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NEUTRALIZATION OF AN ACIDIC EFFLUENT USING MAGNESIUM HYDROXIDE

by

Kawai Tam

A Thesis submitted to the Faculty of Graduate Studies and
Research in partial fulfillment of the requirements
for the degree of Master of Engineering

July, 1994

Department of Chemical Engineering

McGill University, Montreal

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ABSTRACT

Metal and acid containing effluents generated by industry are most commonly treated with lime which neutralizes the acid and precipitates the dissolved metals. The resulting sludge contains gypsum which has a high water content and requires large landfill volumes. It is therefore desirable to find a neutralizing agent which has a good neutralizing capacity and a dense precipitate which can be easily dewatered at low cost. A dense, fast settling sludge would also reduce the cost of the process and the volume to be landfilled. Magnesium hydroxide has been examined in this research as a neutralizing agent for a simulated iron-containing acidic solution. The effects of reaction temperature, dosage, rate of $Mg(OH)_2$ addition, and recycle on the neutralization of acidic iron solutions with magnesium hydroxide were studied. Magnesium hydroxide was found to be an effective precipitating agent removing over 98.3% of the iron from solution and an effective neutralizing agent exhibiting a buffering effect which stabilized the pH between 8.8 to 9.7 even with overtreatment. Observation of precipitate colour suggested that at lower pH values (2.2 to 4.3) ferric hydroxide was formed in the sludge whereas at higher pH values (9.3 to 9.7) the sludge consisted primarily of ferrous hydroxide. Increasing reaction temperatures from 10°C to 25°C did decrease reaction time but had insignificant effects on sludge production or characteristics. However, slow $Mg(OH)_2$ addition to the acidic iron solution as well as the use of a recycle both resulted in the production of larger sludge particles which resulted in a denser, fast-settling sludge.

RÉSUMÉ

Les effluents industriels acides contenant des métaux subissent le plus souvent un traitement à la chaux, qui neutralise l'acide et précipite les métaux en suspension. Les boues résultant de ce traitement contiennent du gypse, qui a une forte teneur en eau et occupe d'importants volumes dans les décharges. Il est donc souhaitable de trouver un agent offrant une bonne capacité neutralisante et produisant un précipité dense qui soit facile et peu coûteux à déshydrater. La production de boues denses se déposant rapidement réduirait également le coût du procédé et le volume à enfouir. La présente étude a examiné les possibilités que présente l'hydroxyde de magnésium pour la neutralisation d'une solution acide ferrugineuse simulée. Les effets de la température de réaction, du dosage, du taux d'addition de $Mg(OH)_2$ et du recyclage sur la neutralisation par l'hydroxyde de magnésium de solutions ferrugineuses acides ont été étudiés. L'hydroxyde de magnésium s'est révélé un agent précipitant efficace qui a éliminé plus de 98.3 % du fer contenu dans la solution, et un agent neutralisant efficace, dont l'effet tampon a stabilisé le pH entre 8.8 et 9.7. L'observation de la couleur du précipité a suggérée qu'à un pH faible (2.2 à 4.3), il s'est formé de l'hydroxyde ferrique dans les boues, alors qu'à un pH plus élevé (9.3 à 9.7), les boues se composaient avant tout d'hydroxyde ferreux. L'augmentation des températures de

réaction de 10°C à 25°C a réduit le temps de réaction, mais n'a pas eu d'effets significatifs sur la production des boues ou sur les caractéristiques de ces dernières. L'ajout lent de $Mg(OH)_2$ à la solution ferrugineuse acide et le recyclage ont entraîné la production de plus grosses particules; il en est résulté des boues plus denses, qui se déposent plus rapidement.

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I wish to express my sincere gratitude to the following people who contributed to the work presented in this thesis.

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To my parents

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NOMENCLATURE

% Solids = percent solids in the precipitated and settled sludge (%)

Mi = mass of the wet precipitated sludge sample that has settled (g)

Mf = mass of the dried sludge sample (g)

PC = (precipitation capacity) percentage of iron removed from simulated acidic iron solution (%)

Ci = initial iron concentration in the simulated acidic solution (ppm)

Cf = final iron concentration in the solution after neutralization (ppm)

CHAPTER 1

INTRODUCTION

As governmental regulations become more stringent, industries in all sectors of the economy have to control the quantities and contents of their effluents. Companies have had to change their priorities in order to achieve these standards.

Hundreds of mine sites within Canada alone discharge an acidic effluent called acid mine drainage (AMD). AMD is formed when sulphide bearing mine waste that has been exposed to air, water and to the catalyzing bacterium *Thiobaccillus ferrooxidans*, is oxidized to produce sulphuric acid. Pyrite is the most abundant sulphide mineral and can result in the production of sulphuric acid by the following chemical reactions: (Environment Canada, 1987)

$$FeS_{2(s)} + 7/2\ O_2 + H_2O \ \text{-->}\ Fe^{2+} + 2SO_4^{2-} + 2\ H^+ \qquad (1.1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \ \text{-->}\ Fe^{3+} + 1/2\ H_2O \qquad (1.2)$$

$$Fe^{3+} + 3H_2O \ \text{-->}\ Fe(OH)_{3(s)} + 3\ H^+ \qquad (1.3)$$

$$FeS_{2(s)} + 14Fe^{3+} + 8\ H_2O \ \text{-->}\ 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (1.4)$$

The oxidation of pyrite in equation 1.1 produces ferrous ions and free acid. The ferrous ions are then oxidized to ferric ions according to equation 1.2. The ferric ions react with water to produce ferric hydroxide and additional acid in equation 1.3. Finally, the overall rate of acid production is increased by several orders of magnitude by the rapid cyclic reactions of equations 1.2 and 1.4 (Singer and Stumm, 1970).

1.1 Acid Mine Drainage in the Environment

AMD or any other acidic discharges increase the acidity of the soil or nearby bodies of water. The decreased pH of the water kills many species of desirable aquatic and plant life, and allows less desirable fungi and mosses to proliferate (Goudie, 1986). The acid also leaches out metals from surrounding rocks and thus, the effluent not only has a pH of 2 to 3, but it also contains potentially toxic metal ions. This contaminates the drinking water and reduces the capacity of the land to sustain vegetation (Sobocinski et al., 1992).

AMD can arise as mine water from open pits as well as underground mine workings, or as surface drainage and seepage from tailings dispcsal facilities and waste rock dumps. The quality of AMD varies from mine to mine, often exceeding regulatory standards for metals and acidity by several orders of magnitude. Hence, treatment is required in order for the industrial emissions to conform to regulatory standards. In the case of iron, the maximum permissible concentration in the environment is 1.0 ppm according to the International Standards of water quality (Lester,1987).

1.2 Neutralization and Metal Precipitation

The most common treatment process for acidic effluents from both active and many non-active mines in Canada is chemical treatment, which usually involves neutralization of the acid with an alkali and precipitation of the dissolved metals in the hydroxide form. Metals will selectively precipitate out of solution as insoluble hydroxides depending on the pH of the solution. Solubility plots of metal hydroxides as functions of pH are available for various metal ions (Figure 1.1).

