The treatment of SAMD oxidized with hydrogen peroxide before neutralization with calcium hydroxide led to results generally similar to the iron sulfate-sulfuric acid treatment under similar conditions. However, there were two differences; sludge volume was slightly greater, and sludge solids content was greater. It should be emphasized that oxidation of ferrous iron before neutralization is similar to a treatment of 100 percent ferric iron SAMD.

The dependence of sludge volume on aging and pH is shown in Figure 13. The low sludge volume at low pH after one hour settling was due to incomplete settling of fine particles formed, and does not represent a true sludge volume. By comparing Figure 13 to Figure 8, volume differences are noted. The SAMD sludge was more pH dependent and at neutral pH values has a volume of 6 percent after 24 hours settling compared to 5 percent for the pure iron solution sludge. The solids content of the SAMD sludge was also pH

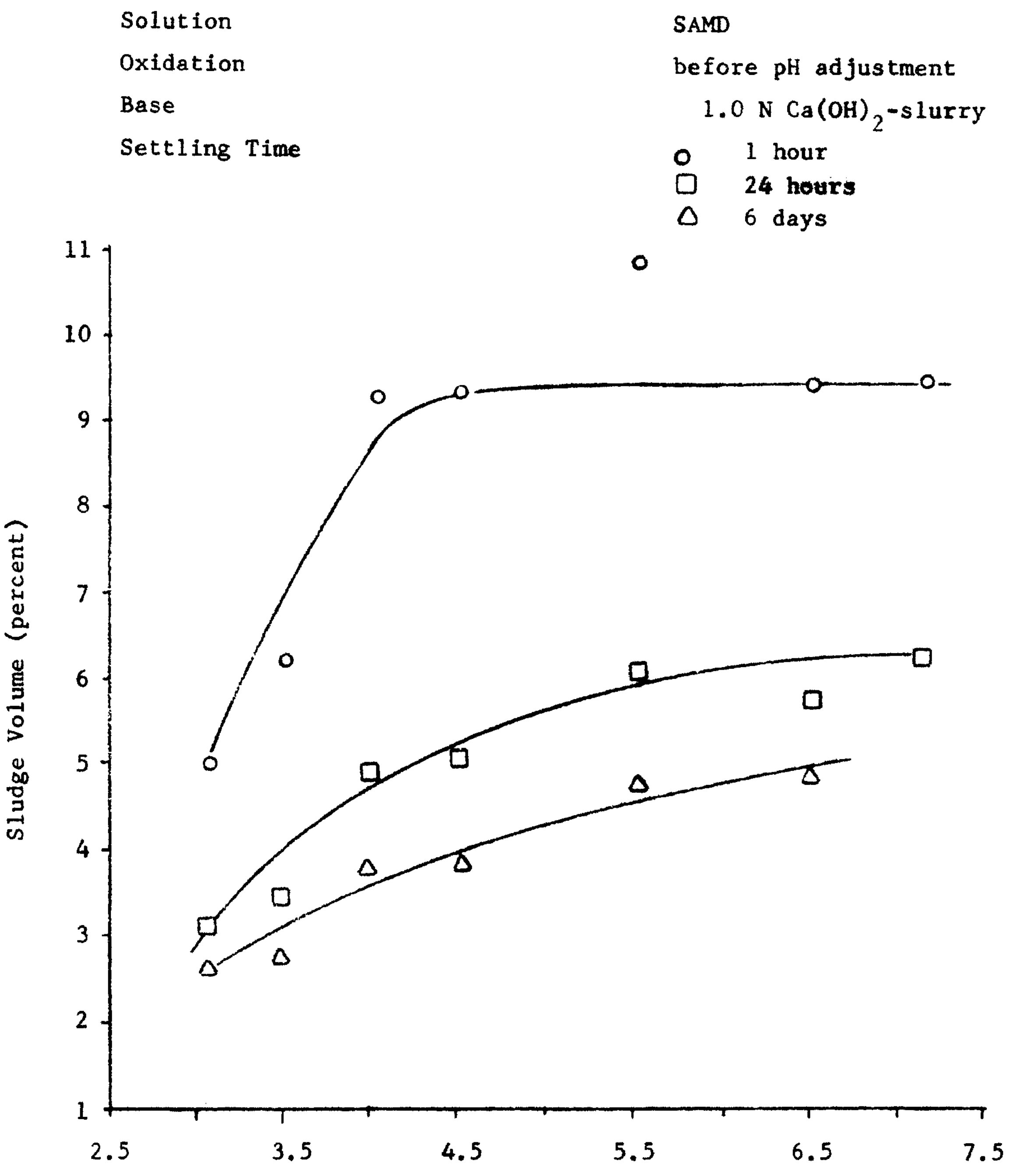


Figure 13

Final pH vs. Sludge Volume

dependent, ranging from 0.362 grams at a treatment pH of 3.5 to 0.388 grams at treatment of pH of 7.3 per liter of SAMD treated. Both of these effects can be related to the aluminum ion. As was mentioned earlier in the section on the treatment of pure aluminum sulfate-sulfuric acid solutions, the precipitation of aluminum occurs at higher pH (4 and above) than does the precipitation of iron. The precipitated aluminum hydroxide will add weight to the sludge, and the voluminous amorphous aluminum hydroxide will add volume to the total sludge. Aluminum remaining in the supernatant solution decreased with increasing pH until at pH 5.5 and above, the aluminum concentration dropped to less than 1.0 mg/l. At pH 4.0, one-half of the aluminum (7.6 mg/l) remained in the supernatant, and at pH 4.5, dropped to 1.8 mg/l. The iron remaining in the supernatant solution after 24 hours settling was below 1.0 mg/l at pH above 4.0.

The sludge formed at the pH 4.0 was fine grained, of yellow color, and settled slowly, indicating the possible presence of goethite, but the sludge formed at higher pH was reddish brown, flocculent, and of the typical appearance of amorphous ferric hydroxide. After settling, it yielded a clear supernatant. At pH 4.0, the sludge volume was 4.0 percent with a solids content of 0.72 percent, while at pH 7.3 the sludge volume was 6.2 percent with a solids content of 0.58 percent. The large sludge volume and its low solids content are factors which emphasize the need for a high density AMD treatment process and justifies the efforts presently directed toward the development of such a process.

Recalling the results of Bethelehem Steel's high density sludge process (5) and results obtained in the present work by treating pure ferrous sulfate-sulfuric acid solutions with calcium hydroxide and sludge "recirculation", a series of runs were performed with SAMD to simulate the recycle process on a laboratory scale by treating batches of SAMD with 100 percent sludge return. The main purpose of this work was to observe the effect of pH, the sludge recycle number and the physical and chemical properties of the sludge solids on the suldge volume and solids content after settling.

The experimental procedure was similar to that used in work on the pure ferrous sulfate-sulfuric solutions. Calcium hydroxide was added to the recycled sludge and then the calcium hydroxide-sludge slurry was added to the SAMD. Another variable investigated was the point of hydrogen peroxide addition during the recycle sequence. One oxidation procedure was to add the hydrogen to the SAMD before the recycled sludge and calcium hydroxide were added. Oxidation before increasing the pH is analogous to the treatment of 100 percent ferric iron AMD. The alternative procedure was to add the hydrogen perodixe after the recycled sludge calcium hydroxide slurry had been added to the SAMD. This simulated the treatment of a ferrous iron AMD.

Preliminary settling and supernatant iron analysis showed that good iron removal and clear supernatant were achieved with twelve hours settling. Four sets of recycle runs were conducted as described below:

Run 1. The SAMD was oxidized before it was treated with calcium hydroxide and the recycled sludge. Treatment was to a final pH of 4.5, and the time intervals between recycles was twelve hours for a total of sixty recycles.

Run 2. Identical to Run 1 with the final pH of 5.5

Run 3. The recycled sludge-calcium hydroxide slurry was added to the new SAMD before oxidation with hydrogen peroxide. During the oxidation, the pH was maintained at 4.5 with a final pH of 4.5. The time between recycles was twelve hours, for a total of thirty recycles.

Run 4. Identical to Run 3 except the pH during oxidation and the final pH were maintained at 5.5.

Figure 14 compares the sludge volumes of Runs 1 and 2. The effect of pH is obvious: the sludge volumes formed at pH of 4.5 are considerably lower when compared with the sludge volumes formed at pH and 5.5. Figure 14 also shows that the sludge volume increased up to approximately 10 recycles, but from the 20th recycle to the termination of the run, the sludge volume remained essentially constsnt. Figures 15 and 16 show the increase of solids content of the sludges with respect to recycle number. It is significant that the sludge solids content increased nearly linearly with the recycle number in the region where the sludge volume remained constant.

The large number of recycles without a sludge volume increase seemed to indicate that once a certain mass of sludge was in the system, the volume would no longer increase. To verify this hypothesis, samples of sludge were taken from Runs 1 and 2 after 60 recycles. The size of samples were taken such that the samples contained a sludge solids mass equal to the total sludge solids mass in the units after 10 and 15 recycles respectively. If the critical mass hypothesis were correct then the sample sludge volumes, when subjected to another recycle, should not increase. For example, the mass present in Run 1 sludge after 10 recycles should occupy a sludge volume of 2.0 percent. If this sludge were recycled, the resulting settled sludge should still occupy a volume of only 2.0 percent. However, the sludge after recycle occupied 2.5 percent. When a volume of sludge was taken to represent 15 recycles of Run 1, the final volume was 3.1 percent and not 2.7 percent as expected. Similar results were found using Run 2 sludges. The sludge volume increases indicated that the mass of recycled sludge in the system was not the only factor controlling the sludge volume. On page 75 the process of dense sludge formation from pure ferrous sulfate-sulfuric acid solutions was discussed. It

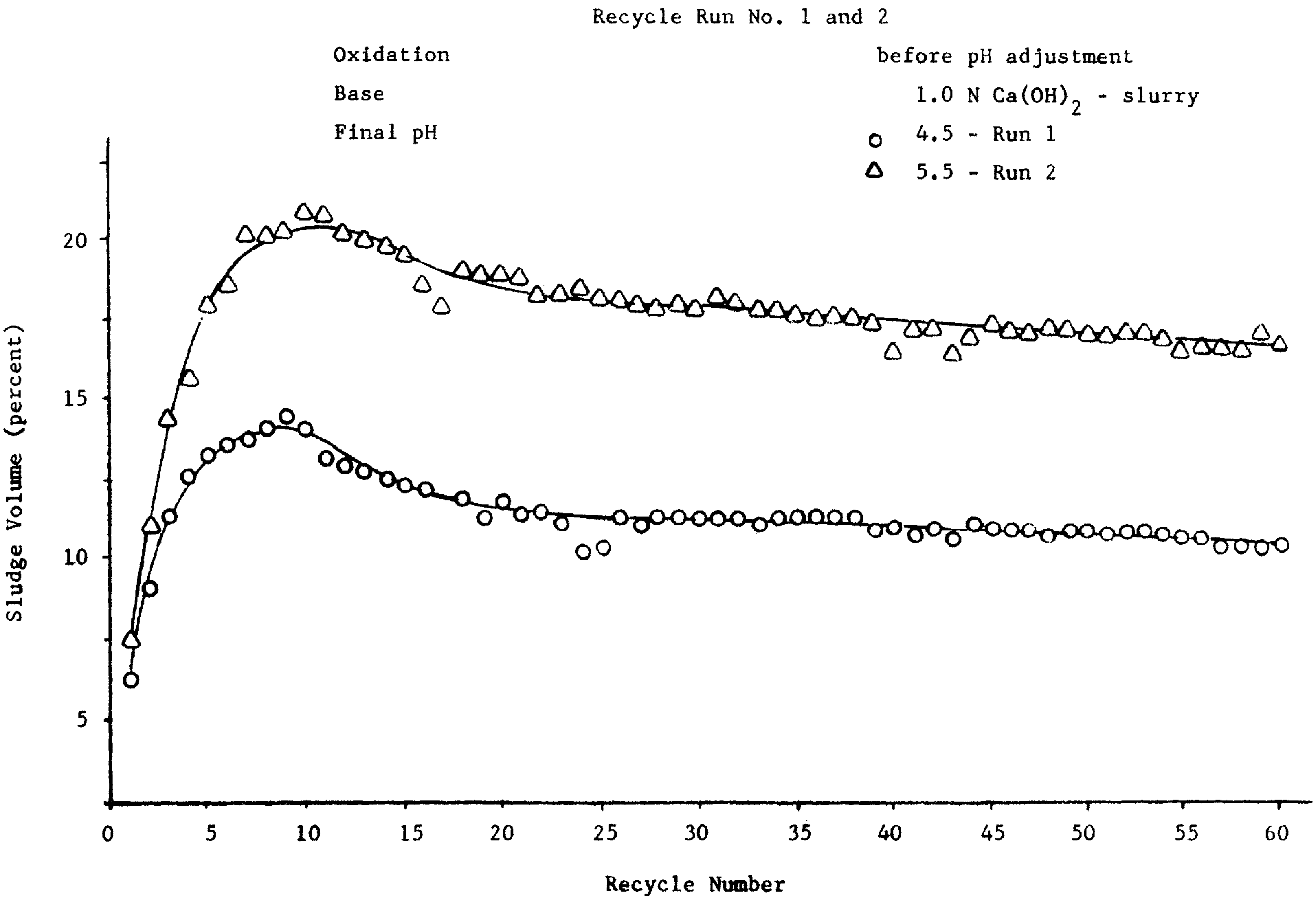


Figure 14

Number of Recycles vs. Sludge Volume

Recycle Run No. 1

Oxidation	before pH adjustment
Base	1.0 N $Ca(OH)_2$-slurry
Final pH	4.5
Sludge Volume	○
Sludge Solids	△

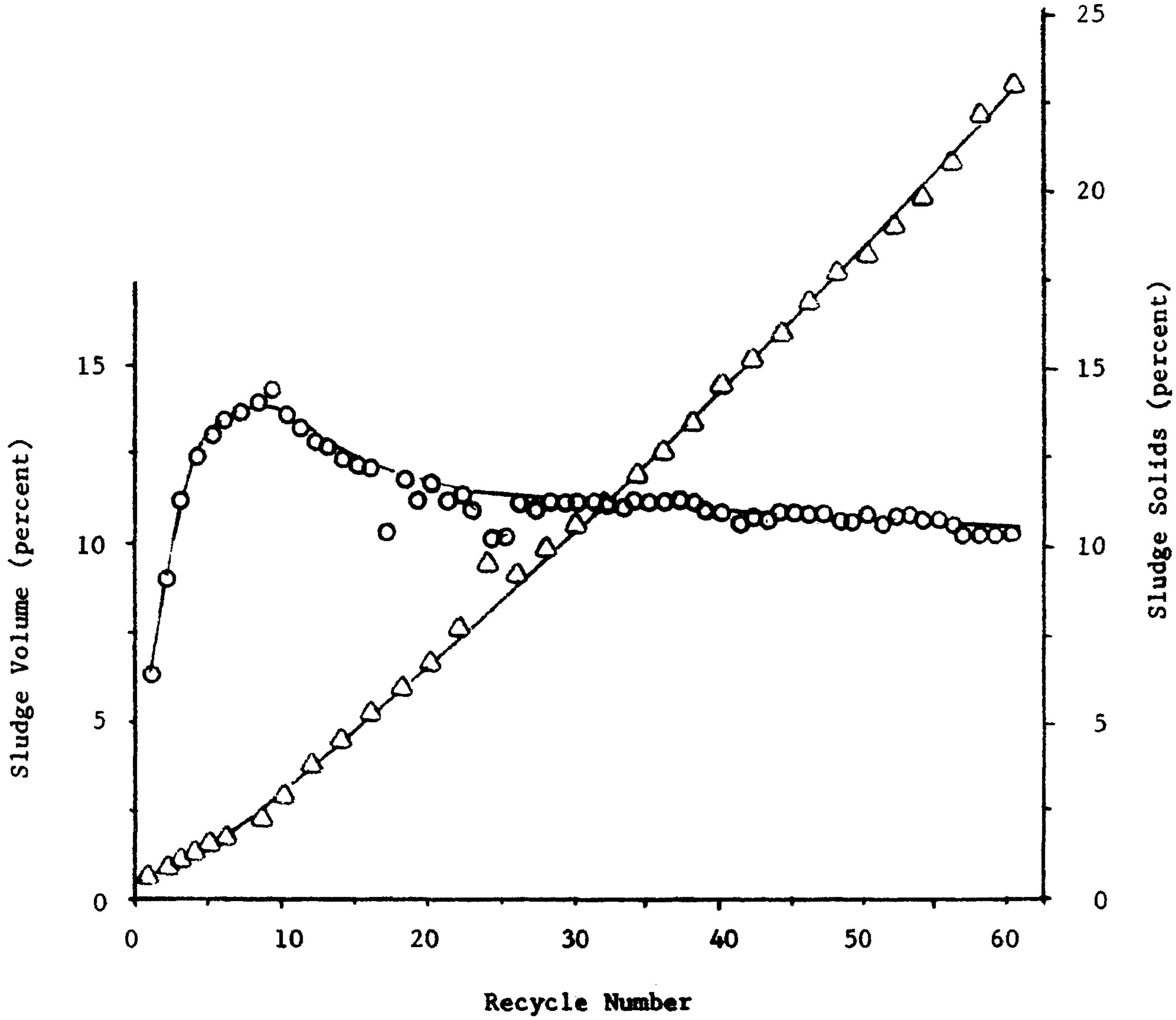
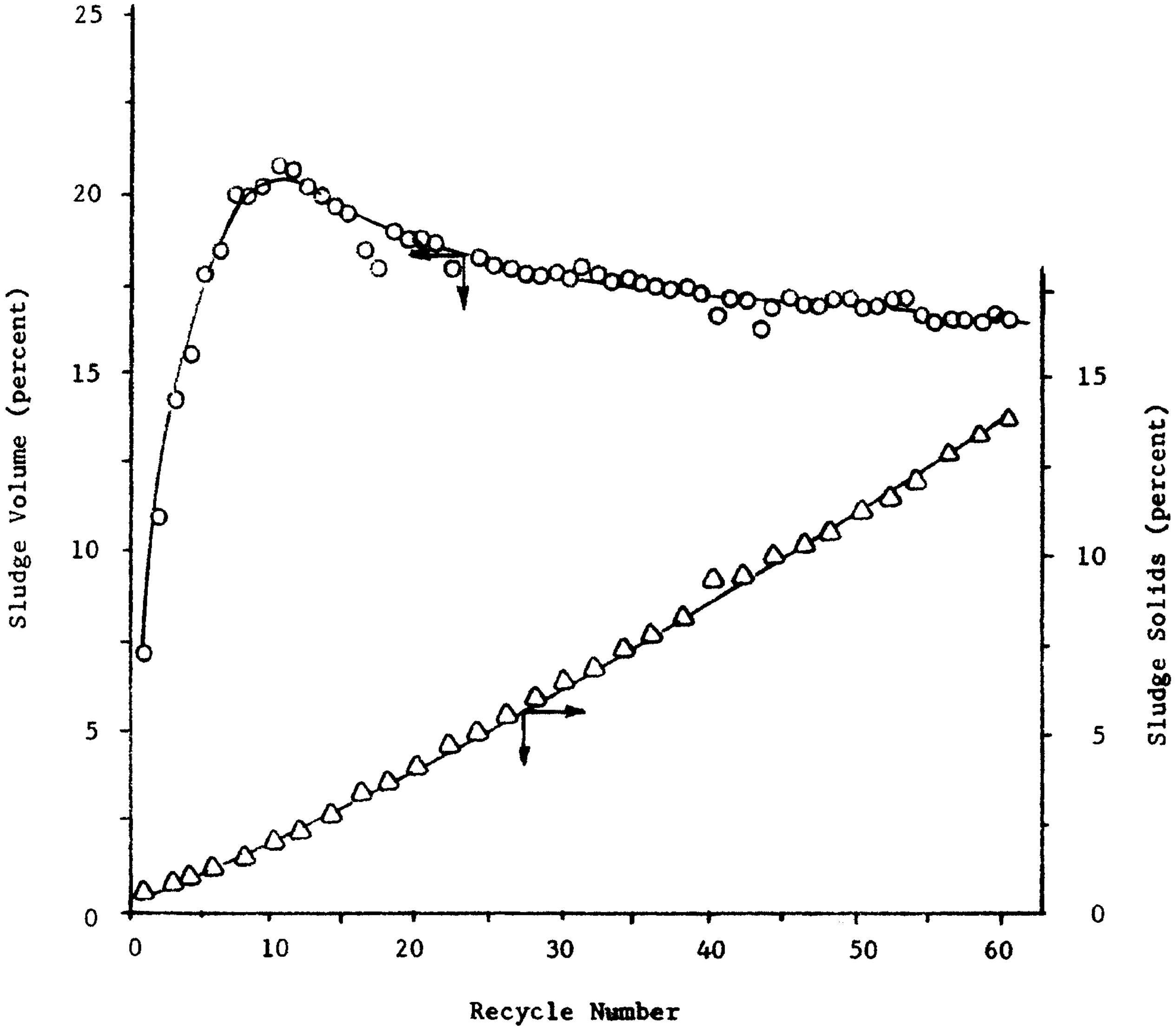