There are many alkaline agents used in industry and the choice is based on neutralizing capacity, characteristics of the by-products, as well as cost. It is advantageous to find an alkaline agent that has good neutralizing capacity, and a dense precipitate that can be easily dewatered at low cost. A denser sludge reduces the volume to be landfilled since solids disposal has recently become problematic with the shortage of landfill space. Table 1.1 gives an overview of findings reported in the literature for processes using the following alkaline agents:

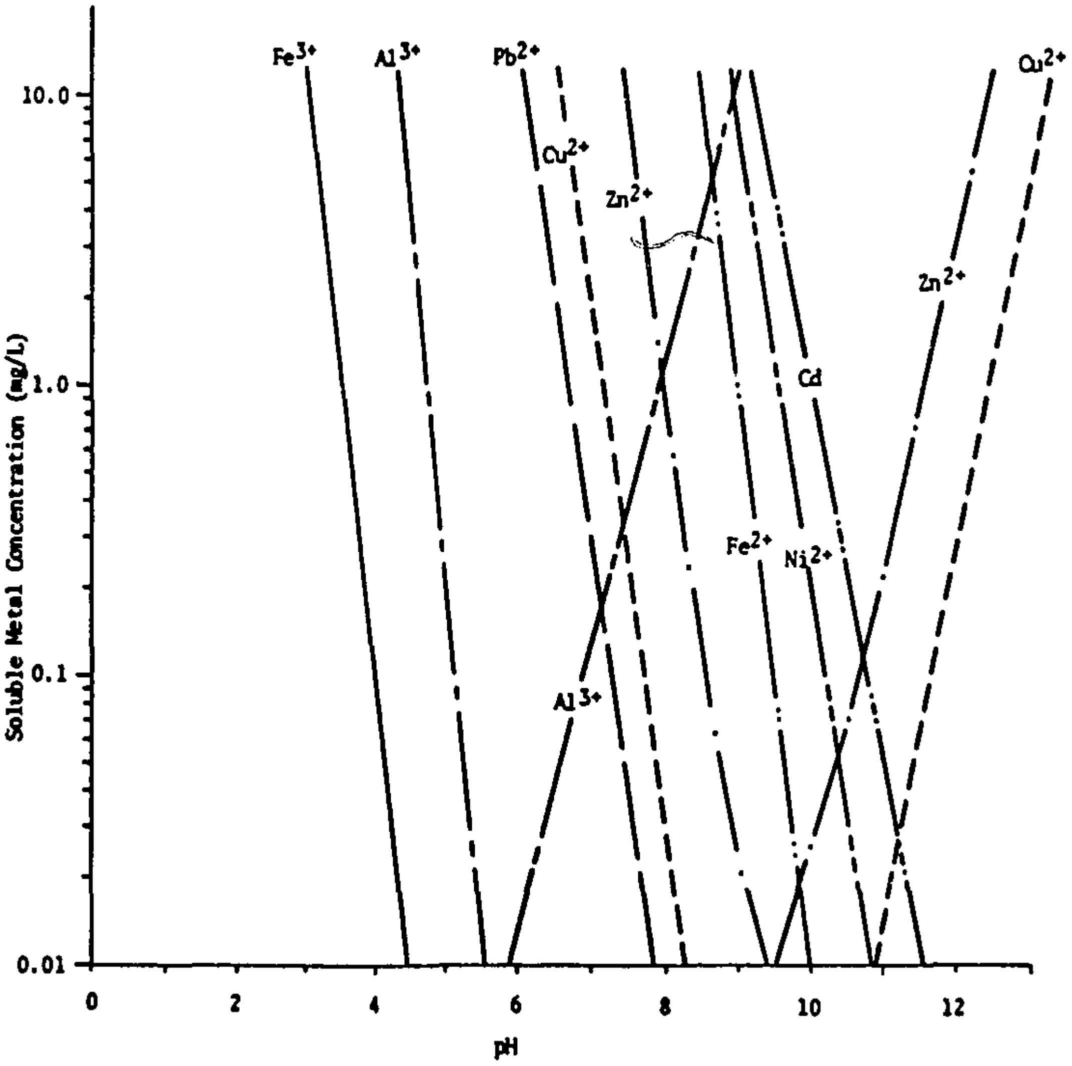

Figure 1.1 Solubility of metal hydroxides (Environment Canada, 1987)

NEUTRALIZING AGENT	CALCIUM COMPOUNDS			MAGNESIUM COMPOUNDS			DOLOMITIC COMPOUNDS			SODIUM COMPOUNDS	
TYPE OF EFFLUENT	**CaO**	**Ca(OH)2**	**CaCO3**	**MgO**	**Mg(OH)2**	**MgCO3**	**CaMgO2**	**CaMg(OH)4**	**CaMg(CO3)2**	**NaOH**	**Other**
ACID MINE WATERS	Bell, A.V., Phinney, K.D., Behie, S.W., (1975) Bosman,D.J., (1983) Boling,S.D., Kobylinski,E.A. (1992) Kemmer,F.N., Odland,K., (1968) Kuit,W.J., (1980) Oko,U.M., Taylor,W.L.W., (1974) Stefanoff,J.G., Kim,Y.K., Mavis,J.D., (1992)	Hoak,R.D., Lewis,C.J., Hodge,W.W., (1945) Davison,W., House,W.A., (1988) Harrison,V.F., (1969)	Campbell,A.B., Howes,W., Ode,W.H., (1932) Davison et al. (1988)				Harrison,V.F., (1969)		Campbell et al., (1932) Lewis,C.J., (1949)	Stefanoff et al. (1992) Davison et al., (1988)	Boling et al., (1992) [Na2CO3] Davison et al., (1988) [Na2CO3]
METAL PROCESSING: Metal Finishing /Metal Plating	Noda,K., Uchida,S., Miyazaki,M., (1989)		Noda et al., (1989) Pandey,G.S., Seth,P.C., (1983)		Teringo III, J., (1986) Teringo III,J., (1987) Teringo III,J., (1990)					Pardue,M.J., Regan,R.W., (1989) Brooks,C.S., (1990)	McAnnaly,S., Benefield,L., Reed,R.B., (1984) [Na2CO3]
PULP & PAPER MILL			Blackwell,B.R., Sikes,J.E.G., Wong,T., (1989) Santoro,L., Ciambelli,P., Volpicelli,G., (1973)							Blackwell et al. (1989)	
PRINTING PLANT		Nakazawa,H., Miyamoto,T., Sato,H., (1990)	Nakazawa, et al. (1990)							Nakazawa et al. (1990)	

Table 1.1 Literature Survey

NEUTRALIZING AGENT	CALCIUM COMPOUNDS			MAGNESIUM COMPOUNDS			DOLOMITIC COMPOUNDS			SODIUM COMPOUNDS	
TYPE OF EFFLUENT	CaO	Ca(OH)2	CaCO3	MgO	Mg(OH)2	MgCO3	CaMgO2	CaMg(OH)4	CaMg(CO3)2	NaOH	Other
SUGAR PLANT			Volpicelli,G., Caprio,V., Santoro,L., Ciambelli,P., (1981)								
TITANIUM DIOXIDE PROCESS	Trees,W.E., Roberts,G.L., Priesing,E.P., (1979)		Trees et al. (1979)		Trees et al., (1979)	Trees et al.,(1979)				Trees et al., (1979)	Trees et al., (1979) [Na2CO3]
HYDROCHLORIC ACID SOLUTION		Teringo,J., (1987)	Uchida,S., Wen,C.Y., McMichael,WJ (1974)		Teringo III,J., (1987)					Teringo III,J., (1987)	
PHARMACEUTICAL PLANT										Okey ,R.W., Chen,K.Y., (1978)	Okey et al. (1978) [NaHCO3]
DOMESTIC SEWAGE	Dziubek,A.M., Kowal,A.L., (1984) Flentje,M.E., (1927) Leentvaar,J., Rebhun,M., (1982)								Dziubek et al., (1984) Dziubek et al., (1989)		
CONTAMINATED GROUNDWATER	Sobocinski,R.W., Myers,J., (1992) Zanoni,P.D., Rogers,J., (1992)									Zanoni et al., (1992)	Zanoni et al., (1992) [Na2CO3] Zanoni et al., (1992) [NaS]
ACIDIC LAKES		Davison,W., House,W.A., (1988)	Davison et al. (1988) Molot,L.A., Hamilton,J.G., Booth,G.M., (1986)							Davison et al., (1988)	Davison et al., (1988) [Na2CO3]
PRODUCTION OF BATTERY STORAGE	Altmansberger,D.S. Huss,S.L. Kroger,H.H. (1984)										

Table 1.1 (continued)

- Calcium compounds (CaO, $Ca(OH)_2$, $CaCO_3$)
- Sodium Compounds (NaOH, Na_2CO_3)
- Dolomite ($CaMgO_2$, $CaMg(OH)_4$, $CaMg(CO_3)_2$)
- Magnesium compounds (MgO, $Mg(OH)_2$, $MgCO_3$)

1.3 Neutralization Using Calcium Compounds

As early as the 1920's, calcium compounds have been used in the pulp and paper industry (Blackwell et al.,1989), mining industry (Harrison,1969) as well as the electroplating industry (Noda et al.,1989).

Lime (CaO) has a high initial degree of neutralization and is the most commonly used precipitation chemical in industry. Unfortunately, it produces large quantities of calcium sulphate or gypsum in the treated effluent. The gypsum forms a film which causes a retarding effect on the dissolution of the neutralizing mineral, thus requiring more "fresh" lime for neutralization to the desired pH. In addition, the flocs obtained while neutralizing with lime are very light and friable, and tend to require long periods of time before settling to a gelatinous sludge. It should be noted that these drawbacks are associated with all calcium containing compounds (CaO, $Ca(OH)_2$, $CaCO_3$), including dolomite compounds.

Harrison (1969) found that lime is more effective when slaked with water to form hydrated lime, which reacts in the following manner:

$$2\ FeSO_4 + 2\ Ca(OH)_2 + 5\ H_2O + 1/2\ O_2 \longrightarrow 2\ Fe(OH)_3 + 2\ CaSO_4 \cdot 2\ H_2O \quad (1.5)$$

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 \cdot 2\ H_2O \quad (1.6)$$

Aeration was also found to help the oxidation of the ferrous ion (Fe^{2+}) to the ferric ion (Fe^{3+}), the latter of which has a lower solubility and when present in sufficient quantity, precipitates out of solution at pH 4.3 as compared to pH 9.5 for the ferrous ion.

When the cost of lime increased, more attention focused on the use of less expensive limestone. Although limestone ($CaCO_3$) has a lower reactivity than lime, it produces a faster settling and higher density sludge (Noda et al.,1989). For example, after a settling period of one day, the sludge volume from limestone neutralization was found to be less than a quarter of that produced using the lime process.

1.4 Neutralization Using Sodium Compounds

Sodium hydroxide, also known as caustic soda, has been utilized in the mining, electroplating and pulp and paper industries. Its use is attractive due to its high neutralizing capacity (high solubility) and the lack of gypsum by-product formation. However, for the same degree of neutralization, it is generally 3-4 times the cost of limestone or slaked lime, and hence is generally considered to be economically unviable. Other alkaline metals such as MgO has been used in conjunction with NaOH in order to offset its high cost in treatment processes (Noranda,1992).

McAnnaly, Benefield, and Reed (1984) found that precipitation of heavy metal carbonates with Na_2CO_3, also known as soda ash, was beneficial since dense sludges were formed which could be easily removed from solution.

Davison and House (1988) conducted further studies on NaOH and Na_2CO_3, and found that sodium products in general dissolved better than calcium compounds. It was also reported that when effluents were treated with the above sodium products, the resulting solution was buffered, enabling it to tolerate further supplies of atmospheric acid precipitation.

1.5 Precipitation Using a Mixture of Magnesium and Calcium Compounds

Flentje et al. (1927) found that a combination of calcium and magnesium precipitates were useful in the treatment and clarification of domestic sewage wastewater. The addition of lime and magnesium chloride to raw wastewater caused $Ca(OH)_2$ and $Mg(OH)_2$ to form. Their findings indicated that these precipitates had good coagulation properties. The precipitates substantially reduced the turbidity, colour, COD (chemical oxygen demand), and phosphates of the raw wastewater.

In 1984, Dziubek and Kowal continued the studies on the coagulation effect of $Mg(OH)_2$ on lime treatment and extended their investigation to include the effect of $Mg(OH)_2$ on dolomite treatment of domestic sewage. Dolomite was selected for study because it consists of the carbonates of both calcium and magnesium. It contains approximately 46% $MgCO_3$ and 54% $CaCO_3$. Through thermal dissociation and hydration of dolomite, both the hydroxides of calcium and magnesium can be obtained.

The conclusion of the above study was that the coagulation and absorbing properties of $Mg(OH)_2$ depend on the method by which it had been formed. While high efficiencies were achieved with $Mg(OH)_2$ precipitated from the wastewater by lime treatment, somewhat lower efficiencies of $Mg(OH)_2$ were obtained from the magnesium component of dolomite. Nevertheless, it was also concluded that the application of dolomite coagulants were promising but require further study.

The application of dolomite was also extended to the treatment of AMD (Harrison,1969), but in different proportions of calcium and magnesium compounds. Dolomitic lime which consists of approximately 30% CaO, 22% MgO, 48% CO_2, and impurities such as silica, clay and feldspar, was used. This effectively neutralized the AMD with decreased production of gypsum due to the production of the soluble $MgSO_4$ salt.

1.6 Neutralization Using Magnesium Compounds

The use of magnesium compounds such as magnesium oxide, magnesium hydroxide and magnesium carbonate (magnesite), has been applied in the industry of electroplating. These magnesium compounds are classified as relatively safe substances to handle. In fact, magnesium oxides and hydroxides can be found in common stomach antacids such as Maalox®. Magnesium is also one of the most common elements on earth and is an essential nutrient for normal plant, animal and human growth.

Teringo (1987) compared neutralization methods using NaOH, lime and $Mg(OH)_2$ and found that magnesium hydroxide was effective in removing undesirable metal contaminants from electroplating and metal finishing wastewaters. In addition, a lower volume and more dense metal hydroxide sludge was obtained when $Mg(OH)_2$ was used. Since longer reaction times are required for the reaction using magnesium hydroxide, there is more time for crystal growth, resulting in large particles and dense sludge. This sludge also had increased porosity and permeability, facilitating the process and cost of dewatering the sludge.

To neutralize and remove metals in a given volume of acidic solution, the $Mg(OH)_2$ had 37% and 27% more hydroxyl ions than NaOH and $Ca(OH)_2$, respectively. Thus, less magnesium hydroxide would be required to neutralize a sulphuric acid solution than NaOH or $Ca(OH)_2$. In addition, less magnesium sulphate is present as total dissolved solids in the neutralized effluent than sodium sulphate. Teringo (1990) found that neutralization using magnesium hydroxide as compared to lime and sodium hydroxide, was a cost effective method when sludge disposal costs were also considered.

An additional advantage to the use of magnesium hydroxide as a neutralizing agent is its buffering effect (caused by the equilibrium between a base and its salt in an aqueous solution) at a pH of 9.0, which coincides with the Clean Water Act of 1976 for effluent discharge. Therefore, overtreatment of an acidic solution using magnesium hydroxide would not be problematic. The buffering effect is advantageous because pH stabilization is very important in neutralization processes and prevents the resolubilization of metals precipitated.