Figure 15

Number of Recycles vs. Sludge Volume and Solids

Recycle Run No. 2

Oxidation	before pH adjustment
Base	1.0 N $Ca(OH)_2$-slurry
Final pH	5.5
Sludge Volume	○
Sludge Solids	△



<u>Figure 16</u>

Number of Recycles vs. Sludge Volume and Solids

has shown that the process of dense sludge formation was associated with the concentration and size of the seed crystals introduced in the solution by recirculated sludge as well as by the mass of recirculated sludge. Generally, the same approach may be applied to describe the results of Run 1 and 2, but there are other factors which affect the sludge volume. The insolubilization of ferric iron on increasing the pH with calcium hycroxide proceeds much faster than the oxication of ferrous iron with air. The aluminum present in SAMD is also insolubilized and according to Kakabadse (88) is preferentially adsorbed on the ferric hydroxide. It is therefore expected that the formation of crystaline ferric oxihydroxides should be retarded. This retardation effect was experimentally verified by precipitation of ferric and ferric-aluminum-sulfuric acid solutions with calcium hydroxide and aging of the sludge formed. The ferric iron sludge, after 60 days aging, showed presence of geothite, but the aluminum-ferric iron sludge was x-ray amphorous.

The sludges of Run 1 and 2 were x-ray amphorous, with a yellow-brown color. Schellmann and Schwertmann (55)(56) noted that the color change from the red brown of ferric hydroxide gel to a yellow indicated the presence of geothite. Also in our work with pure iron solutions it was shown that the color change to yellow was associated with the formation of geothite. The color change of sludges of Runs 1 and 2 may also indidate the presence of geothite, but if so it is of such a small crystal size as to be undetectable by x-ray analysis.

Samples of recycled sludges from Runs 1 and 2 and freshly precipitated sludge samples were examined with a phase contrast microscope. The sludge samples from Runs 1 and 2, after 60 recycles, showed a particle of brown color, and within each particle there were well ordered dark brown dots. The freshly prepared sludge floc, however, appeared blue in color. The significance of the different colors is that it indicates a change in index of refraction, and thus, a different floc structure. The sludge samples of Runs 1 and 2 after only several recycles showed the presence of gel like brown floc, but the dark brown dots evident in the flocs were not ordered in any pattern. The absence of blue colored particles suggested that no new flocs of iron compound were formed, but that the insolubilized iron formed on the particles already present, apparently filling the voids and forming a denser and more or less orderly steric arrangement. The dark brown dots were assumed to be clusters of very tiny crystals of ferric oxihydroxide compound not detectible by x-ray analysis. The evidence discussed is a possible explanation of the phenomenon of the sludge volume remaining constant during repeated recycles, while the sludge density increases. The supernatant from Runs 1 and 2 became increasingly more cloudy as the number of recycles were increased, and that of Run 1, at the lower pH, was much more turbid than the supernatant of Run 2. The iron in the supernatant also increased as the turbidity increased. The aluminum remaining in the supernatant remained constant at 1.5 mg/l for Run 1 and at 0.8 mg/l for Run 2. The supernatant iron of Run 2 never exceeded 6 mg/l while supernatant iron of Run 1 attained a value as high as 12 mg/l. When the supernatants from Run 1 and 2 were allowed to settle for several days, or when the supernatant was filtered through Whatman No. 42 filter paper, the iron remaining in solution decreased by 5 or 6 mg/l. The turbidity can be related to very fine, slow-settling particles in the supernatant. The mechanism of the formation of the very small particles may be attributed to the same process described in the section on insolubilization of pure ferrous sulfate-sulfuric acid solutions.

Another factor investigated was the raising of the pH of the supernatant from Runs 1 and 2 to 7.0. The raising of the pH of Run 2 supernatant produced no additional sludge. Run 1 supernatant, however, produced a sludge of a volume of 0.25 percent and a mass of 0.005 grams per liter of supernatant treated. The iron analysis before and after this secondary treatment indicated that it was the iron removal that produced the additional sludge, demonstrating the higher iron removal efficiency of Run 2 (pH 5.5) as compared to Run 1 (pH 4.5).

The sludge volume of Runs 3 and 4 are compared in Figure 17. The scatter of points in this figure was due to a variation in the time between recycles of from ten to fourteen hours. The points above the curve are due to the resulting shorter settling time, while the points below the curve showed the result of the sludge having more time to age, and to settle and compact. The sludge volume never reached a constant in these two runs as it did in Runs 1 and 2. However, the rate of volume increase did decrease with increasing recycle number. Figure 17 also shows that denser sludges were formed at the lower pH.

Figures 18 and 19 show how the solids content of the sludge increased with each recycle. Even though the sludges in Runs 3 and 4 did not reach a constant (after 30 recycles), they still represent an improvement over unrecycled sludges. For example, in Run 4 at the end of the first cycle, the sludge volume was 9 percent. If the sludge did not increase in density as it was recycled, then at the end of six recycles the sludge volume would be 54 percent. However, even after thirty recycles the sludge volume was under 54 percent.

Runs 3 and 4 yielded a reddish brown, sludge, which after settling yielded a clear supernatant of less than one mg/l of total iron. The sludge color was similar to the color of amorphorous, flocculent, gel like precipitates of ferric hydroxide. The structure of ferric hydroxide gel is not certain. Some researchers feel that the gel is truly $Fe(OH)_3$, while other

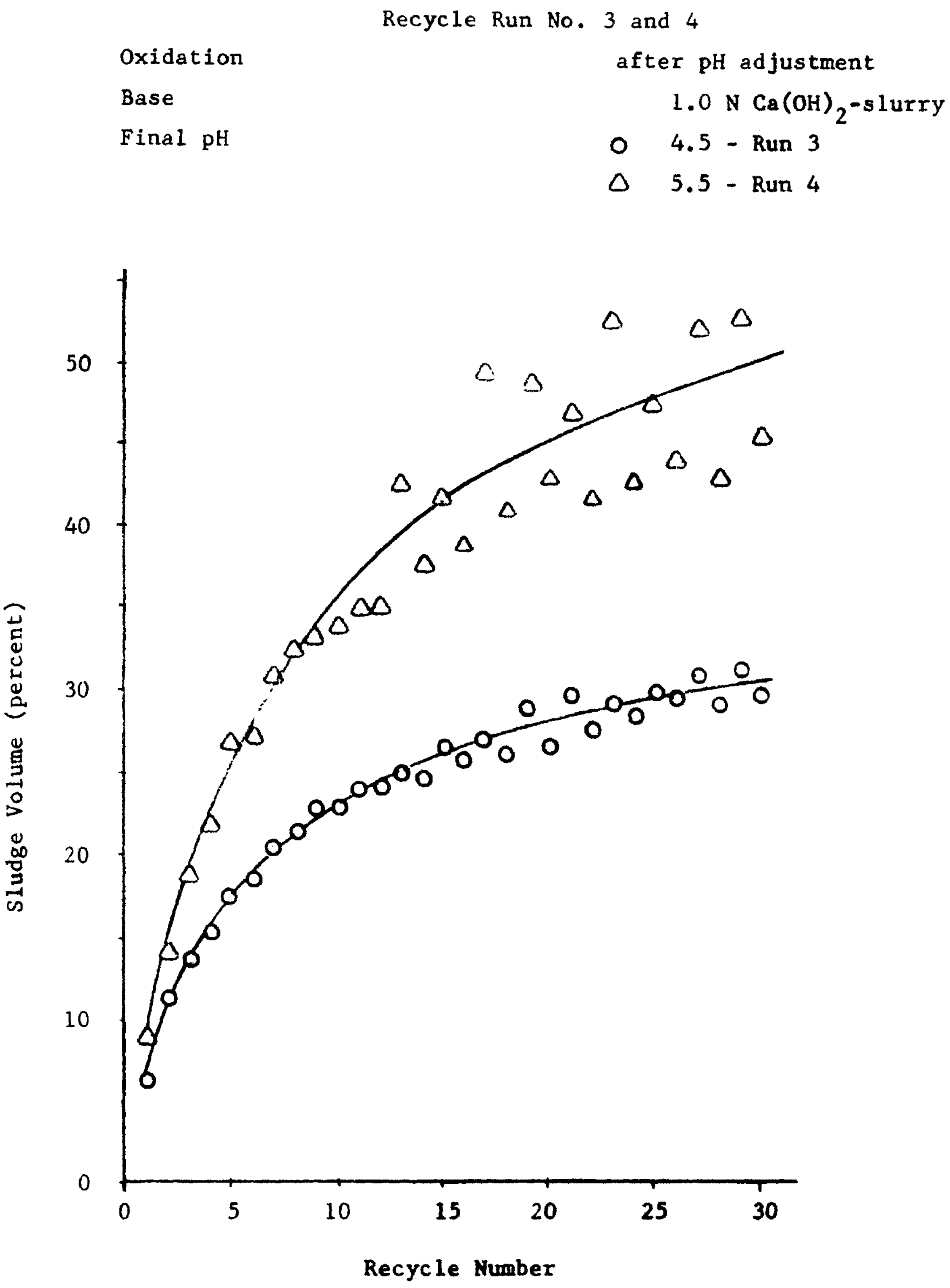


Figure 17

Number of Recycles vs. Sludge Volume

Recycle Run No. 3

Oxidation	after pH adjustment
Base	~1.0 N $Ca(OH)_2$-slurry
Final pH	4.5
Sludge Volume	○
Sludge Solids	△

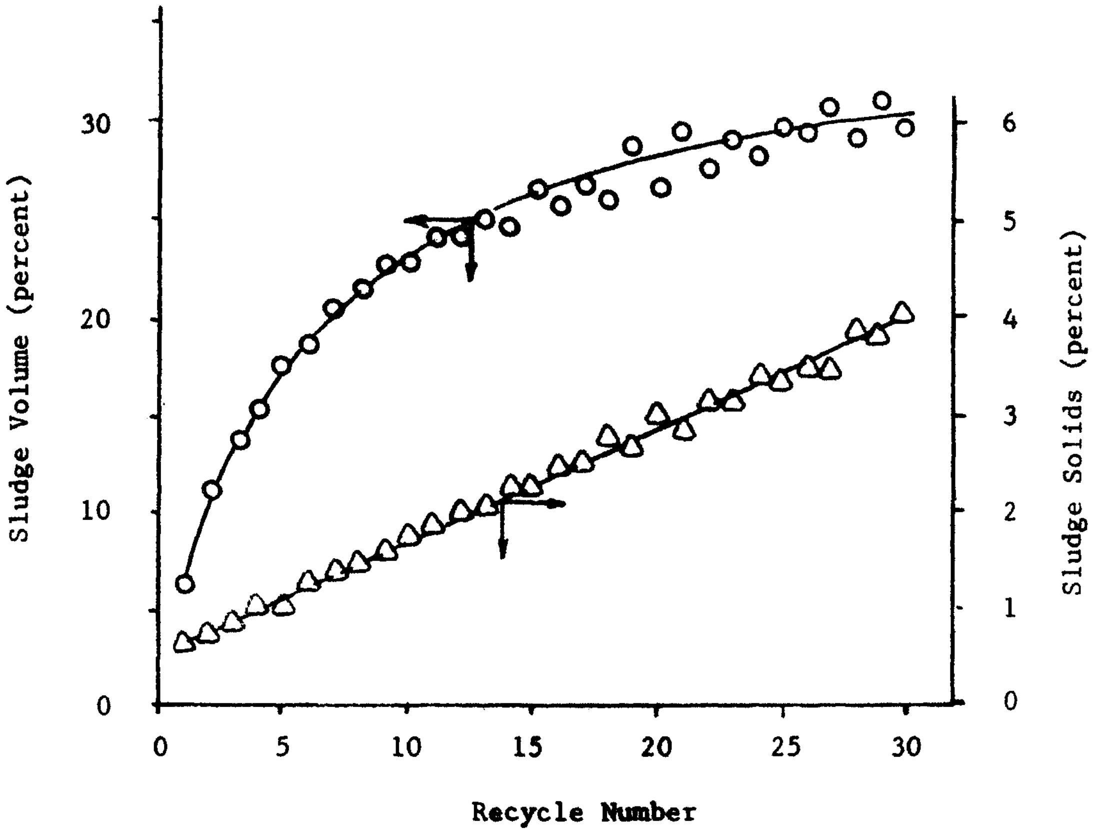


Figure 18

Number of Recycles vs. Sludge Volume and Solids

Recycle Run No. 4

Oxidation	after pH adjustment
Base	$\sim$1.0 N $Ca(OH)_2$-slurry
Final pH	5.5
Sludge Volume	○
Sludge Solids	△

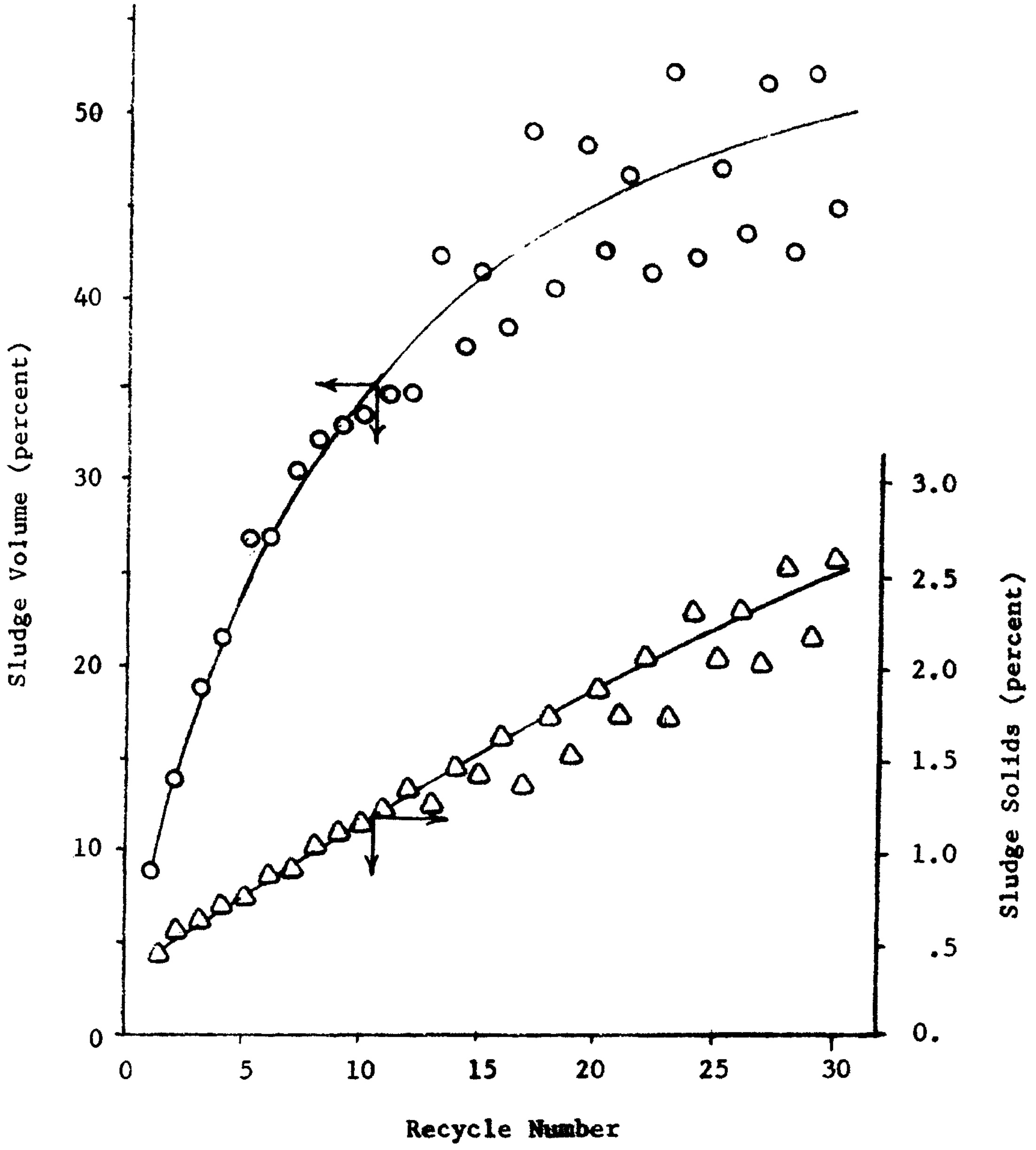


Figure 19

Number of Recycles vs. Sludge Volume and Solids

researchers feel that the gel contains certain microcrystals of ferric hydroxi or oxide compounds. If it is assumed that the ferric hydroxide gel contains some microcrystaline compounds the sludge density increase with recycle number may be attributed to formation of crystals which grow with increasing recycle number but still remain small enough to not be detected by x-ray analysis. It should be noted that the x-ray analysis of sludge samples of Runs 3 and 4 were x-ray amorphous. When the sludges were viewed under the microscope, the flocs were both blue and brown. The brown flocs did not contain the well ordered dark brown dots evidenced in the sludges from Runs 1 and 2. The presence of small blue flocs in Runs 3 and 4 sludge indicated the presence of freshly formed flocs which had not grown on older floc particles. This presence of these new flocs may explain why the sludge volume of these runs continued to increase up to 30 recycles.