The latest study in the use of $Mg(OH)_2$ for the treatment of acidic waste streams, was done by Foreman (1993) and it was found that the buffering effect of $Mg(OH)_2$ occurred at a pH range from 9.0 to 9.5. Other findings in his study confirmed those found by Teringo (1990).

In summary, the above studies using magnesium compounds as neutralizing and metal precipitating agents showed that magnesium compounds potentially have the following advantages over calcium and sodium compounds for the treatment of AMD. Firstly, magnesium compounds have a buffering effect on the resulting solution. Secondly, less neutralizing agent is required. Thirdly, resulting sludge characteristics are favourable in terms of density and handling properties. Finally, magnesium is a safe substance to handle and is not damaging to the environment.

The purpose of this Master's project was to further investigate magnesium hydroxide as a neutralizing agent for iron-containing acidic solutions by varying process parameters such as neutralizer quantity and concentration, reaction temperature, rate of neutralizer addition, and recycle. Precipitation capacity, neutralization times, settling rates, quality of treated effluent, and percent solids in the precipitated sludge were the primary factors of comparison. The investigation was carried out using a simulated iron-containing acidic effluent in a batch process.

CHAPTER 2

RESEARCH OBJECTIVES

The overall objective of this Master's project is to evaluate the effectiveness of magnesium hydroxide as a neutralizing agent for a simulated iron-containing acidic solution through the variation of several process conditions.

2.1 Statement of Objectives

1. To evaluate and determine the reactor hydrodynamics necessary for a well mixed laboratory reactor system.

2. To investigate the effect of precipitation of iron hydroxide on the sulphuric acid titration process using magnesium hydroxide.

3. To investigate the effect of a series of process variables such as neutralizing agent concentration, reaction temperature, rate of neutralizer addition, and recycle of iron hydroxide sludge particles.

4. To evaluate the results from the investigations of the above process variables based on neutralization effectiveness, treated effluent quality, and resultant sludge characteristics.

CHAPTER 3

MATERIALS AND METHODS

In this chapter, the procedures used to prepare a simulated acidic effluent and a neutralizing agent slurry are described. The experimental equipment and methods used in the neutralization reactions, and for data acquisition are also presented. Finally, the methods used for characterizing the precipitated sludge are discussed.

3.1 Experimental Procedures

3.1.1 Acidic Effluent Simulation

The ingredients used to prepare the simulated acidic effluent were: ferric hydroxide ($Fe(OH)_3$) paste purchased from Pfaltz and Bauer, laboratory-grade sulphuric acid (H_2SO_4) obtained from J. T. Baker Inc., and distilled water.

Thirteen liters of effluent were prepared by combining 16.0 g ferric hydroxide with 15 liters of distilled water and sufficient sulphuric acid to reach a pH of 2. After allowing the mixture to stand for 48 hours, the supernatant was decanted and stored for use throughout the experimental period as simulated acidic effluent. The concentration was found to be 23.5 ± 1.5 ppm of iron by atomic absorption spectrophotometry. The concentration of the iron in the initial acidic effluent stayed constant with respect to time throughout a block of experiments as shown in Figure 3.1.

The iron content in the simulated initial acidic effluent is representative of the iron concentration found in industrial wastewaters from Canadian mines and mills, which ranges from 10 to 1200 ppm (Environment Canada, 1987). The sulphate concentration of 480 ppm in the simulated acidic effluent is lower than the concentration found in industrial wastewater which normally ranges from 800 to 1800 ppm. Even though the concentration of sulphates is lower than that normally found in industrial wastewaters, the data does provide relevant information concerning neutralization and iron removal efficiency.

3.1.2 Neutralizer Slurry Production

$Mg(OH)_2$ was purchased as a powder with a particle size of approximately 1 to 2.5 microns from Fisher Scientific. In order to produce a 20% $Mg(OH)_2$ slurry, 50.0 grams of magnesium hydroxide was slowly stirred into 200.0 cm^3 of distilled water. A magnetic stirrer was used to keep the slurry in suspension. The amounts of magnesium hydroxide

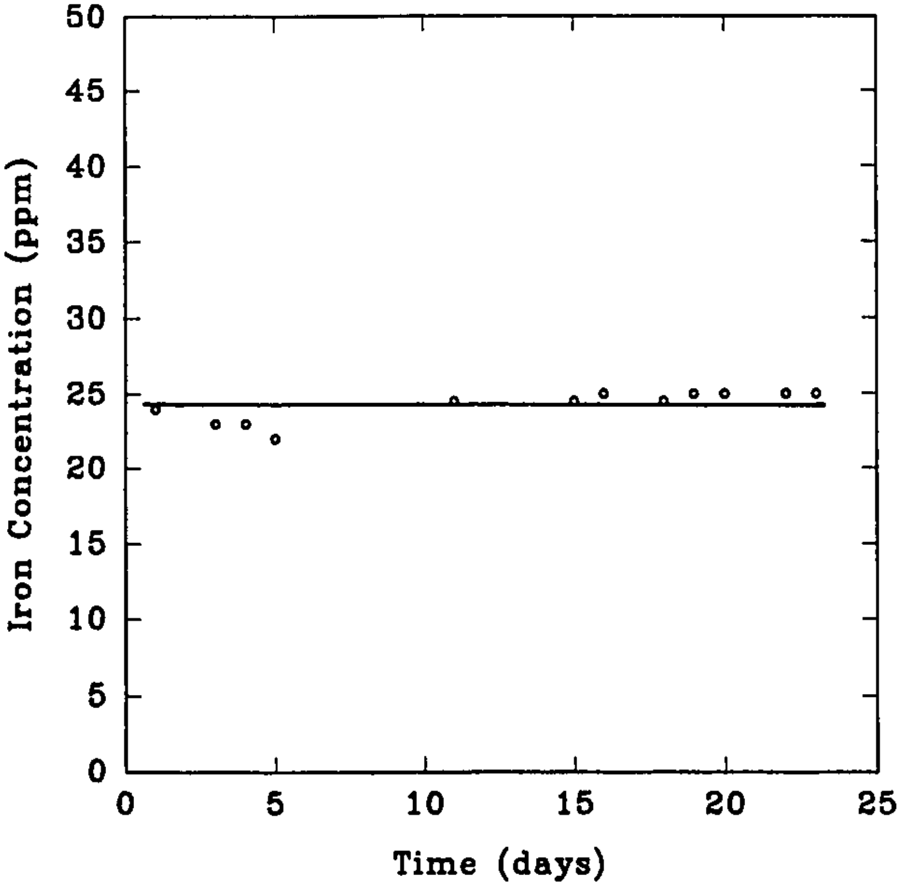

Figure 3.1 Iron concentration of simulated acidic effluent over time for a set of experiments

used in 10% and 30% $Mg(OH)_2$ were 22.0 g and 85.7 g respectively per 200 cm^3 of distilled water.

The slurry form of the neutralizing agent was used as opposed to the dry powder form because the slurry is an easier form to handle since problems such as static electricity associated with the use of fine powders are eliminated. In addition, industrial processes use slurries of the neutralizing agent because they can be pumped.

3.1.3 Experimental System

The experimental system is shown in Figure 3.2. Neutralizer was fed using a disposable pipette into a 1000 cm^3 beaker reactor which contained 500 cm^3 of acidic effluent. The resulting solution was mixed at 645 rpm using an overhead CAFRAMO stirrer Type RZR1-64 equipped with an impeller having a diameter of 5 cm.