When the sludge shown in Figure 19 are compared with the sludge volumes from pure ferrous sulfate-sulfuric acid solutions (Figure 11), the much larger sludge volumes of the Run 4 are obvious. Figure 11 shows a sludge volume of 7.5 percent after 30 recycles, while Figure 19 shows a sludge volume of 50 percent after 30 recycles. Both runs were made at similar conditions, except that in Run 4 hydrogen peroxide was used for oxidation of ferrous iron instead of air, and aluminum precipitated from the SAMD is included in the Run 4 sludge. The large sludge volume of Run 4 is attributed to the rapid oxidation of ferrous iron, and to presence of aluminum precipitates.

Table VIII shows the results of sludge analyses of Runs 1 through 4. Note that the sum of the constituents analyzed for was less than 100 percent However, if the iron were expressed as FeOOH, and aluminum as $Al(OH)_3$, the sum would increase over 90 percent. Also, since the sludge was dried at 105°C for 24 hours, some water undoubtedly remained in the dried sludge, and the

TABLE VIII

Sludge Analysis from the Recycle Runs

Run No.	Treatment pH	Alkali	% Fe_2O_3	% Al_2O_3	% CaO	% MgO	% MnO	% SO_4^{-2}	TOTAL
1	4.5	$Ca(OH)_2$	71.5	7.2	0.081	0.014	0.019	8.88	87.69
2	5.5	$Ca(OH)_2$	69.5	7.4	0.095	0.011	0.035	7.61	84.65
3	4.5	$Ca(OH)_2$	71.5	6.1	0.056	0.033	0.057	9.51	87.26
4	5.5	$Ca(OH)_2$	71.5	6.4	0.090	0.005	0.019	6.28	84.29

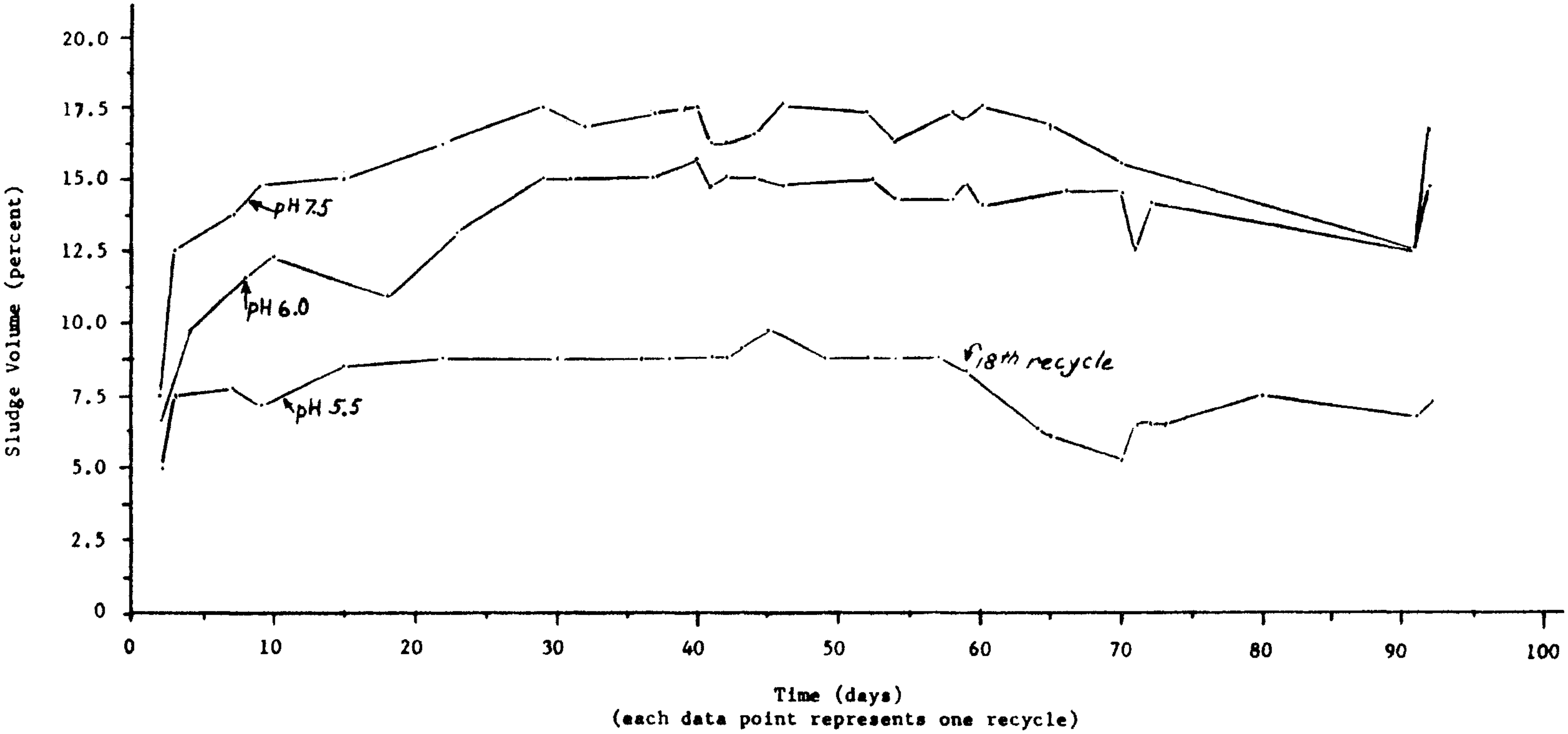
weight of this component was not determined. The sulfate content of the sludge decreased when the treatment pH increased, and was present probably in the form of ferric hydroxisulfate.

b) Oxidation with Air

The experiments involving air oxidation of SAMD prior to neutralization were performed in a manner similar to the experiments with pure ferrous sulfate-sulfuric acid solutions. Experiments were conducted at pH 7.5, 6.0, and 5.5, with the results shown in Figure 20.

The pronounced effect of pH is obvious. The initial sludge volume at pH 6.0 was 6.5 percent with a solids content of 0.50 percent, while at pH 7.5, the volume was 7.5 percent with sludge solids of 0.47 percent. The sludge volume of the runs at pH 6.0 and 7.5 reached a maximum value after 6 recycles and then remained reasonably constant at 15.0 percent and 17.5 percent respectively until termination of the runs. The terminal sludge solids content at pH 6.0 and 7.5, after 24 and 22 recycles, was 5.9 and 5.4 percent respectively, showing an approximately tenfold solids content increase from the initial values.

The initial sludge volume at pH 5.5 was 5.0 percent, with a solids content of 0.60 percent. The sludge volume increased to 8.7 percent in 4 recycles and remained constant up to 17 recycles, attaining a solids content of 6.8 percent. After the 17th recycle the sludge was split into two parts and only one half, corresponding to a volume of 4.4 percent, was carried through the remainder of the recycle series. At the 18th recycle the sludge volume increased to 6.2 percent, then decreased to 5.1 percent, then again increased and leveled off at 7.5 percent. If the mass of the recirculated sludge had been the only factor determining the total sludge volume, then the total sludge volume should have remained constant at 4.4 percent; the



<u>**Figure 20**</u>

SAMD Sludge Volume vs. Time

results showed that this was not the case. Here again it is suggested that the physical properties of the recirculated sludge, particularly the size and concentration of seed particles introduced per unit volume of the SAMD to be treated, is the primary factor determining the volume of sludge formed. This phenomenon was discussed more thoroughly eariler in this chapter. At the termination of the pH 5.5 run, after a total of 26 recycles, the volume of the sludge was 7.5 percent with a solids content of 10.4 percent.

Figure 20 indicates a relatively small effect of aging on sludge volume, suggesting that a close packing of particles occurs during settling, and that relatively small changes in the physical properties of the sludge solids occur on aging.

The sludge formed at pH 5.5 was of yellow color, fine grained and slow settling. The supernatant was clear for the first several recycles, with an increasing number of recycles, became more turbid. The color, the particle size, and the settling characteristics of this sludge were similar to the sludge solids formed from pure ferrous sulfate-sulfuric acid solutions at pH 5.5. These properties suggest the presence of goethite, and x-ray diffraction analysis of the solids did indeed show the presence of goethite. When viewed through the microscope the sludge solids appeared as brown particles within which there were well ordered dark brown dots. The dark brown dots were relatively larger and closer spaced than those observed in sludges of Runs 1 and 2, which employed hydrogen peroxide for ferrous iron oxidation. The microscopic observations seem to support the assumption that the observed dark brown dots are clusters of randomly oriented fine goethite crystals. The sludge volume of the pH 5.5 run, Figure 20, remained constant for an extended time at 8.7 percent, and there is evidence that sludge volume will remain constant for many more recycles. It is to be recalled that this sludge resulted from the treatment of SAMD, which includes aluminum and other constituents in addition to iron. The sludge volume from pure ferrous sulfate-sulfuric acid solution under similar conditions, Figure 11, remained constant for many recycles at 7.5 percent. Comparing the two sludge volumes, it appears that constituents other than iron in the SAMD, particularly aluminum, had a minor effect on the sludge volume formed. On the other hand, comparing the pH 5.5 air oxidized SMAD sludge volume of 8.7 percent (17 recycles, Figure 11) with pH 5.5 hydrogen peroxide oxidized SAMD sludge volume of 40 percent (17 recycles, Figure 19), it is obvious that a major factor determining sludge volume is the rate of oxidation of ferrous iron, provided the other conditions of the process are identical. It should be remembered that the rate of oxidation of ferrous iron by air increases rapidly with increasing pH, and therefore the change of pH is also associated with a rapid change of the oxidation rate over the pH range of these experiments.

The sludges of the runs at pH 6.0 and 7.5 were yellow-brown, darker at pH 7.5, more flocculent than at pH 5.5 and on settling, yielded a clear supernatant. The sludge formed at pH 6.0 showed an x-ray diffraction pattern of amorphous material with some poorly formed goethite. The x-ray analysis of the sludge formed at pH 7.5 was partly amorphous, but with some poorly developed lepidocrocite. On treatment of the SAMD at pH 7.5, the formation of dark green precipitate was observed, probably a ferrous-ferric hydroxi compound, which turned brown on oxidation. According to Schwertmann (55), oxidation of $Fe(OH)_2$ with oxygen at pH from 5 to 8 leads to the formation of γ-FeOOH (lepidocrocite); thus, our observations are in agreement with Schwertmann's. According to Nitschmann (68) the γ-FeOOH is termodynamically unstable at the conditions of our experiments and is converted α-FeOOH (goethite). Our observations also showed that with prolonged aging of the sludges the fraction of α-FeOOH increased relative to γ-FeOOH.

The supernatant analysis for SAMD treated at the indicated pH values are shown below:

Iron and Aluminum Concentration
In Supernatant

SAMD	Aluminum mg/l		Iron mg/l	
Treatment pH	48 hour settling	Filtered Whatman 42	48 hour settling	Filtered Whatman 42
7.5	0.29	0.20	0.33	0.04
6.0	0.35	0.13	0.38	0.06
5.5	0.44	0.05	0.81	0.08

The results show good iron and aluminum removal. These samples were taken under conditions of clear supernatant. With increasing turbidity the supernatant total iron concentration increased.

Two runs were performed using modified SAMD with 122.5 mg/l ferrous iron and 77.5 mg/l ferric iron, the concentration of the other constituents remaining unchanged. This ferrous-ferric ratio was chosen so that when the dissolved oxygen in the SAMD was completely used for ferrous iron oxidation, the final mole ratio of ferric to ferrous iron should be two to one. The pH of two samples of SAMD was adjusted with $Ca(OH)_2$ suspension to 9.0, a dark green precipitate, probably green rust II, was formed, and the dissolved oxygen concentration dropped to near zero. From this point on the treatment of the suspension was different for the two samples, both of which were subjected to treatment with sludge recycling. In the first run, the suspension was slowly stirred in a beaker open to the air and the slow oxidation of the precipitate was accomplished by oxygen slowly diffusing in from the air. In the second run, oxidation was accomplished by passing a lively stream of dispersed air through the suspension giving a more rapid oxidation rate of the ferrous iron. The difference in oxidation rates was readily observed by the rates of change of the color of the precipitates from dark green to brown. The sludges were then allowed to settle for 24 hours, separated from the supernatant, combined with $Ca(OH)_2$-suspension, and sludge - $Ca(OH)_2$ slurry was recirculated to a fresh batch of modified SAMD. It was speculated that the oxidation of green rust II might lead to denser sludge formation.

The sludge volume of the slow oxidation run increased from an initial volume of 8.7 percent, with a solids content of 0.52 percent, to 16.3 percent with a solids content of 2.5 percent after 9 cycles.

The sludge volume, of the rapid oxidation run, increased from an initial value of 6.9 percent with a solids content of 0.66 percent to a volume of 25 percent with a solids content of 1.7 percent after 9 recycles.

The runs were terminated after 9 recycles because the sludge volumes were still increasing nearly linearly with recycle number, and the large volumes of low solids content of the sludges after 9 recycles did not indicate any advantage over treatment of SAMD at lower pH values.

X-ray analysis of the sludge of the slow oxidation run showed the presence of lepidocrocite, but the sludge solids of the rapid oxidation run were x-ray amorphous. The conclusion may be drawn that the oxidation rate of ferrous iron has a pronounced effect on the formation of crystalline ferric hydroxi compounds, and hence, on sludge density.

The results of treatment of pure ferrous sulfate-sulfuric acid solutions and of SAMD with lime and oxidation of ferrous iron with hydrogen peroxide or air showed that denser sludges were obtained by sludge recycling. Further, the volume of the recycles sludge was determined by the physical and chemical properties of the recycled sludge solids, which were in turn strongly affected by the pH and the rate of ferrous iron oxidation. The decrease of the recycled sludge volume with decreasing pH and the associated rapid decrease of the oxidation rate of ferrous iron by air indicate that a process conducted at lower pH should yield the denser sludge. An actual AMD treatment process utilizing air for oxidation of ferrous iron at low pH would be associated with large volume oxidation tanks and high power consumption for contacting AMD with air. On the other hand, the smaller recycled sludge volume should decrease both the pumping costs for the recycled sludge, and the costs of sludge disposal. Considering all the economic factors associated with a particular case, an estimation of the optimal values of process variables could be made. Experience has shown that ferrous iron oxidation with air is an important factor in the economics of an AMD treatment process, and therefore the following was done to determine the effect of sludge recycling on oxidation rate.

During the work with pure ferrous sulfate-sulfuric acid solutions, it was observed that the rate of farrous iron oxidation with air increased with increasing number of sludge recucles. At the time of the experiments, it was initially thought that the oxidation rate increase was associated with biochemical processes, due to the large number of dead bacteria present in the recycled sludge when viewed under microscope after HCI treatment to dissolve the ferric iron. Chemical catalysis due to the sludge itself was not expected since Stumm (13) had noted that amorphous ferric hydroxide did not affect the oxidation rate of ferrous iron with air.

By observation, however, it appeared that the oxidation rate increase was also associated with the color change of the recycled sludge, indicating the formation of geothite. To eliminate the possible effect of microorganisms, both the reagent solutions and the recycled sludge were boiled for 30 minutes.

These experiments were made with pure ferrous sulfate-sulfuric acid solutions, 400 mg/l Fe^{2+} and 1200 mg/l total SO_4^{2-}, using the same procedure of sludge neutralization and dilution with fresh acid-iron solution applied to the prior runs. Ferrous iron concentration was determined on samples taken at specified time intervals with the samples being filtered immediately, acidified with $HCl-H_3PO_4$ mixture, titrated with 0.01N $K_2Cr_2O_7$ solution. The solution oxidized with air contained 7.5 grams per liter of recycled sludge solids. The sludge used in these experiments was taken from the sludge obtained from the previous runs at pH 5.5 after the termination of the recycle runs with pure ferrous sulfate-sulfuric acid solutions. The ferrous iron oxidation with suldge reclcle was conducted at constant pH of 5.5, and are compared with runs made under similar conditions withour sludge recycling. Figure 21 shows the recycling results of the duplicate run plotted as the log of ferrous iron concentration (mg/l) versus time (minutes). It is noted that the data fit closely the representation of a first order reaction;

$$-\frac{dc}{dt} = KC; \quad \log \frac{Co}{C} = \frac{k}{2.303} t$$

It should be emphasized that there were not enough data to verify the order of the reaction, and the plot should be considered more or less a data fitting attempt for convenient use in discussion of the results. The apparent specific rate constant, K, estimated for the runs without sludge recirculation is 0.045 $min.^{-1}$ and for the runs with sludge recirculation show a constant 0.179 $min.^{-1}$ indicating an oxidation rate four times faster than without sludge recirculation. It should be also mentioned that there are other factors affecting the oxidation rate, including the manner of addition of calcium hydroxide, stirring rate and probable local high pH, the alternate option of treatment of the mixture with calcium hydroxide after addition of the sludge to the ferrous sulfate-sulfuric

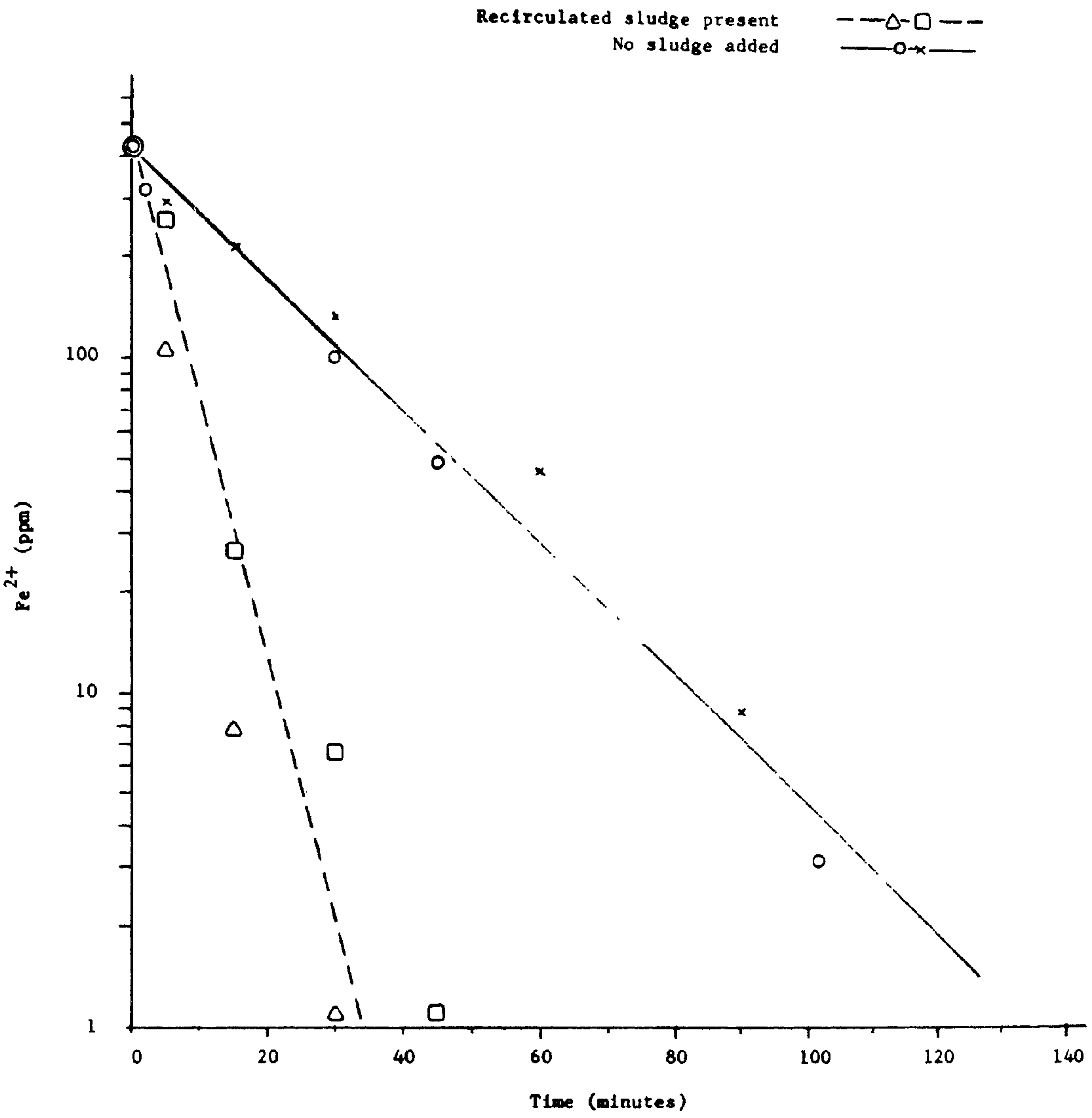


Figure 21

Ferrous Iron Concentration vs. Time

acid solution, the rate of air flow through the solution. However, the overall results clearly indicate the positive effect of sludge recirculation on the oxidation rate of ferrous iron. It is assumed that goethite or lepidocrocite are catalizing the ferrous iron oxidation rate, but more work would be required to verify this assumption. Stumm (13) showed that the oxygenation rate of ferrous iron in solution was first order with respect to ferrous iron concentration, and estimated of the specific reaction rate constant, K, to be 0.00016 min.^{-1} at pH 5.5. Stauffer and Lovell (89) performed ferrous iron oxidations in sulfuric acid solutions and arrived at a rate constant of 0.040 min.^{-1} at pH 5.5. The apparent discrepancy between Stumm's rate constant estimate as compared to Lovell's and ours (K=0.045 min.^{-1}) may be explained by Stumm's use of perchloric acid instead of sulfuric, working with very low initial ferrous iron concentrations, and utilizing buffers to maintain constant pH. On the other hand, Lovell's and our reaction rate constants might appear high because of the transient local high pH which develops by addition of base to the reaction solution to maintain constant pH. Lovell attributed his high reaction rate constant, K, to the formation of insolubilized $Fe(OH)_2$ which was oxygenated at a very high rate. Recent experiments in our laboratory not covered in this report showed a somewhat lower reaction rate constant at pH 5.5, and a pronounced catalytic effect of ferric oxyhydrosides on the oxygenation rate of ferrous iron solutions.

The observation that the oxidation rate of ferrous iron was increased from 4 to 6 times when the sludge was recycled as compared with the oxidation rate without sludge recirculation, led to the expectation that the oxidation rate of ferrous iron with air should be higher with sludge recycling in SAMD treatment with lime. Concurrently with the experiments with SAMD and sludge recycling, observations were also made on the time required for essentially complete oxidation of ferrous iron (residual concentration of Fe^{2+} approximately 10 mg/l). The end point of the ferrous iron oxidation was determined by observing when the pH after mixing of the lime-treated sludge with fresh SAMD ceased drifting downward, and settled at a stable value for at least 15 minutes. The oxidation of ferrous iron with oxygen is described by equation

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ + = Fe^{3+} + \frac{1}{2} H_2O$$

and the hydrolysis of the ferric iron formed is shown by the equation

$$Fe^{3+} + 3 H_2O = Fe(OH)_{3(s)} + 3H^+$$

or by the overall reaction

$$Fe^{2+} + \frac{1}{4} O_2 + 2\frac{1}{2} H_2O = Fe(OH)_{3(s)} + 2H^+$$

The overall reaction equation shows that the oxidation process is associated with a release of hydrogen ions and consequently with a decrease of pH, thus providing a basis for estimating oxidation time from pH readings. Figure 22 shows the results. Each dot indicates the time required for almost complete oxidation of ferrous iron, corresponding to the experiments shown on Figure 20. The determination of the oxidation end point was not precise but the results show clearly the overall trend. It might be argued that the oxidation rate increase with time and increasing recycle number was associated with an increasing microorganism population. That this was not the case is shown by the experiments conducted after the termination of the runs, in which all solutions and the recycled sludge was sterilized by boiling for 30 minutes. The oxidation rates with sterilized solutions were the same as the rates of the last experiments in the series, prior to boiling. The overall results show an oxidation time decrease from approximately 200 minutes after a few

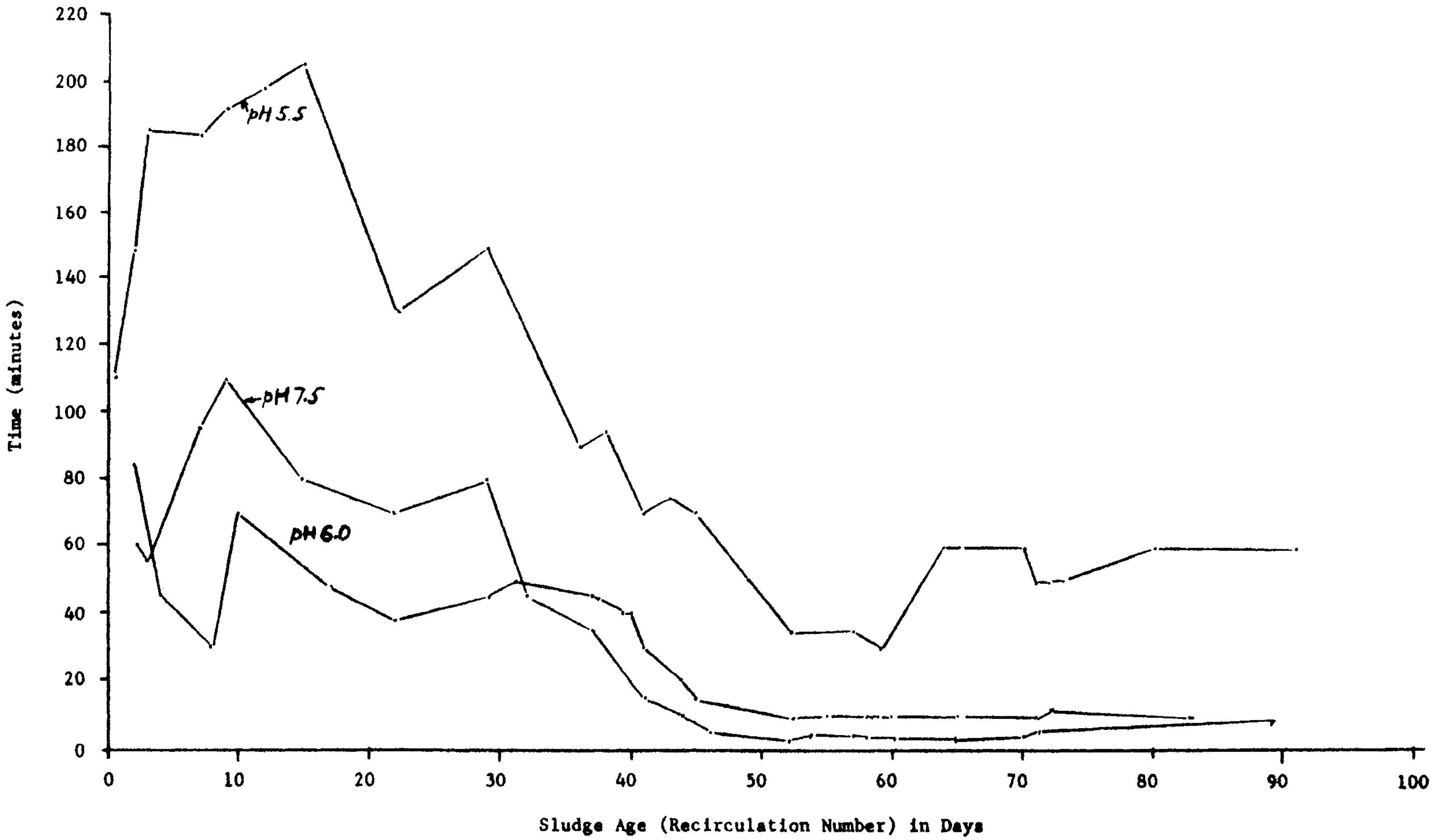


Figure 22

SAMD-Sludge Oxidation Time vs. SAMD-Sludge Age (Recirculation Number) recycles, or an approximate sevenfold oxidation rate increase, at pH 5.5. After the 17th recycle, (pH 5.5) one half of the accumulated sludge was used for the 18th recycle. The oxidation time increased from 30 to 60 minutes, showing that the oxidation rate of ferrous iron was directly associated with the quantity of the recycled sludge. The nearly proportional decrease of the oxidation rate with respect to the decrease of recycled sludge quantity, or the surface of the sludge solids, indicates a process of heterogeneous catalysis. Several experiments were also made with other ferrous iron to aluminum mole ratios. The results showed that the oxidation rate of ferrous iron decreased in the presence of sludge having a lower ferric iron to aluminum mole ratio, indicating a possible interference of aluminum on the catalytic properties of the recycled sludge.

4. The Role of Iron Oxidizing Bacteria in Mine Drainage Treatment Processes

As noted above, the catalysis of iron oxidation at low pH values, over and above the rates observed in solution (13) may be due either to chemical catalysis associated with the ferric iron precipitate surfaces present, or to the effect of iron oxidizing autotrophs of the Ferrobacillus-Thiobacillus group. The following experiments were performed with the intent of determining the relative importance of these two phenomena under conditions of pH and sludge recirculation pertinent to the treatment of acid mine drainage. A detailed report of the findings in this section are found in the thesis of Chao (92). The following material outlines the procedures and results of these experiments.

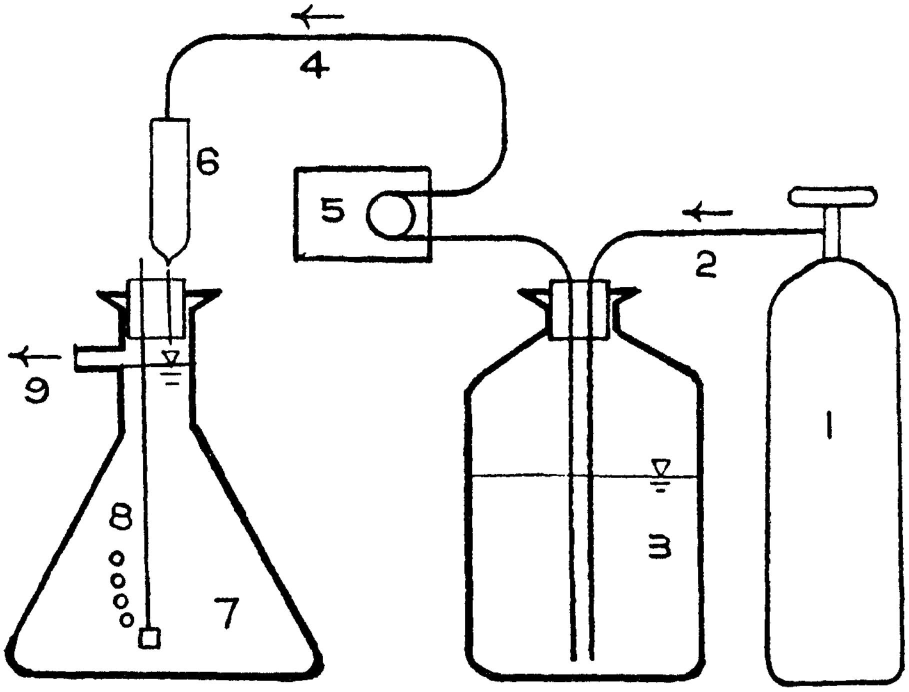
Background

Iron oxidizing bacteria having acidophilic and chemoautotrophic characteristics have long been associated with the oxidation of pyrite, and attempts have been made to utilize their iron oxidizing abilities in the treatment of acid mine drainage. Although the acidophilic iron oxidizing chemoautotrophs have been differentiated as separate species, with T. ferrooxidans and F. ferrooxidans being most prominent in the literature, there is increasing opinion that these two strains may, in fact, be variants of a single species, thus the iron oxidizing bacteria associated with acid mine drainage are often referred to generally as the Thiobacillus-Ferrobacillus group. The organisms used in the experiments described below are a mixed culture of iron oxidizers, obtained from mine drainage samples taken from Vinton County, Ohio. These organisms grow well in the SAMD used in this research, particularly if an inorganic nitrogen source such as ammonium nitrate is added.

Apparatus

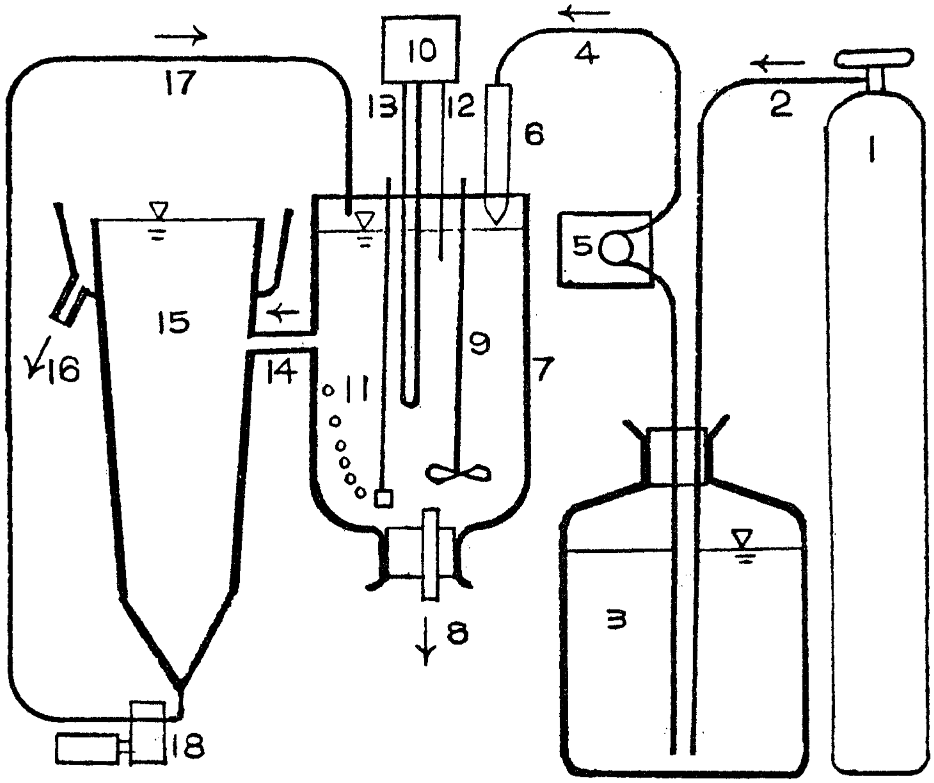
The basic intent of this work was to compare the oxidation rates observed at pH values varying from 2.5 to 5.5, with and without bacterial catalysis, and both with and without sludge recycle. To accomplish this, three types of laboratory scale diffused air oxidation systems were used, all of which employed complete mix hydraulic conditions in the aeration tanks. These units are shown in Figures 23 through 26. Figure 23 shows the Type I unit employed when working in the range of pH from 2 to 3, in which no settleable iron precipitates were obtained. In this case, no return sludge system was required, and no attempt to operate the unit under sterile conditions was required, since chemical oxidation rates at this pH are almost immeasurably slow.