The temperature in the reactor was regulated by a constant temperature water bath which limited the reactor temperature fluctuations to less than 1°C.

pH and temperature measurements of the reactor were taken with a standard pH electrode (Sensorex S200C) and an automatic temperature compensation probe (ATC probe) attached to a Cole Parmer Microprocessor pH meter and a Type

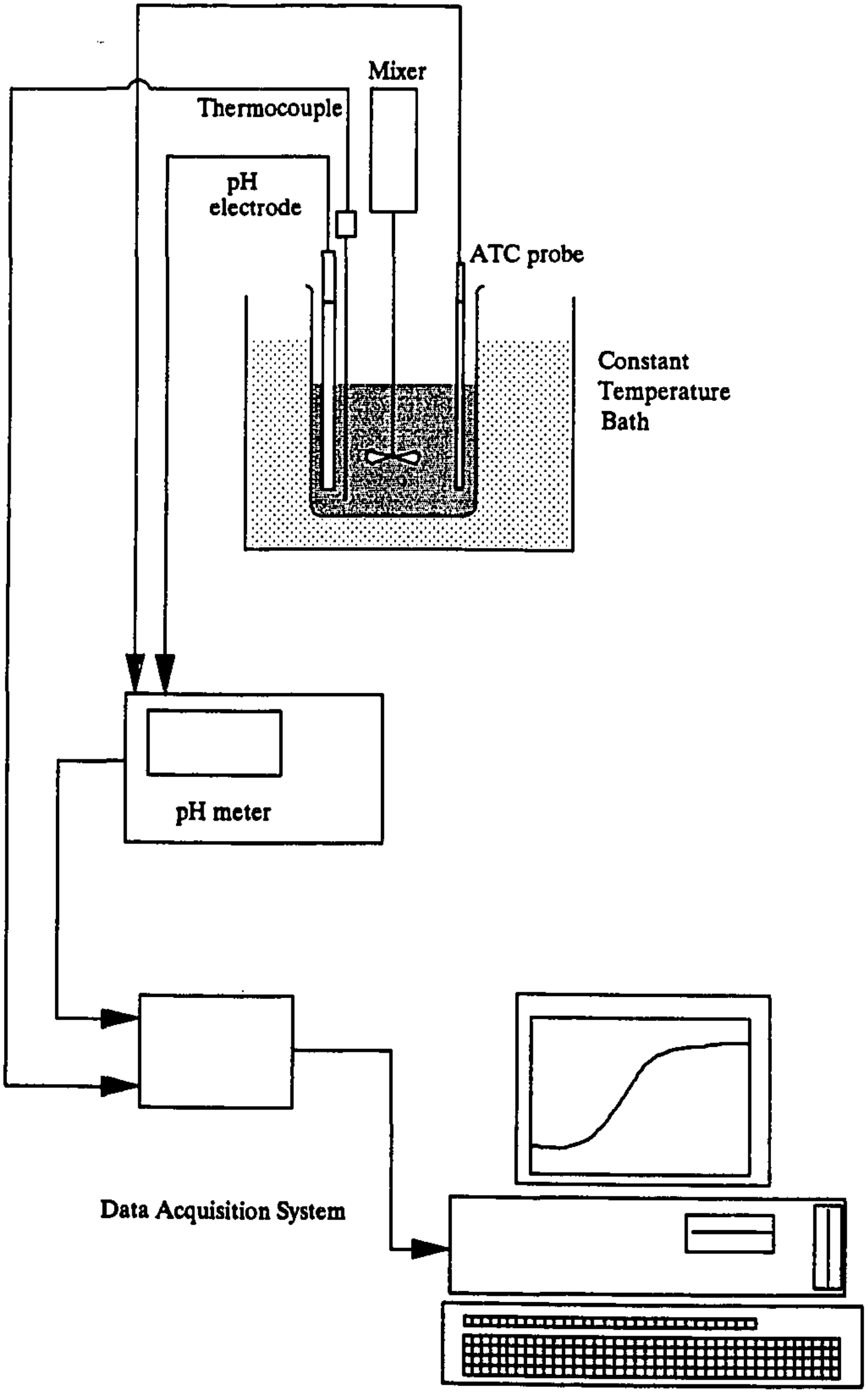

Figure 3.2: Experimental apparatus

K thermocouple. The pH electrode had a response time at 95% in less than 1 second and the thermocouple was coated with PFA teflon in order to withstand the acidity of the solution.

Both the pH meter and the thermocouple were connected to a data acquisition system (WB-ASC-TC interface card from Omega Engineering Inc.). This system enabled continuous monitoring and recording of the pH and temperature in the reactor. Since the pH and temperature responses were recorded every ten seconds and could be viewed either graphically or numerically at any time, an accurate picture of the reaction as it occurred was obtained.

3.1.4 Experimental Procedure

Before and after neutralization, the iron and magnesium concentrations in the solution were measured using an atomic absorption spectrophotometer(Thermo Jarell Ash Corp. Model Smith-Hieftje II). Iron and magnesium hollow cathode lamps (Visimax II) were used.

The atomic absorption spectrophotometer was calibrated each day of analysis using iron and magnesium atomic absorption standard solutions purchased from Aldrich, WI. The calibrations were also verified after each five samples and replicates were performed. Error associated with the measurements was typically within 5%. In all cases, iron was the only element detected in the solution before neutralization while in all but one case, magnesium was the only element detected in the solution after neutralization. The atomic absorption detection limits for iron and magnesium are 0.4 ppm and 0.03 ppm respectively.

Experiments were carried out in the temperature range of 10°C to 25°C at 5°C intervals. Neutralizer weight percentages of 10%, 20%, and 30% $Mg(OH)_2$ were investigated. Preliminary experiments on the reactor system were also performed by varying the positions of neutralizer addition and rate of agitation.

At the beginning of each day of experimentation, the neutralizer slurry was resuspended and the pH meter was recalibrated. The scale and offset of the data acquisition had to be recalculated to ensure that the proper readings for pH and temperature were recorded.

For each experimental run, a volume of 500 cm^3 of acidic effluent was added to the reactor and the mixing was started. At the onset of mixing, the pH reading fluctuated. Approximately 5 minutes of mixing were required before stable pH readings were obtained. The neutralizer was not added until the pH reading showed a stable reading for at least ten minutes.

After the addition of the neutralizing agent, the pH and temperature readings were recorded until the pH readings were once again constant. This procedure was repeated for each set of reaction conditions. Figure 3.3 demonstrates the reproducibility of the experimental system in terms of the rate of neutralization.

In the case of the titration experiments, 40 μl quantities of 3.9 M $Mg(OH)_2$ were added using a calibrated pipette to the acidic solution and once again the pH and temperature readings were recorded.

3.2 Data Evaluation

Three parameters were used to characterize the neutralizations: 1) final iron concentration, 2) precipitation capacity, and 3) time to reach pH 7. Iron concentration data obtained from the atomic absorption spectrophotometer was used to determine the quality of the treated effluent. As stated in the introduction, according to the International standards for water quality, the maximum permissible concentration of iron for discharge is 1.0 ppm. Therefore, this criteria was used as the standard in the evaluation of the effectiveness of this neutralizing agent.

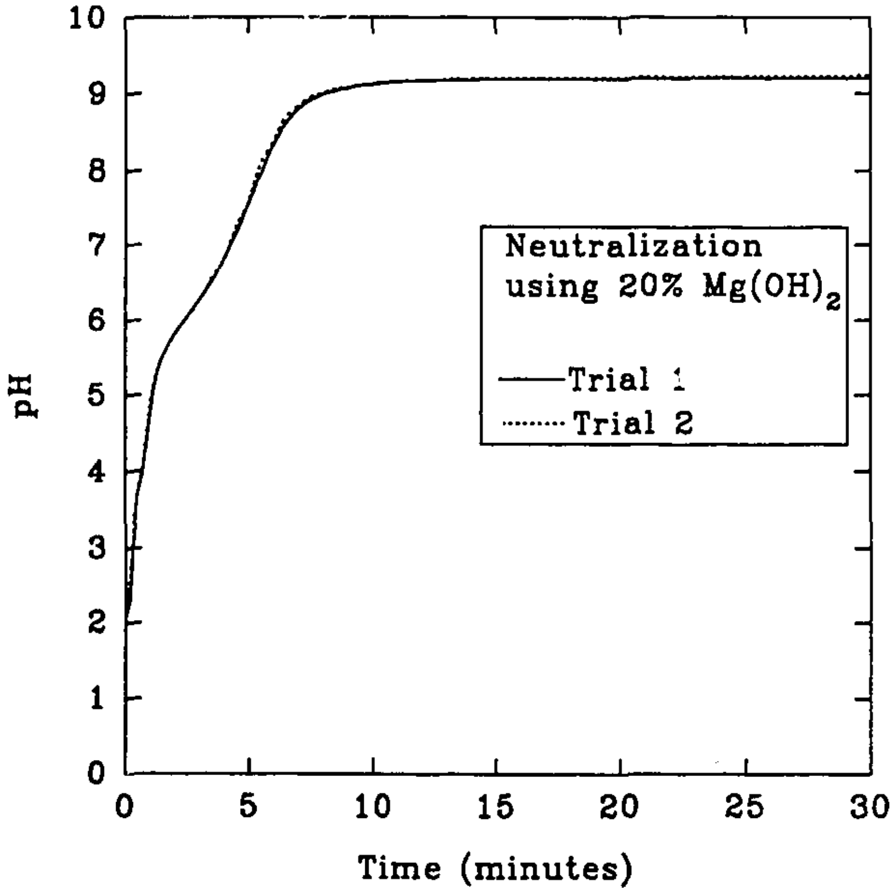

Figure 3.3 Reproducibility of experimental system

Precipitation capacity is another important characteristic that was determined from the iron concentration data. Neutralizing capacity is defined as the percentage of iron removed from the solution due to neutralization and metal precipitation. This is calculated by the following equation:

$$PC = \frac{(Ci - Cf)}{Ci} \times 100\% \qquad (3.1)$$

where PC = percentage of iron removed from the solution (%)
Ci = initial iron concentration in the solution (ppm)
Cf = final iron concentration in the solution after neutralization (ppm)

Finally, data acquisition results for pH and temperature as functions of time were used to evaluate the reaction times required for neutralization in the experiments. The reaction time of neutralization is defined as the time taken for the pH to increase from approximately 2 to a pH of 7. This refers to the period of time from when the neutralizer is first added to the acidic effluent until neutralization is reached. This definition of the reaction time gives an indication of neutralization rate and is therefore useful for comparing the experimental parameters.

3.2.1 Sludge Characterization Methods

Three different methods of sludge characterization were used to evaluate the sludge produced after neutralization: a settling rate test, percent solids determination in the sludge and laser diffraction analysis.

1) Settling Rate Test: A modified version of the American Society for Testing and Materials (ASTM, 1990) Method C110-87 for the settling rate of hydrated lime was used for the determination of the settling rate of the neutralized sludges. Initially, the ASTM method called for 10 g of sample to be diluted to the 100 cm^3 level in a 100 cm^3 graduated cylinder. Preliminary experiments showed that it was impossible to obtain 10.0 g of sludge and that sludge resuspension was a common occurrence.

The modified version of the settling rate test involved taking a 200 cm^3 sample of the homogeneous solution of neutralized effluent and pouring it into a modified and calibrated settling rate column as shown in Figure 3.4. The bottom section of the settling rate column was narrowed in order to more precisely measure the volume of sludge that settled. This modification was required since preliminary experiments showed that sludge volumes which were obtained from a 200 cm^3 sample were normally between 0.3 and 2.5 cm^3 (0.35 g and 2.9 g, respectively). Standard 200 cm^3

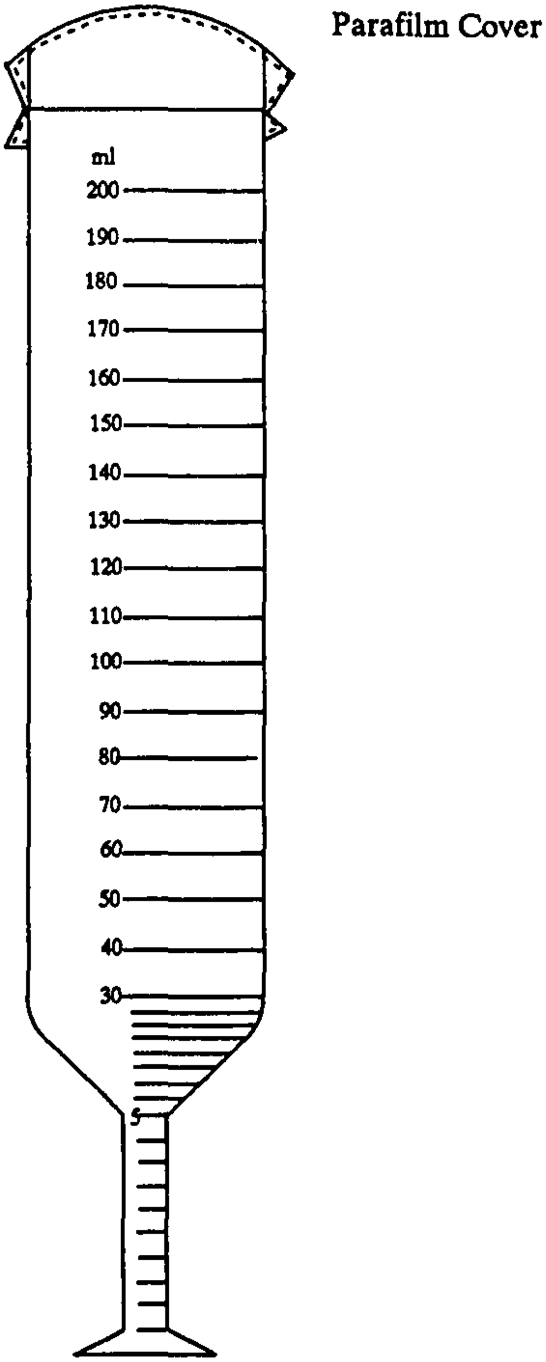

Figure 3.4: Settling rate column

graduated cylinders are accurate to within 10 cm^3, insufficient for the sludge volumes being handled.

After pouring the neutralized solution into the settling rate column, the column was sealed with Parafilm and mixed again by inverting the column twenty times. The column was then allowed to stand undisturbed at room temperature for 24 hours. The volumes of the clear, cloudy, and sludge regimes were recorded in cm^3 at 0.0, 0.25, 0.5, 0.75, 1.0, 2.0, 4.0 and 24.0 hours.

The time required for complete settling, when only the two distinct clear and sludge regimes remained, was used as the basis for comparing settling rates between experiments.

2) Percent Solids Determination: Wet sludge is defined as the layer of wet particles present after 24 hours of settling. Approximately 1.25 ± 0.75 cm^3 of wet sludge samples were dried for 6 hours in a convection oven at 100°C. The sludge samples were weighed both before and after drying. The weight difference was used to calculate the percent solids according to the following equation:

$$\%Solids = \frac{(Mi - Mf)}{Mi} \times 100\% \qquad (3.2)$$

where Mi = the mass of the wet sludge sample (g)

Mf = the mass of the dried sludge sample (g)

3) Laser Diffraction: The Malvern Series 2600 Droplet and Particle Sizer was used for the determination of particle size distributions for the neutralized sludges. The set-up of the optical experiment is shown in Figure 3.5. The main components include the helium-neon laser, the cell where the particles are suspended, the receiver lens, and the detector plane.