Figure 24 shows the Type II unit employed when working in the pH range from 4 to 5.5, where iron precipitates accumulate to high concentrations, and where it was anticipated that both chemical and biological catalysis would have measurable effects on the iron oxidation rates. In this case, the unit



1. nitrogen gas tank
2. nitrogen gas flow
3. SAMD reservoir
4. SAMD flow
5. peristaltic pump
6. SAMD surge tank
7. culture flask
8. air diffuser
9. effluent

Figure 23
Schematic Diagram of Continuous Culture Units



1. nitrogen tank
2. nitrogen inlet
3. SAMD reservoir
4. SAMD flow
5. peristaltic SAMD pump
6. SAMD surge tank
7. aeration tank
8. aeration tank sampling valve
9. stirrer
10. automatic titrator
11. air diffuser
12. titrator delivery tip
13. titrator electrode
14. mixed liquor flow
15. settling tank
16. effluent
17. sludge return flow
18. sludge return pump

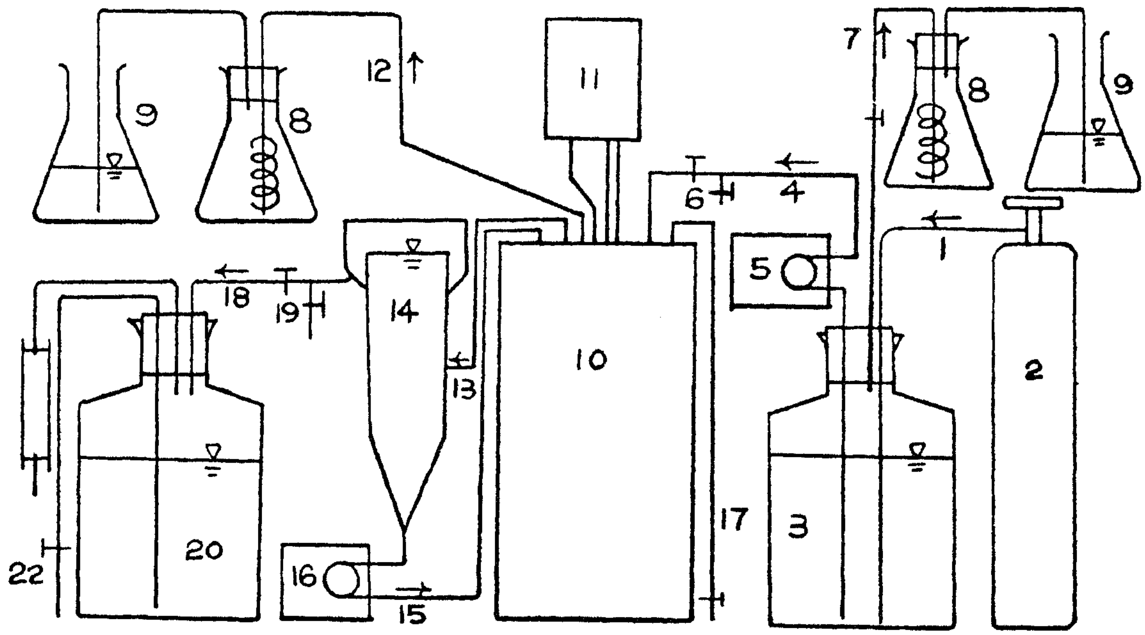
Figure 24

Schematic Diagram of Continuous Flow Activated Sludge Type Unit was equipped with an automatic titrater feeding 20% KOH, in order to keep the pH relatively constant. Problems with electrode fouling precluded precise pH control, but control within the range of ± 0.2 pH units was feasible. The aeration tank, having a volume of 3.385 liters, was left open to the atmosphere and no attempt was made to use this unit under sterile conditions.

Figure 25 shows the Type III unit adopted for use in the range of pH 4 to 5.5, where recycle capability became a requirement due to the high sludge solids concentrations precipitated, and where it was necessary to operate the system under sterile conditions to eliminate the possible effect of bacterial catalysis. In this case, the aeration tank consisted of a 5 liter New Brunswick fermenter, modified to allow continuous pH control, sludge recirculation, and allowing sterilization of all components by autoclave prior to beginning of an experimental run. Details of the aeration tank assembly are shown in Figure 26.

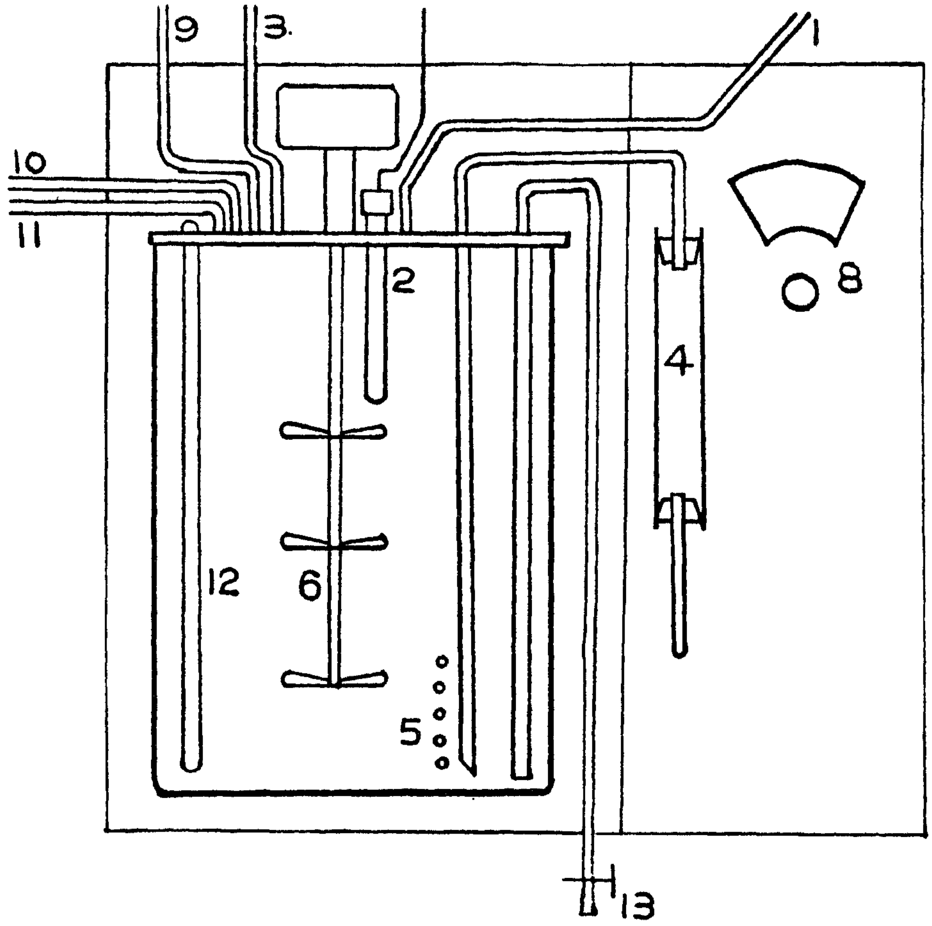
Procedure

The SAMD used in this phase of the research was modified by addition of sufficient ferrous sulfate to result in a total ferrous iron concentration of 1000 mg/l. When growth of iron oxidizing bacteria was to be encouraged, 2.58 mg/l of ammonium nitrate were also added to provide a nonlimiting source of nitrogen. Runs were made at nominal pH levels of 2.5, 4.0, and 5.5. In the case of the pH 2.5 runs, the pH of the feed was adjusted to 2.3, which resulted in a pH in the aeration tank of very close to 2.5, the increase being due to hydrogen ions consumed in the oxidation of ferrous to ferric iron. In the case of runs at pH 4.0 and 5.5, precipitation of ferric iron in the form of ferric hydroxides resulted in the release of hydrogen ions, and there was no way to compensate for this release other than to provide continuous pH adjustment through use of an automatic titrator. In these



1. nitrogen inlet
2. nitrogen tank
3. SAMD reservoir
4. SAMD flow
5. peristaltic SAMD pump
6. SAMD sampling valve
7. nitrogen outlet
8. glass wool filter
9. mercuric chloride solution
10. fermentor
11. automatic titrator
12. air outlet
13. mixed liquor outlet
14. settling tank
15. sludge return flow
16. peristaltic sludge return pump
17. mixed liquor sampling valve
18. effluent
19. effluent sampling valve
20. effluent reservoir
21. effluent discharge valve

Figure 25
Schematic Diagram of Continuous Flow Activated Sludge Type Unit under Aseptic Conditions



1. SAMD in
2. automatic titrator electrode
3. titrator delivery tip
4. air filter
5. air inlet
6. stirrer
7. stirrer speed control
8. air outlet
9. mixed liquor flow outlet to settling tank
10. sludge return inlet
11. thermometer
12. mixed liquor sampling valve

Figure 26

Schematic Diagram of Fermentor

runs, no pH adjustment of the feed was used, other than the addition of sufficient sulfuric acid in making up the feed to provide a pH of 2.1 , preventing the rapid chemical oxidation of iron in the feed carboys. Further insurance against the oxidation of iron in the feed carboys was provided by purging the feed with nitrogen to sweep out dissolved oxygen, and maintaining a partial pressure of nitrogen in the feed carboys of 2-3 psig.

When runs were made at pH 4.0 and 5.5 under sterile conditions, the SAMD was autoclaved at 121°C for one hour without the ferrous salts, which were added later. The 20% KOH used in the automatic titrator burette was also unsterilized, as was the nitrogen cylinder gas used in the feed carboys to maintain pressure. These sources were felt to be free of contamination by iron oxidizing autotrophs, a contention which was checked by bacterial counts run on the units at the beginning and end of the experimental runs. No evidence of bacterial contamination resulting in detectable growth was found.

Initially, it was hoped that direct bacterial counts using a counting chamber and a phase contrast microscope would be useful in estimating the extent of bacterial growth, and thus, of bacterial oxidative activity. Except in the case of runs at pH 2.5, where there was very little ferric iron precipitation direct counts were too inaccurate to be of quantitative value. Processes utilizing the dissolution of iron floc with HCI were tried, and while better counts could be made under these conditions, variability was still quite high, and direct counts were abandoned as a means of estimating bacterial oxidation rates. While the qualitative presence of bacteria in numbers probably sufficient to result in significant bacterial catalysis was easily detectible by direct counting under any pH conditions, no quantitative application of counting data was made.

It was also initially hoped that runs under sterile conditions would not be necessary, based on the contention that elimination of nitrigen from the SAND feed would result in sufficient limiting of bacterial growth to allow us to discount bacterial effects in regard to any oxidation rate catalysis observed. While nitrogen elimination from the feed did decrease bacterial populations in the aeration units, the extent of this decrease was marginal, and the decision was made to insure sterility of the system through autoclaving of both the apprartus and the feed.

To provide a common basis for the comparison of oxidation rates from one set of experimental conditions to another, including pH, aeration tanks, oxidation rate constants were calculated for each experimental run. This calculation was based on the known ferrous iron concentration in the influent, the measured average ferrous iron concentration in the effluent calculated over a period of operation during which oxidation rates were relatively stable, and the assumption that the reaction is first order in respect to ferrous iron concentration. Since the continuous flow units could be operated at fairly constant flow rates through the use of peristaltic feed pumps, the aeration rates were sufficiently high to insure nearly saturated dissolved oxygen and a complete mix hydraulic condition in the tank, then the following relationships were used to define the reaction rate constants used in presenting the results to follow:

$-\frac{dc}{dt} = KC$; and at steady state,

$QCo - KCV = QC$, where:

Q = feed flow rate, vol/time
Co = initial ferrous iron concentration in feed
C = ferrous iron concentration in aeration tank
V = volume of aeration tank
K = reaction rate constant, time^{-1}

While the reaction rates may not have been strictly first order with respect to ferrous iron, such a procedure allowed at least an approximate correction of experimental results for detention time and ferrous iron variations, and considering the range of rate constants presented below, the general conclusions made can be considered valid. It should be noted that all runs were made at room temperature, which was subject to daily variation, but was nominally about 25°C.

Results

Table IX shows the results of five experimental runs, spanning the nominal pH range from 2.5 to 5.5, and incorporating both sludge recirculation and bacterial catalysis at pH 4.0.

TABLE IX

Iron Oxidation Rate Constants at Various pH Values

Run No.	pH	$K(hr^{-1})$	Sludge Recirculator	Bacterial Catalysis
1	2.58	0.877	without	with
2	4.02	0.0453	with	with
3	4.17	0.0212	with	without
4	4.05	0.0208	without	without
5	5.5	6.50	without	without

Discussion of the individual runs are given below:

Run 1 was made in the Type 1 unit, and represents relatively ideal conditions for growth of the Ferrobacillus group of bacteria. Over the 31 day period for which operating conditions were averaged, the detention time of the aeration tank was 8.6 hours, the aeration tank pH was 2.58, and the per cent oxidation of ferrous iron through the tank was 88.3%. This resulted in calculation of a rate constant of 0.877 hr^{-1}. During the period of operation over which this run was made, the bacterial concentration in the unit averaged 1.13×10^7 cells/ml, which represents a normal bacterial concentration for continuous flow units under these conditions of operation. The cells were fully dispersed, and tended to show a high degree of motility. While ferric iron did not form a flocculent precipitate at this pH, colloidal ferric iron was present, and iron precipitated out slowly on the walls of the flask. If this precipitate layer was allowed to accumulate, and was then removed by acid cleaning, the relative oxidation rate of the unit could be made to drop by as much as 50%. Whether the catalytic effect of the precipitate on the flask wall was of a biological nature due to possibly higher concentrations of bacteria in and around the precipitate, cannot be answered from the data available. The authors tend to feel that this phenomenon is more biological than chemical.

Run 2 was made in the Type 2 unit, and due to the volume of iron precipitated, an attempt was made to recycle the sludge. Sludge concentrations in the aeration tank tended to increase continuously during the run, reaching an equilibrium value of 20 grams per liter by the end of this 28 day run, but the increasing sludge solids had little effect on the per cent iron oxidation through the aeration tank, which was fairly stable, and averaged 53.03 per cent. The pH averaged 4.02, and with an average detention time of 24.28 hours, the rate constant is calculated to be 0.045 hr^{-1}, a considerable drop from the rate constant seen in the case of Run 1. Direct bacterial counts indicated the presence of numerous bacterial cells, but the presence of the sludge solids prevented an accurate count, and the contribution of these cells to the observed oxidation rates cannot be estimated on the basis of these data alone.

Following a wasting of suspended solids back to a level of 14 g/l, the operation of the unit was continued until the solids reached an equilibrium value of 24 g/l. During this period, the daily percent iron oxidation values were observed to be quite sensitive to pH, with a pH increase of 0.1 unit giving a percent oxidation increase of nearly 10 per cent. This pH sensitivity is indicative of a significant degree of chemical catalysis, an observation which is reinforced by the detection by x-ray diffraction analysis of geothite and lepiodocrocite in the suspended solids.

In an attempt to resolve the question of the relative importance of bacterial and chemical catalysis of the relative importance of bacterial and chemical catalysis of iron oxidation at pH 4.0, the decision was made to run a series of experiments under completely sterile conditions, constituting Runs 3, 4, and 5 described below.

Run 3 was made in the Type III unit, utilizing a sealed 5 liter New Brunswick fermentor operated under sterile conditions, and with continuous flow of feed throuth the unit. The unit was operated for 23 days at a nominal pH of 4.0 and a nominal detention time of 24 hours. Sludge was recirculated during this run, resulting in a suspended solids increase continuously in the unit from an initial value of 6.2 g/l to a terminal value of 12.3 g/l at the end of the run. The solids initially present were the result of a prior run without sludge recirculation.

During Run 3, the pH averaged 4.17, and the average detention time was 23.07 hours. With an average per cent iron oxidation of 32.78, the iron oxidation rate constant was calculated to be 0.0212 hr^{-1}, or approximately one half of that calculated for Run 2. As in the case of Run 2, the daily per cent iron oxidation was sensitive to pH, with a 0.1 increase in pH value resulting in an increase in per cent iron oxidation by approximately 6 per cent. X-ray diffraction analysis of the suspended solids showed well developed geothite and lepidocrocite formation.

Run 4 was run under conditions similar to Run 3, with the exception that no sludge recirculation was used. Thus, during the 11 day operation of this run, suspended solids tended to quickly reach a solids equilibrium, due to the continuous loss of solids in the unit effluent, which balanced the precipitation of new solids in the unit. The initial solids concentration at the beginning of the run was approximately 6.0 g/l, and the solids remained essentially constant, with an average value for the run of 6.2 g/l.

The average pH during the run was 4.05, and the detention time of the unit averaged 25.03 hours. With an average per cent iron oxidation of 33.75, the iron oxidation rate constant was calculated to be 0.0208 hr^{-1}, or about the same as in Run 3. The suspended solids generated during Run 4 showed the presence of goethite and lepidocrocite, but less well defined than in the case of Run 3, which featured sludge recirculation.

Run 5 was run in the Tupe III unit, as were Runs 4 and 3, but at a pH of 5.5. Due to the rapid iron oxidation rate at this pH, it was necessary to decrease the detention time of the unit in order to avoid complete oxidation. After an 8 day period of operation at a detention time of 24 hours, during which the suspended solids reached an equilibrium value of 7 g/l, and during which the iron oxidation was complete, the detention time was decreased to 6 hours, and the per cent iron oxidation allowed to reach a new equilibrium value. This took only 24 hours, with the new equilibrium per cent iron oxidation being 97.5. Calculation of the corresponding iron oxidation rate constant yielded a value of 6.50 hr^{-1}, which is markedly greater than in the case of Runs 1 thorugh 4.

Discussion

Difficulties in the precise control of temperature and of suspended solids levels in Runs 1 through 5 described above make it difficult to state any conclusions as to the effects of these variables on iron oxidation rates. However, the relative values of the iron oxidation rate constants listed in Table IX provide supporting evidence for some fairly certain conclusions regarding the relative importance of bacterial and chemical catalysis of iron oxidation as a function of pH. Figure 27 shows a plot of oxidation rate constant as a function of pH. The two curves shown are largely a matter of conjecture, due to the lack of additional data points, but are believed by the authors to be compatible with present knowledge of the behavior of the bacterial and chemical systems involved. The rate constant for Run 2, which included both chemical and bacterial catalysis, is 0.043 hr^{-1}, or approximately twice the rate constants for Runs 3 and 4 (0.0212 and 0.0208 respectively), indicating that bacterial and chemical effects are roughly equivalent at pH 4. Further, the cheimcal rate constant curve has a slope of approximately 2, which is in agreement with the Stumm-Lee rate law for iron oxidation (13), and there is little doubt that the catalysis at pH 2.5 is entirely bacterial, with no appreciable chemical component. Thus, it is strongly suggested that iron oxidation processes should be carried out below pH 3, where bacterial catalysis controls the reaction rate, or above pH 5.0, where chemical catalysis is the controlling factor. The region around pH 4 should be avoided, due to the inordinately long reaction times which would be required for reasonably complete conversion of ferrous to ferric iron. The process results desired, as dictated by considerations other than iron oxidation alone, will dictate whether bacterial or chemical catalysis is the most desirable choice.