The light from a low power helium-neon laser, typically 1 cm in diameter, is directed through the cell which contains the particles in a surfactant solution (Tween 20). The light scattered by the particles and the unscattered light is brought to a focus on the detector, passes through a small aperture in the detector and out of the optical system. The sample volume concentration can be determined from the amount of power that passes out of the optical system. Calculations performed in the Malvern computer for the diameter of the particles is based on the assumption that the particles are spherical (Malvern, 1985).

When a particle scatters light, it produces a unique light intensity characteristic with angle of observation. The scattering angle is related to the particles' diameter. Large particles scatter at low angles, whereas small particles scatter at high angles.

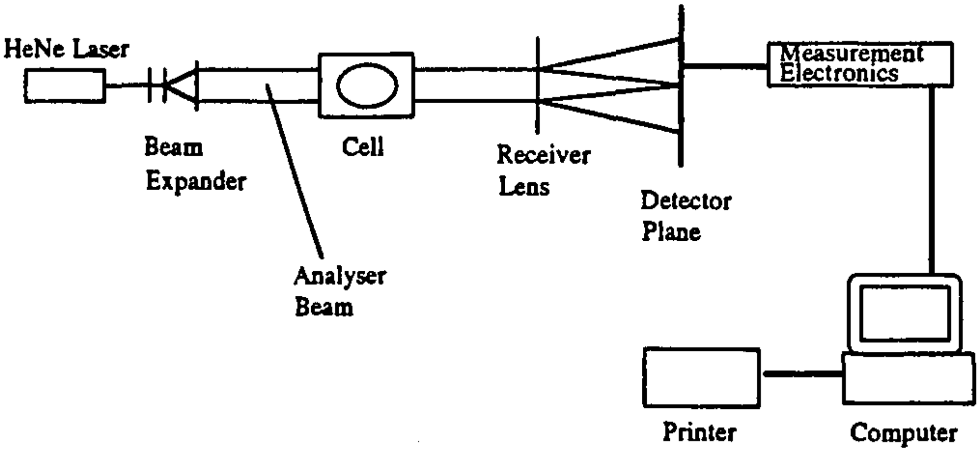

Figure 3.5 Laser Diffraction Experiment Set-up

Solutions of neutralized effluent were mixed in order to resuspend any settled particles and ensure homogeneous sampling. A sample was then taken by pipette and slowly added to the cell containing the surfactant solution.

In using this method for particle size distribution analysis, it was important to sample the particles soon after neutralization (less than 6 hours), in order for the assumption of consistent particle shapes to be valid. After this period of time, the results were irreproducible because the particles agglomerated in solution and broke up during resuspension in an inconsistent manner.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the effect of several process parameters including neutralizer concentration, reaction temperature, rate of neutralizer addition and recycle on the quality of the treated effluent and on the characteristics and quantity of metal hydroxide sludge produced is presented. The chapter is divided into eight sections. The first section includes the results and discussion of hydrodynamics in the reactor system. The second section describes results of the effect of iron concentration on the titration process, while the third section describes the results of various neutralizer concentration experiments. The fourth and fifth sections present results of reaction temperature variation and rate of magnesium hydroxide addition, respectively. Finally, the last section examines the results of a neutralization reaction in the presence of recycled sludge particles.

4.1 Reactor Hydrodynamics

The purpose of this section is to present data which was used to evaluate the mixing properties of the reactor as well as the effect of the slurry injection method on the reactor performance and sludge characteristics.

4.1.1 Effect of Point of Neutralizer Addition

Mixing properties of the reactor had to be tested in order to ensure that the reactor was a well mixed system. This was achieved by adding a small volume of red tracer to the reactor and recording the time required for the tracer volume to diffuse throughout the entire solution volume in the reactor. Having used a Cole Parmer tachometer Model(8213-20) to set the agitation rate of the stirrer at 645 rpm, three positions in the reactor were tested by tracer injection. The first position examined was located at the center of the reactor where the impeller was situated and is denoted as the "central addition" (Figure 4.1a). The next position tested was a "side addition" located at the forefront of the reactor halfway between the impeller and the wall of the reactor (Figure 4.1b). The last configuration tested was a "sweep addition" where the tracer volume was swept along the front of the reactor solution (Figure 4.1c).

Results from the tracer tests indicated that the reactor system was well mixed since between one and two seconds were required for complete mixing when central addition was used and between two to three seconds when dye injections were made at the other two positions. In all cases, no dead volumes could be identified.

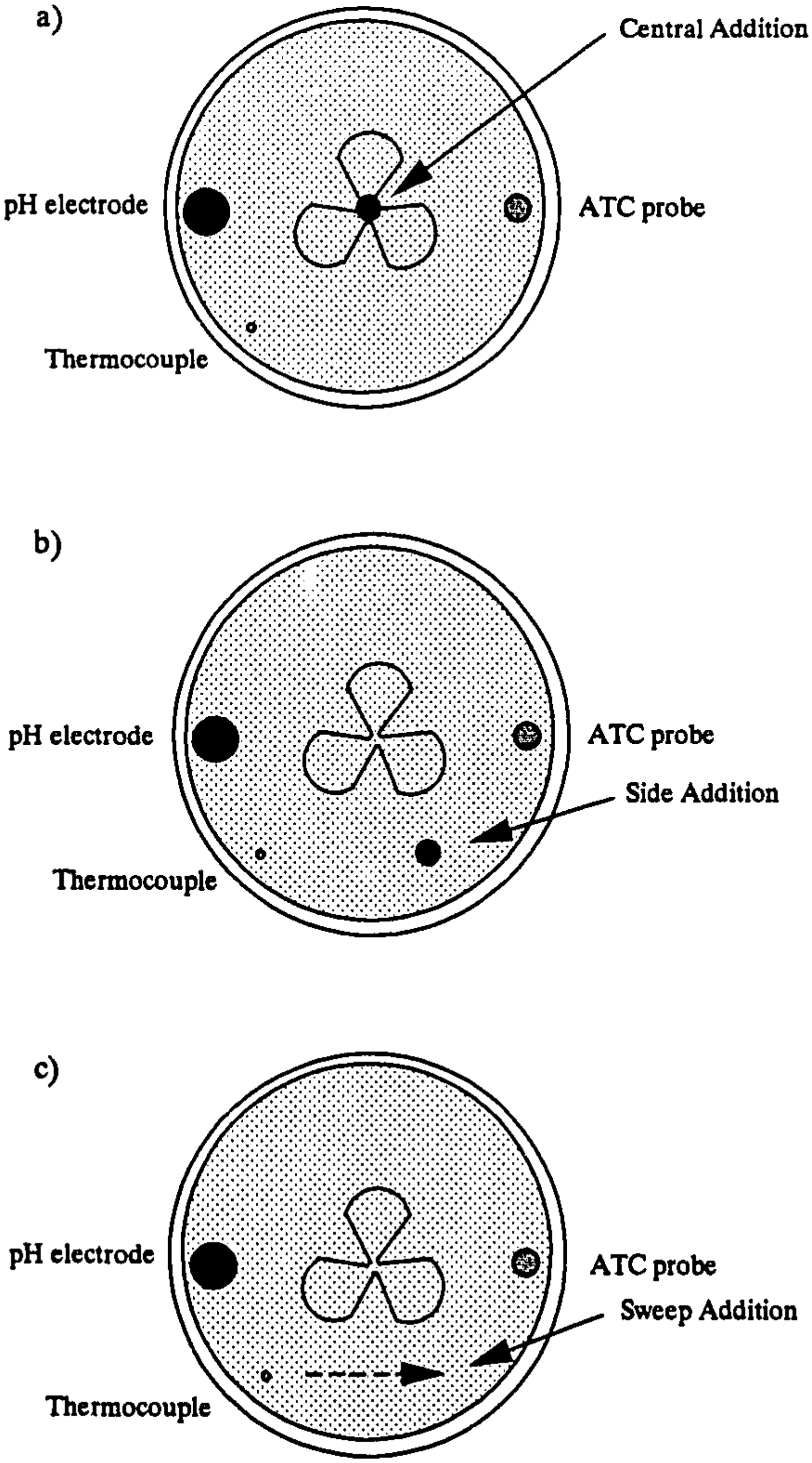

Figure 4.1: Points of tracer addition (top view of reactor)
a) central addition b) side addition c) sweep addition