In regard to the effect of iron precipitate surfaces on the chemical

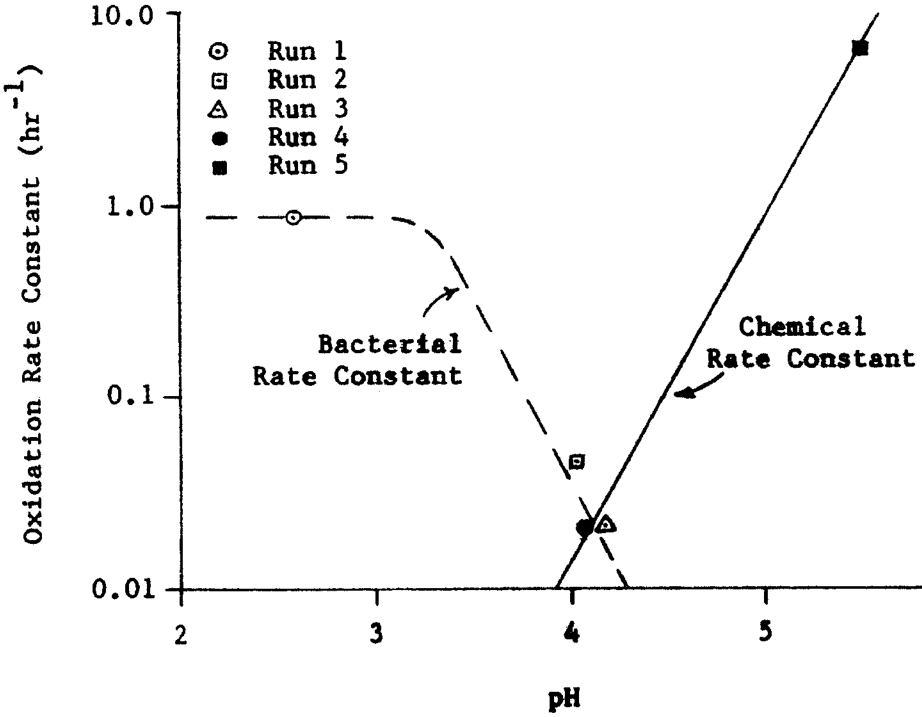


Figure 27

Oxidation Rate Constant vs. Time

catalysis of iron oxidation, it is informative to compare the Run 3 and Run 4 rate constants with those obtained by Singer and Stumm (13), as shown in Table X.

TABLE X

Iron Oxidation Rate Constants

	From Ref. 13	From Ref. 13	Run 4	Run 3
pH	4.0	4.0	4.05	4.17
K (day^{-1})	5.03×10^{-4}	1.58×10^{-2}	4.99×10^{-1}	5.088×10^{-1}
Remarks	uncatalized Ferrous Iron oxidation	Al_2O_3 catalytic surface	without sludge recirculation; suspended solids concentration 6.2 g/l	with sludge recirculation; suspended solids varied from 6.2 to 12.3 g/l

The greater catalytic effect, under sterile conditions, of the suspended solids present in Runs 3 and 4 is readily apparent, and is believed to be due to the presence of goethite and lepidocrocite in the iron precipitates.

The experiments described above on the chemical oxidation of ferrous iron with air in a SAMD treatment process using lime neutralization and sludge recycling was of an exploratory nature. Much more work would be required to determine the various factors affecting the oxidation rate. Considering the importance of oxidation rate of oxidation rate of ferrous iron in an AMD treatment process, the extension of work on the oxidation of ferrous iron in the presence of recycled sludge appears justified.

Conclusions

The following major conclusions appear to be supported by the results obtained during the course of this study:

The percent sludge volume formed by treatment of pure ferrous sulfate-sulfuric acid solutions or of a synthetic acid mine drainage (SAMD), employing lime neutralization and oxidation of ferrous iron, generally depends on the concentration of ferrous iron and aluminum in the solution treated provided that the final concentration of calcium sulfate resulting from the treatment does not exceed the solubility limit. Specific observations drawn from our experiments are summarized below:

I. Treatment of pure $FeSO_4$ - H_2SO_4 solutions with lime:
  a) Oxidation with H_2O_2:
    1) The sludge volume formed decreases with decreasing pH.
    2) The final pH should be above 3 to obtain satisfactory iron removal.
    3) The sludge volume decreases on aging and is associated with the formation of goethite (α-FeOOH) as detected by x-ray diffraction analysis.
    4) The color change with time from the red brown color of the initially formed sludge to the light yellow of the older sludge indicates the formation of goethite.
  b) Oxidation with air:
    1) The sludge volume formed decreases with decreasing pH.
    2) The sludge volume decreases on aging due to the formation of goethite.
    3) Exposure of the sludge to high pH during the neutralization step enhances the formation of geothite, which is associated with sludge volume decrease.
  c) Oxidation with air and sludge 'recycling':
    1) Smaller sludge volumes are obtained at lower pH.
    2) The sludge solids content increases with the increasing sludge recycle number; sludges with 30 percent or more solids content are

obtained by sludge recycling under proper conditions.

3) The formation of dense sludge is associated with the formation of geothite (α-FeOOH) or lepidocrocite (γ-FeOOH).

4) The formation of crystaline ferric hydroxy compounds is enhanced by a slow rate of oxidation of ferrous iron, which in turn is determined by the pH of the solution, degree of temporary exposure of the sludge to high pH, and by the quantity and, to a larger extent, the physical and chemical properties of the recycled sludge solids.

5) A balance between ferrous iron concentration and oxidation rate and the optimum concentration of seed particles supplied by the recycled sludge in a definite seed particle size range, has to be maintained to minimize the precipitation of amorphous ferric hydroxide and consequently, to ehhance the formation of dense sludge.

6) An undesired phenomenon, the formation of very fine particles which settle slowly, is associated with the sludge recycling process at lower pH.

II. Treatment of pure $Al_2(SO_4)_3$-H_3SO_4 solutions with Lime:

1) Dense aluminum sludges are formed in the pH range from 5 to 6.

2) Aluminum removal from solutions is incomplete below pH 4.5.

3) The formation of dense aluminum sludge is associated with the formation of gibbsite (γ-$Al(OH)_3$), favored by introduction of seed crystals by sludge recirculation in the proper pH range; sludges of up to 15 percent solids content are obtained.

4) The formation of dense aluminum sludge is very sensitive to pH in the near-neutral range, and to chemical and physical conditions prevailing during the neutralization process. The presence of aluminum in an AMD, particularly at high mole ratios of aluminum

to iron, may cause the formation of voluminous mixed component sludges when the treatment deviates from the optimal conditions.

III. Treatment of SAMD with Lime:

a) Oxidation with H_2O_2 before lime treatment, simulating treatment of an all-ferric SAMD:

   1) Good iron and aluminum removal is achieved at pH 5.5 and higher.

   2) The sludge volume is not strongly dependent on pH, and is voluminous and with low solids content (0.6 to 0.7%). The sludge solids have the typical appearance of amorphous gel-like ferric hydroxide.

b) Oxidation with H_2O_2 before lime treatment but with sludge recycling:

   1) Smaller sludge volumes are formed at pH 4.5 than at pH 5.5 (11 percent and 17 percent respectively, with solids content of 23 percent and 14 percent after 60 recycles).

   2) Iron and aluminum removal at pH 5.5 may be considered as nearly complete.

   3) With an increasing number of recycles the color of the sludge changes from red brown to yellow indicating the formation of goethite, but x-ray analysis did not show the presence of crystaline ferric hydroxy compounds.

   4) The sludge solids show the presence of freshly precipitated ferric hydroxide flocs.

   5) The turbidity of the supernatant solution increases with increasing sludge recycle number, and the small particles settle slowly.

   6) The presence of aluminum shows a retarding effect on the formation of goethite.

c) Oxidation with H_2O_2 after lime neutralization; this process is similar to treatment of an all ferrous AMD with lime, but with very rapid oxidation of ferrous iron:

1) The sludge volume is smaller at pH 4.5 than at pH 5.5 (30 percent and 50 percent respectively, and with solids contents of 4 percent and 2.5 percent after 30 recycles) and shows a density increase with the number of sludge recycles.

2. The sludge solids consist mostly of amorphous ferric hydroxide, probably due to the rapid oxidation rate of ferrous iron by hydrogen peroxide.

d) Oxidation with air and sludge recycling:

1) The optimum pH appears to be close to 5.5 for obtaining dense sludge and achieving high iron and aluminum removal from SAMD when treating with lime.

2) The formation of dense sludge by sludge recycling is associated with the formation of ferric hydroxy compounds; goethite (α-FeOOH) and lepidocrocite (γ-FeOOH).

3) The formation of crystaline ferric hydroxy compounds is favored by low pH, by low oxidation rate of ferrous iron (which is dependent) and by the quantity and physical and chemical properties of the recycled sludge solids. To minimize the formation of voluminous amorphous ferric hydroxide a balance between ferrous iron concentration and oxidation rate and an optimum concentration of seed particles in a definite particle size range in the recycled sludge should be maintained.

4) A temporary exposure of the sludge to high pH favors the formation of denser sludge.

5) The treatment of SAMD at pH higher than 6 favors the formation of lepidocrocite. In general, treatment under conditions that favor

the formation of green rust II, followed by slow air oxidation, leads to the formation of lepidocrocite, but the sludge is voluminous and the accumulated volume increases rapidly with recycle number.

IV. Chemical and biological oxidation rate of ferrous iron.

1) The chemical oxidation rate of ferrous iron with air in pure ferrous sulfate-sulfuric acid solution and in the presence of recycled sludge, increases with the amount of recycled sludge solids and the recycle number (pH 5.5). A four to six fold oxidation rate increase was observed in the presence of 7 grams per liter of recycled sludge solids when compared with the oxidation rate without sludge recycle. The oxidation rate increase is probably associated with the catalytic properties of the recycled sludge solids, and not with biological catalysis.

2) The oxidation rate of ferrous iron with air in the SAMD also increases with the quantity and the number of recycles of the recycled sludge. A seven-fold oxidation rate increase was observed in the presence of the recycled sludge (pH 5.5). The oxidation rate increased nearly linearly with the recycled sludge quantity, indicating a catalytic effect of the recycled sludge. A possible retardation effect of aluminum present with sludge is observed as compared to oxidation rates in the presence of sludge formed from pure ferrous iron solutions.

3) Bacterial catalysis of iron oxidation does not appear to be practical at pH values above 3, due to the decrease in catalytic activity as pH 4 is approached. Iron oxidation rates above pH 4 appear to be due almost entirely to chemical, rather than biological phenomena.

4) More work is required to determine the mechanism of ferrous iron oxidation rate catalysis in the presence of recycled sludge.

Recommendations

1. The effect of temperature on dense sludge formation should be investigated, as all work described above was done at room temperature (26 to 28°C).
2. The effect of the concentration of ferrous iron and aluminum, and particularly the effect of the mole ratio of aluminum to iron on the formation of dense sludge, should be more thoroughly investigated.
3. The effect of precipitation of gypsum on the dense sludge formation in the range where the solubility of gypsum is exceeded, should be investigated.
4. The effect of sludge recirculation on the oxidation rate of ferrous iron must be more thoroughly investigated because the oxidation rate of ferrous iron in an AMD treatment process may determine the economic feasibility of the treatment process.
5. The feasibility of the process in an actual AMD treatment plant should be demonstrated.

SECTION IV

FORMATION OF DENSE SETTLED SLUDGE BY NEUTRALIZATION OF SYNTHETIC ACID MINE DRAINAGE WITH CALCIUM CARBONATE AND SLUDGE "RECIRCULATION".

The following exploratory work done on the formation of dense settled sludge by neutralization of SAMD with calcium carbonate and subsequent oxidation of the ferrous iron is not within the scope of the project as submitted to the sponsor. However, in view of the observations reported by Mihok (9), Glover (10) and Bitumenous Coal Research (7) on the formation of dense sludges by AMD treatment with limestone, and since the experiments required were readily adapted to our equipment and procedures, this was considered justifiable.

The experimental procedure using calcium carbonate for neutralization was similar to that used for neutralization with calcium hydroxide except that accurately weighed quantities of calcium carbonate were added directly in powder form. The calcium carbonate used in these experiments was reagent grade with a surface area of 0.57± 0.06 square meters per gram, a particle size of 3.9 ± 0.4 microns and a calcite crystaline structure. The oxidation of ferrous iron was done with both hydrogen peroxide and air. Oxidation with hydrogen peroxide before the addition of calcium carbonate is analogous to the treatment of an all ferric SAMD, while oxidation with hydrogen peroxide after calcium carbonate is analogous to the treatment of an all ferrous SAMD, as were the experiments employing oxidation of ferrous iron with air.

Figure 28 shows the sludge volumes obtained at different pH values by neutralization of a solution of 200 ppm ferric iron (oxidation prior to neutralization) and 1200 mg/l of total sulfate with calcium carbonate. These are compared with the sludge volumes obtained by neutralization with sodium hydroxide and calcium hydroxide under similar conditions.

Solution	200 ppm iron 1200 ppm sulfate
Oxidation	before pH adjustment
Settling Time	24 hours
Base	○ 1.0 N NaOH □ 1.0 N $Ca(OH)_2$-slurry △ $CaCO_3$

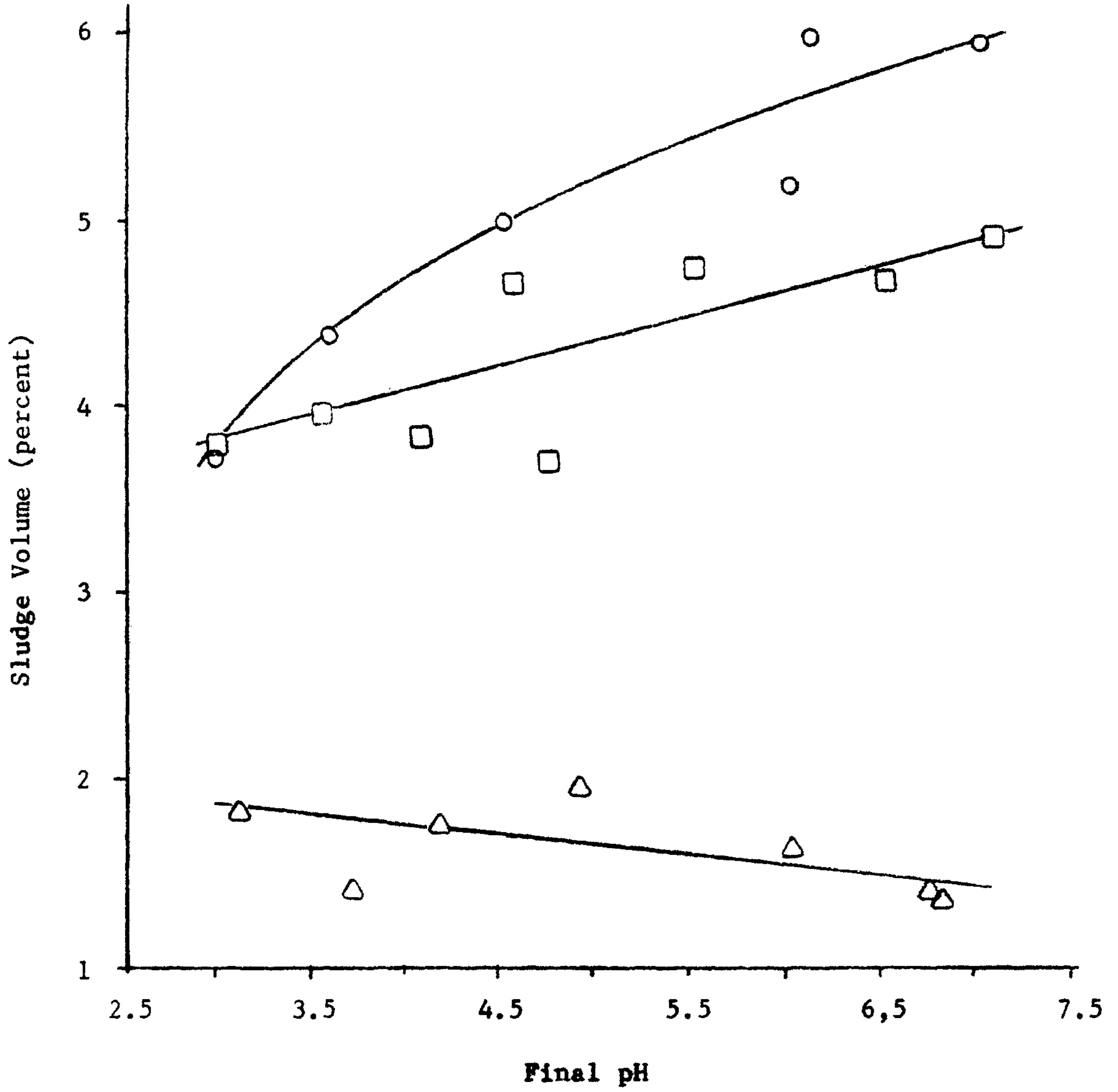


Figure 28

Final pH vs. Sludge Volume

Solution	200 ppm iron 1200 ppm sulfate
Oxidation	before pH adjustment
Base	$CaCO_3$
Settling Time	○ 24 hours △ 6 days

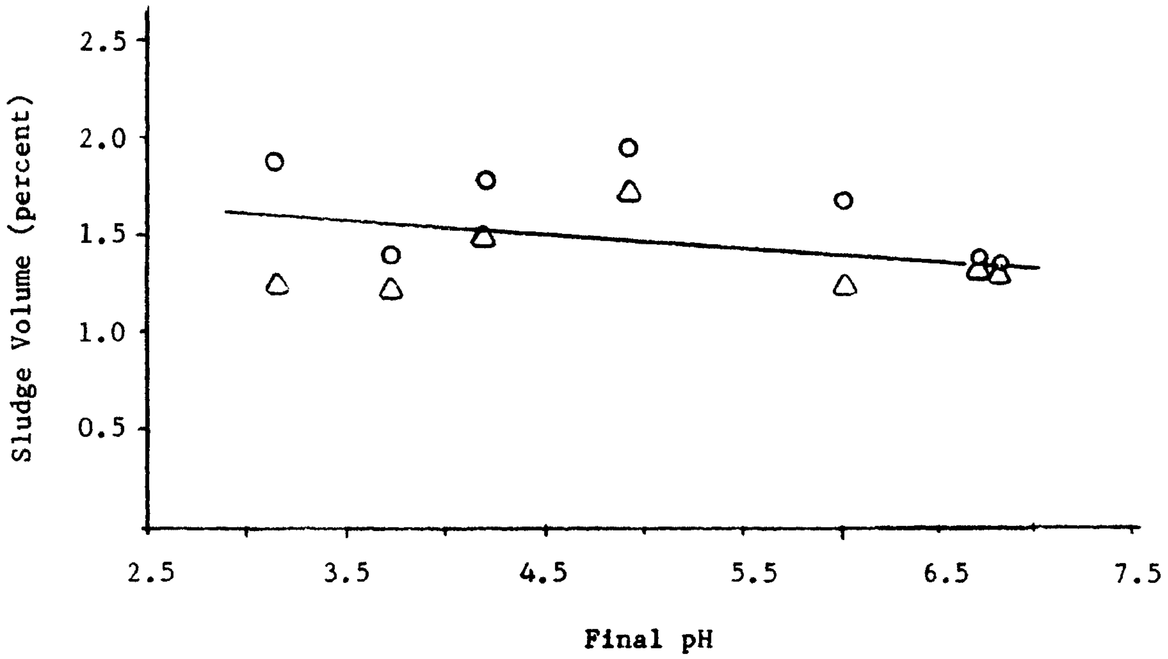


Figure 29

Final pH vs. Sludge Volume

The sludge volume difference is obvious, and the dependence of the sludge volume, from calcium carbonate neutralization on pH is relatively small. The aging effect on the sludge volume was also relatively small, as shown on Figure 29. The weight of calcium carbonate used indicated that nearly 100 percent of it reacted at a pH of 5 and below, but an excess was used at pH 6 and above to overcome the buffering properties of carbonates. Sludge formed by calcium carbonate treatment was pale yellow, fine grained, and settled slowly. The properties of the sludge solids indicated the presence of geothite. Verification of the presence of geothite was provided by x-ray diffraction analysis, which showed fairly well developed crystals. Schellmann (56) showed that geothite is formed in the presence of carbonate or on the hydrolysis of ferric carbonate or bicarbonate. Our findings are thus in agreement with Schellmann's research. The neutralization of ferric iron solutions with calcium carbonate proceeds at a relatively slow rate when compared with the neutralization with sodium hydroxide or calcium hydroxide, because the calcium carbonate-acid interaction is a heterogeneous two phase (solid-liquid) reaction, therefore providing more time for the formation and growth of geothite crystals, probably with an intermediate formation of ferric carbonate or bicarbonate. The fine particles of calcium carbonate may also serve as crystalization centers.

The total concentration of iron in the supernatant after 24 hours settling was less than 1 mg/l at pH values above 5; below pH 5 the residual concentration if iron was as high as 7 mg/l.

The solids content of the sludge was dependent on the final pH of the solution. Below pH 5, the sludge solids were 0.342 grams per liter of solution treated, and above pH 5 the weight of excess calcium carbonate contributed to the measured solids content.

The results of SAMD treatment with calcium carbonate were similar to the results of calcium carbonate neutralization of ferric sulfate-sulfuric acid solution. The sludge volumes were nearly the same, as can be seen by comparing Figure 30 with Figure 29. The effect of aluminum on sludge volume is demonstrated when the slopes of the curves shown on Figure 30 and Figure 29 are compared: The slight sludge volume increase with pH as shown in Figure 30 is associated with the presence of aluminim in the sludge solids. Figure 30 also shows the minor effect of aging on the sludge volume. Figure 31 compares the sludge volumes obtained by calcium hydroxide treatment with those obtained by calcium carbonate treatment. It is seen that the sludge volume resulting from calcium carbonate neutralization is only about one fourth of the volume resulting from calcium hydroxide neutralization; these results agree with the findings of Calhoun (8). The tests employing a single precipitation by calcium carbonate, after oxidation of the SAMD and twenty-four hour settling time, gave the following results: at pH 4.2 the sludge volume was 1.24 percent, with a solids content of 3.2 percent, while at pH 6.6, the sludge volume was 1.4 percent, with a solids content of 3.0 percent. Similar treatment of SAMD with calcium hydroxide gave a sludge volume at pH 4.0 of 4.9 percent with a solids content of 0.72 percent, and a pH 7.3, a sludge volume of 6.3 percent with a solids content of 0.58 percent. The advantage of using calcium carbonate for obtaining dense sludge is obvious.

To observe the effect of sludge recirculation on the sludge volume, while using calcium carbonate for neutralization of SAMD, four series of experiments were conducted:

Run 1: The SAMD was oxidized with hydrogen peroxide before the recycled sludge was added, and the calcium carbonate was added to the recycled sludge before the slurry was added to the new SAMD. The weight of the calcium carbonate added before each experiment was kept constant at 0.900 grams for

Solution	SAMD
Oxidation	**before pH adjustment**
Base	$CaCO_3$
Settling Time	○ 1 day △ **6 days**

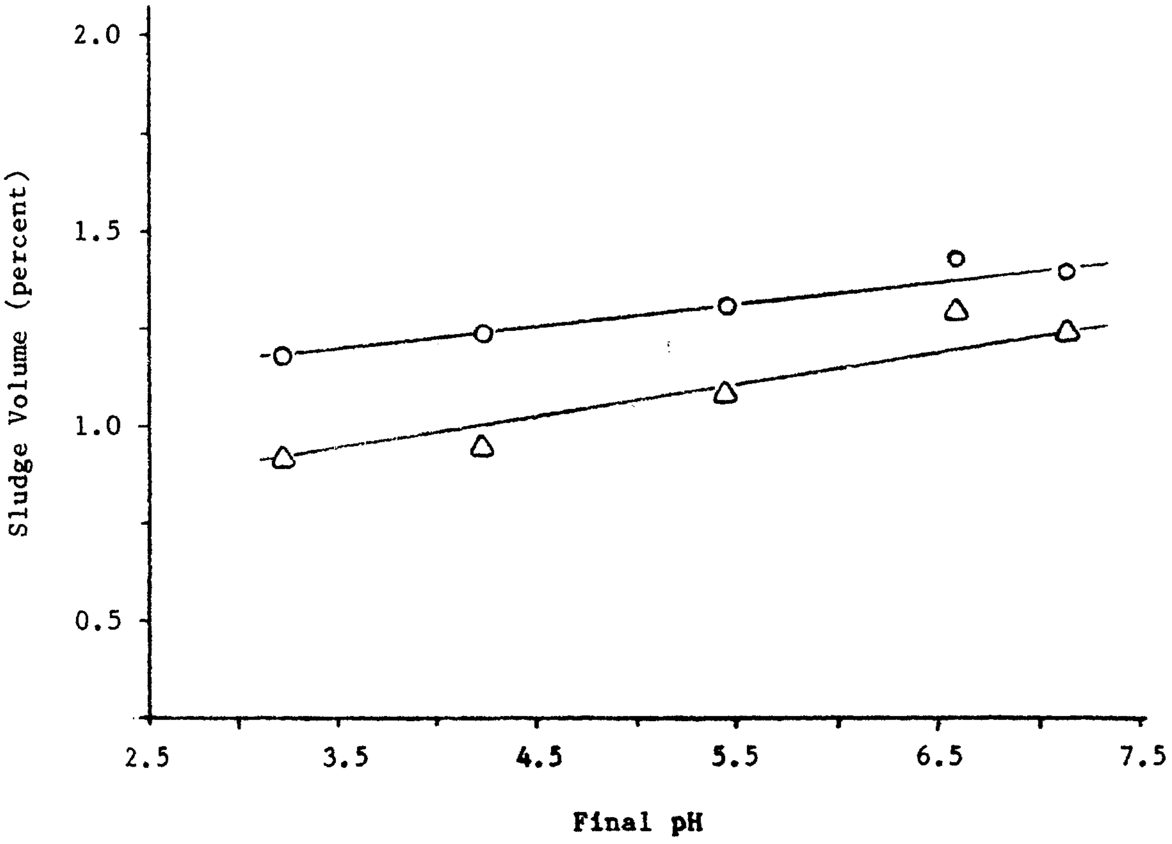


Figure 30

Final pH vs. Sludge Volume

Solution	SAMD
Oxidation	before pH adjustment
Settling Time	24 hours
Base	○ 1.0 N $Ca(OH)_2$-slurry △ $CaCO_3$

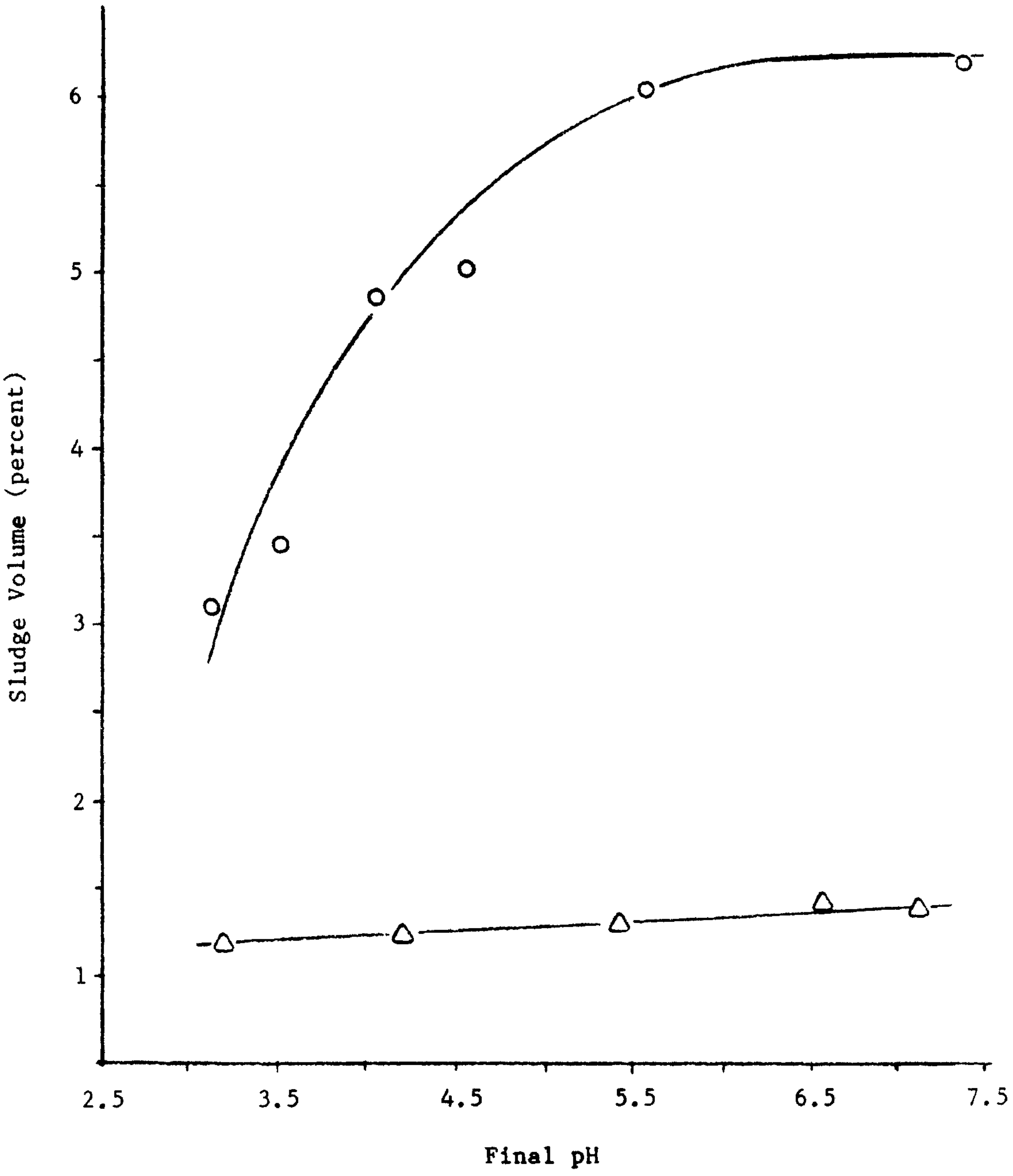


Figure 31

Final pH vs. Sludge Volume

each 800 ml of new SAMD, and the weight of calcium carbonate used was in excess of stichiometric requirements. Agitation was continued until a final pH between 6.3 and 6.6 was reached. The time between recycles was twenty-four hours, for a total of thirty recycles.

Run 2: This run was similar to Run 1, except that the oxidation with hydrogen peroxide was carried out after the recycled sludge and calcium carbonate slurry had been added to the new SAMD. The final pH in this run was also between 6.3 and 6.6. A total of fifteen recycles were conducted.

Run 3: This run was similar to Run 1, except the weight of calcium carbonate was 0.650 grams for each 800 ml of new SAMD. This was less than the stiochiometric requirements for complete neutralization. The final pH for this run was between 3.9 and 4.1, with a total of fifteen recycles.

Run 4: The recycled sludge was mixed with calcium carbonate, added to the new SAMD, and oxidized with dispersed air. The amount of calcium carbonate added for each experiment was such that the final pH of the system was between 4.8 and 5.4 and a total of seven recycles was run.

Figure 32 shows the sludge volume versus recycle number for Run 1 and Run 2. In Run 2, it is observed that after fifteen recycles the sludge volume was still less than 10 percent, and that the sludge volume for Run 1 was still less than 10 percent after 30 recycles. The more voluminous sludge of Run 2 as compared to Run 1 was due to the difference in mode of iron oxidation. It should be pointed out that the oxidation of ferrous iron with hydrogen peroxide, after addition of the recycled sludge-calcium carbonate slurry, was extremely fast as compared to air oxidation. The solids content of the sludges of Run 1 and Run 2 also show an increase with increasing recycles number, as shown in Figures 33 and 34.

Microscopic observation of the sludge solids of Run 1 and Run 2

Recycle Run No. 1 and 2

Base	**0.900 gm. $CaCO_3$ per recycle**
Final pH	**6.0**
Oxidation	**Run 1** ○ **before treatment with $CaCO_3$** **Run 2** △ **after treatment with $CaCO_3$**

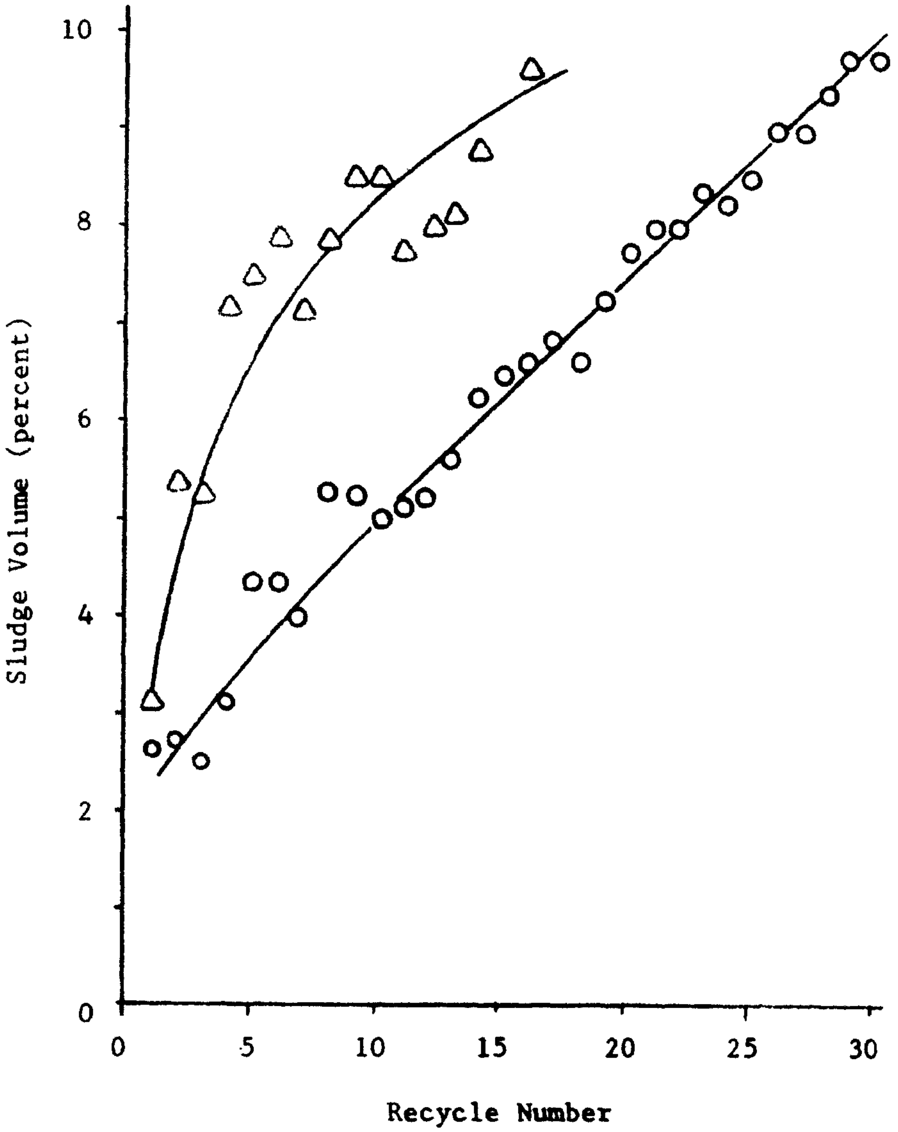


Figure 32

Number of Recycles vs. Sludge Volume

Recycle Run No. 1

Oxidation	**before pH adjustment**
Base	0.900 gm $CaCO_3$ per recycle
Final pH	~6.0
Sludge Volume	○
Sludge Solids	△

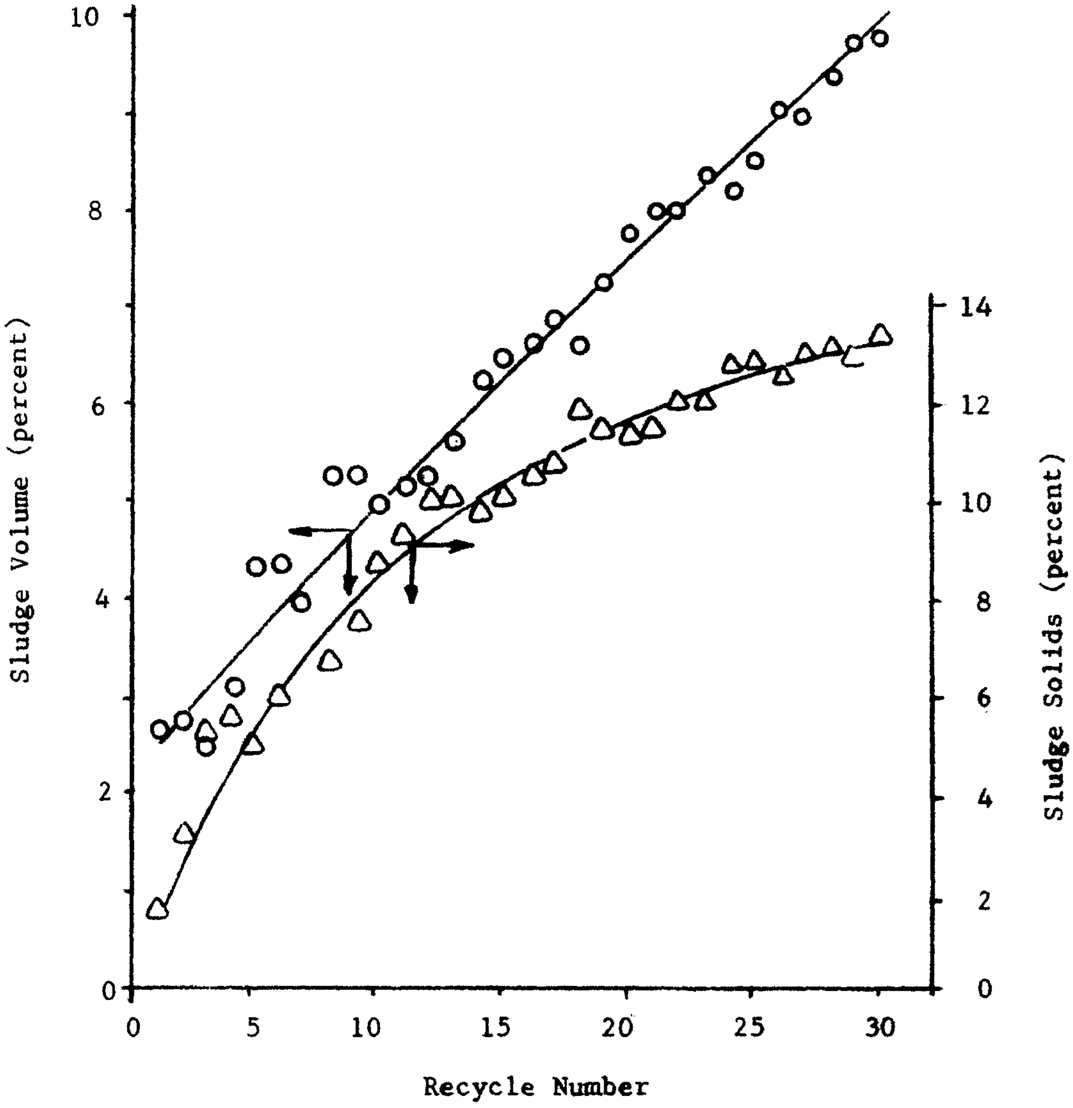


Figure 33

Number of Recycles vs. Sludge Volume and Solids

Recycle Run No. 2

Oxidation	after pH adjustment
Base	0.900 gm $CaCO_3$ per recycle
Final pH	~6.0
Sludge volume	○
Sludge Solids	△

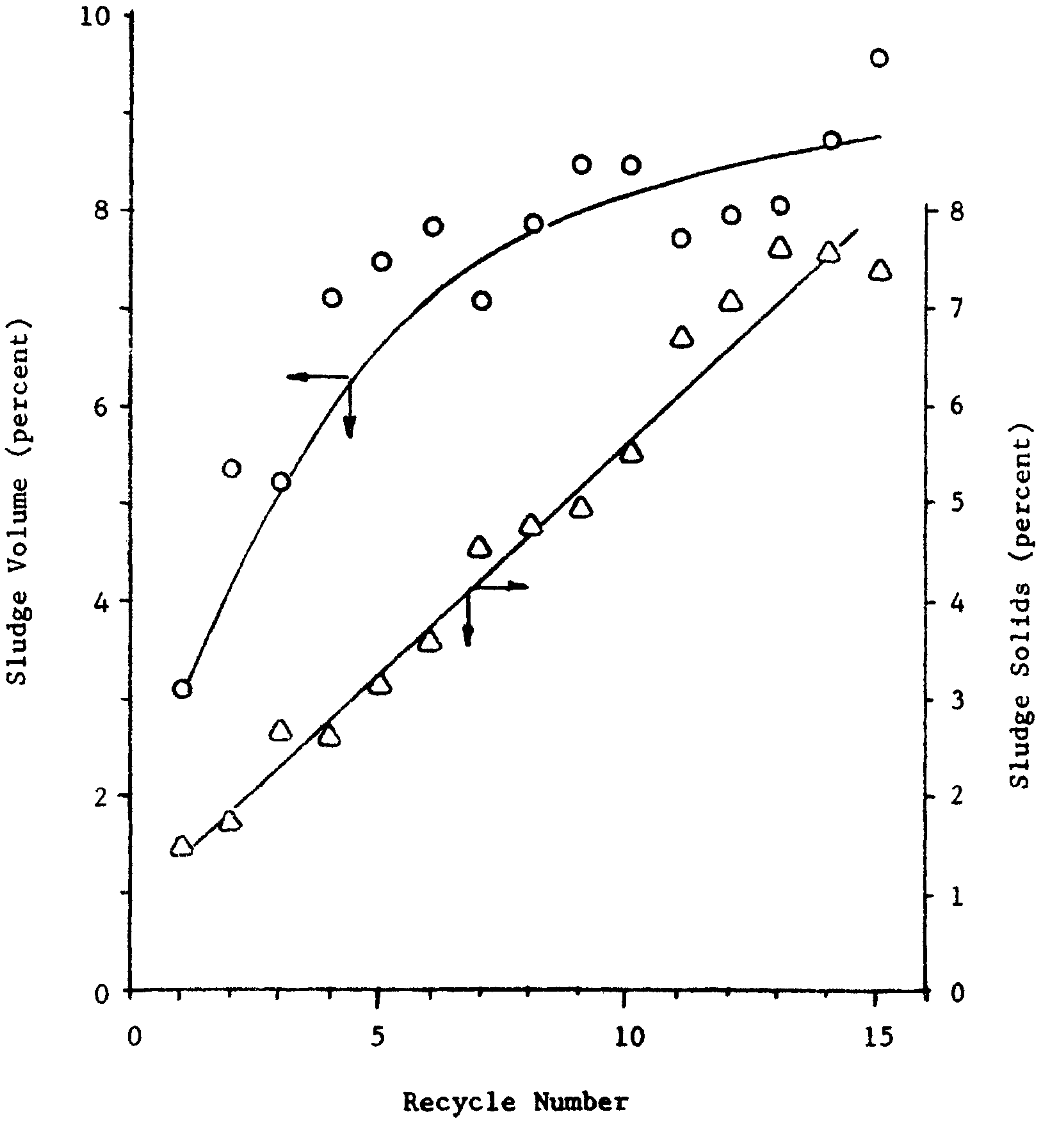


Figure 34

Number of Recycles vs. Sludge Volume and Solids

revealed the presence of many dense dark brown flocs that contained small ordered darker dots. However, there was a very small number of tiny blue flocs. The blue flocs indicated the presence of newly formed particles. The color of the sludges was a dirty yellow, and the small grained particles settled slowly. The observable physical properties of the sludge solids indicated the presence of geothite in very tiny and poorly developed crystals, but these were not detected by x-ray diffraction analysis.

The supernatant solution of both Run 1 and 2, after 24 hours settling time, contained less than 3 mg/l total iron. After filtering on Whatman 42 filter paper, the iron contents were less than 0.1 mg/l. Aluminum remaining in the unfiltered supernatant was less than 0.5 mg/l.

The sludge volumes of Run 3, which did not have an excess of calcium carbonate, and Run 1, with excess calcium carbonate, are compared in Figure 35. The sludge volume of Run 3 remained nearly constant. The solids content increased nearly linearly, ranging from 1.72 percent after one recycle to 23.1 percent after 15 recycles.

The sludge of Run 3, when observed under the microscope, showed small brown particles filled with ordered dark brown dots. The color of the sludge was a pale yellow, and the small grained particles settled slowly. While observed physical properties indicated the presence of geothite, the sludge was x-ray amorphous.

Although the iron removal after the first few recycles was good, leaving less than 2 mg/l in the supernatant, the supernatant iron after 15 recycles was over 10 mg/l. This high iron content was related to the large amount of fine slow settling particles in the supernatant that were slow to settle. Aluminum remaining in the supernatant of Run 3 was at a level of 9 mg/l, and the low aluminum removal of only 40 percent may contribute to the

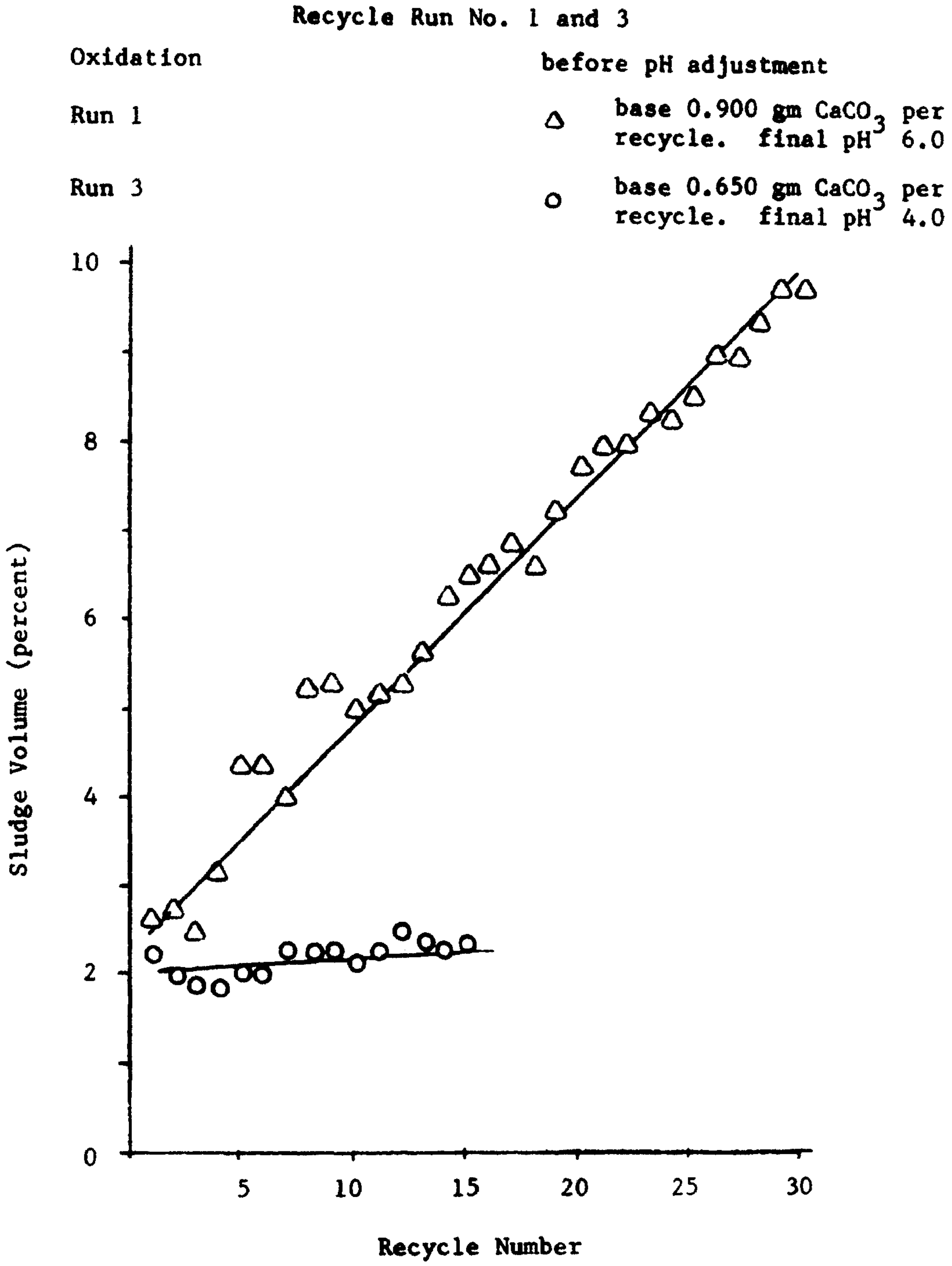


Figure 35

Number of Recycles vs. Sludge Volume

dense sludge formation. Sludge analyses for Runs 1, 2, and 3 are shown in Table XI. Figure 36 shows the sludge volume and solids content versus recycle number for Run 4. The physical properties of the Run 4 sludge solids were very similar to those of Run 3, but x-ray diffraction analysis showed the presence of both geothite and lepidocrocite. The presence of recirculated sludge solids, the presence of carbonate, the slower neutralization rate, and the slower oxidation rate of ferrous iron with air all favor the formation of crystalline ferric hydroxy compounds and consequently the formation of dense sludges, as shown by the results of Run 4. The sludge volume after six recycles was 0.7 percent with a solids content of 22.4 percent. It appears that calcium carbonate treatment of SAMD with sludge recirculation under carefully controlled conditions may yield the most dense sludges, as compared to the other AMD treatment alternatives discussed in this report.

Limited exploratory work was done also on the effect of recirculated sludge, formed by calcium carbonate SAMD neutralization, on the ferrous iron oxidation rate by air. The results indicated that carbon dioxide formed during neutralization may retard the capacity of the recirculated sludge to enhance the oxidation rate of ferrous iron with air. There are probably many ways to overcome carbon dioxide interference but a two step neutralization procedure using limestone and lime appears to be a practical approach to the problem, considering economical factors. A two step neutralization process for treatment of a ferrous AMD is visualized as follows: a slurry of pulverized limestone and recycled sludge is added to the AMD and the ferrous iron oxidized with air, at controlled pH, to a definite residual concentration of ferrous iron. The suspension is then treated with lime and residual ferrous iron oxidized with air at controlled pH. The sludge is then allowed to settle, and a fraction of the settled sludge is recirculated after addition of the

TABLE XI

Sludge Analysis from the Recycle Runs with $CaCO_3$

Run No.	Treatment pH	Alkali	% Fe_2O_3	% Al_2O_3	% CaO	% MgO	% MnO	% SO_4^{-2}	TOTAL
1	6.0	$CaCO_3$	64.5	6.4	5.7	0.002	0.016	2.90	79.52
2	6.0	$CaCO_3$	62.5	5.7	9.4	0.003	0.016	1.94	79.56
3	4.0	$CaCO_3$	72.5	1.9	0.060	0.014	nil	13,40	87.87

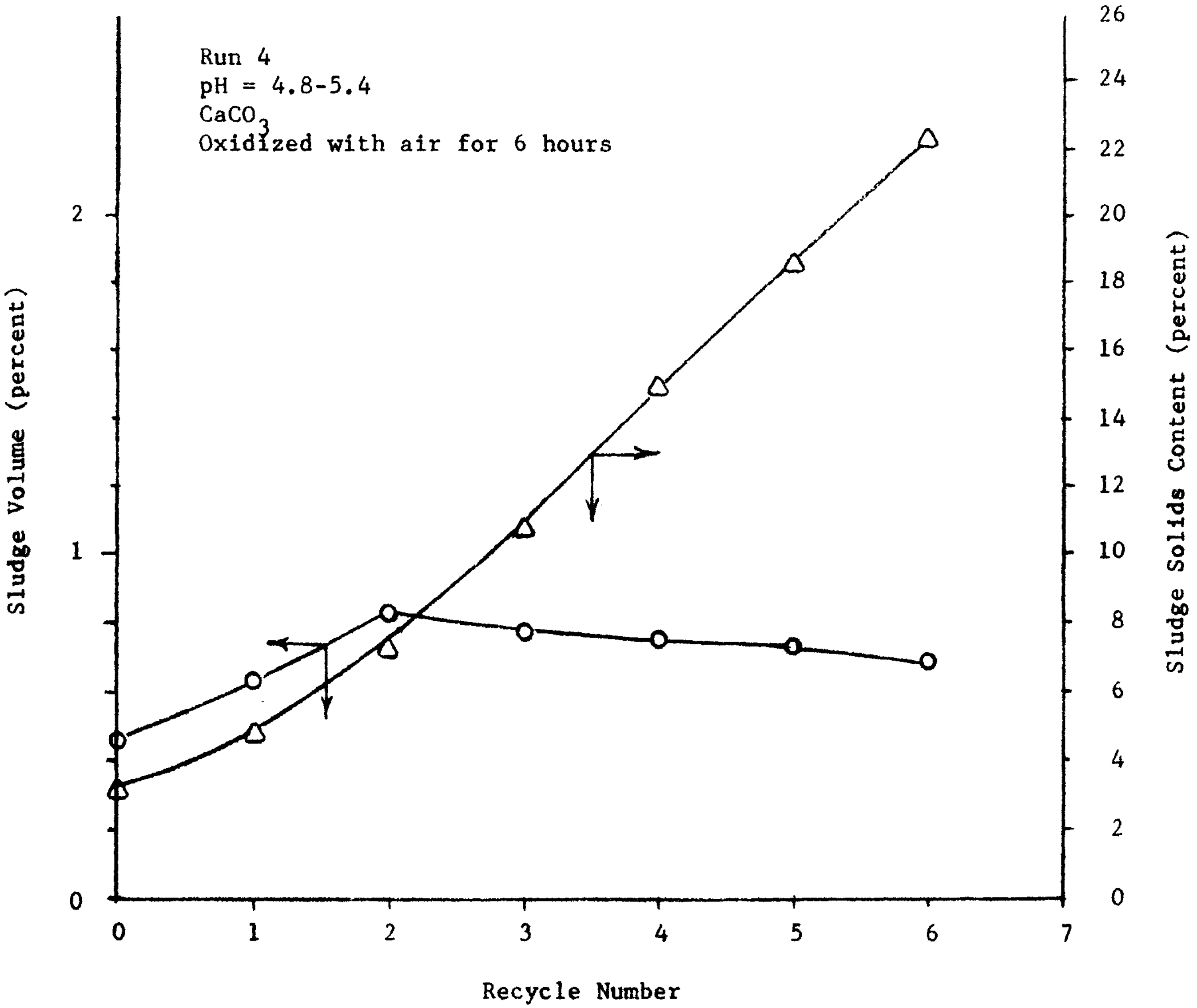


Figure 36

SAMD (Neutralized with $CaCO_3$) Sludge Volume and Solids vs. Recycle Number required quantity of limestone. Many factors affecting the sludge density, such as oxidation rate, the extent of oxidation in each neutralization step, et cetra have to be investigated, and such factors as the consumption of limestone and lime, power, and equipment costs, must be determined. Such considerations could not be covered within the limited budget of this project.

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