Preliminary experiments were also designed to determine the best position in the reactor in which the neutralizing agent slurry should be added. The same positions that were investigated in the mixing properties test with the tracer volume, were tested in these neutralization experiments by adding magnesium hydroxide to the simulated acidic effluent. The results of these experiments were evaluated on the basis of their times for neutralization, precipitation capacity, settling rate, treated effluent quality and sludge properties. All are tabulated in Table 4.1.

Results of these experiments indicate that in all cases the same precipitation capacity was achieved with greater than 98.8% removal of the iron initially in solution, and the treated effluent quality satisfied the standard of iron concentration at less than 1 ppm. In fact, the iron concentration in the neutralized solutions was less than 0.4 ppm, the limit of detection using atomic absorption. In addition, there was no difference in the time required for complete settling of the metal hydroxide sludge particles (24 hours), and the percent solids are all similar to each other (1.63 ± 0.26 % to 1.86 ± 0.25 %).

Figure 4.2 is a plot of pH versus time for the three positions tested. It is shown that the central addition experiment had a neutralization time of 15.5 minutes, 5.3 minutes faster than the other two positions tested. The

Table 4.1

Experimental Results of Various Positions of 20% $Mg(OH)_2$ Slurry Additions

	Central Addition	Side Addition	Sweep Addition
Initial Fe Conc. (ppm)	34.5	34.5	34.7
Reaction Temperature (°C)	19.9	20.0	20.0
Mass of $Mg(OH)_2$ in Slurry (±0.001g)	0.234	0.234	0.233
Mass of Slurry (±0.001g)	1.167	1.169	1.166
Final pH (±0.01)	8.97	8.99	8.74
Reaction Time (minutes)	15.5 ± 0.05	20.8 ± 3.0	20.8 ± 2.9
Fe Conc. after Neut. (ppm)	<0.4 *	<0.4 *	<0.4 *
Neutraliz. Capacity (%)	98.8	98.8	98.8
Time for Complete Settling (hr)	24	24	24
Percent Solids in sludge (%)	1.68 ± 0.29	1.63 ± 0.26	1.86 ± 0.25
Conc. of Mg in solution after neut. (ppm)	166	178	178

* limit of detection on atomic absorption spectrophotometer

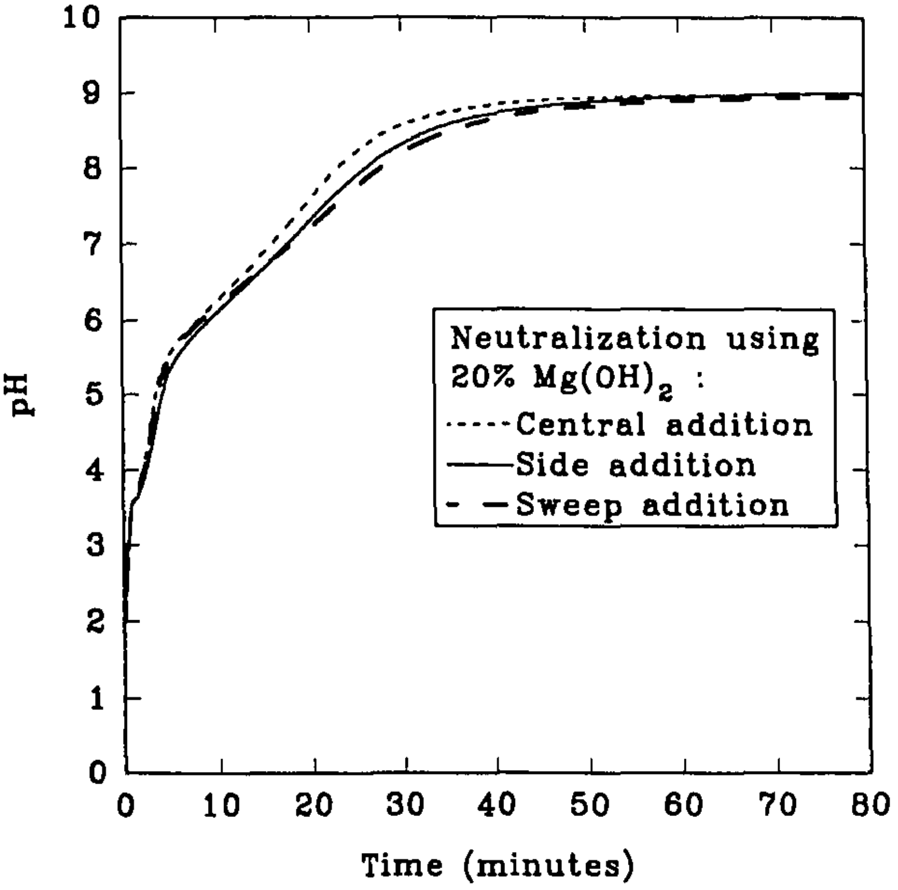

Figure 4.2 Effect of position of neutralizer addition on pH over time

faster neutralization time for the central addition corresponds to a faster rate of reaction. Since mixing was found to be slightly faster when central addition was used, it is concluded that improved mixing improves contact between the acidic solution and the solid particles of $Mg(OH)_2$ in the neutralizer slurry. Given that all sludge properties were found to be the same for all mixing regimes and that faster reaction rates are achieved using central addition, all subsequent experimentation was conducted by injecting the neutralizing agent at the center of the reactor. No baffles in the reactor were required to achieve this.

4.1.2 Effect of Agitation Rate

The effect of agitation rate in the reactor system was also examined. A neutralization experiment conducted at an agitation rate of 345 rpm showed identical results in the settling rate times (24 hours) and the treated effluent quality (Fe concentration less than 0.4 ppm) to an experiment that was performed at 645 rpm, the limit of the equipment set-up (Table 4.2). The percentages by weight of solids in the precipitated sludges were also similar within experimental error for the two agitation rates.

The neutralization times were different at 17.9 minutes for the 345 rpm experiment and 15.5 minutes for the 645 rpm

Table 4.2

Comparison Between Two Agitation Experiments
Using 20% $Mg(OH)_2$

	345 rpm	645 rpm
Initial Fe Concentration (ppm)	35	34.5
Reaction Temperature (°C)	20.0	19.9
Mass of $Mg(OH)_2$ in Slurry (±0.001g)	0.233	0.234
Mass of Slurry (±0.001g)	1.167	1.167
Final pH (±0.01)	8.98	8.97
Reaction Time (minutes)	17.9 ± 0.85	15.5 ± 0.05
Fe Concentration after Neut.(ppm)	<0.4 *	<0.4 *
Neutralization Capacity (%)	98.9	98.8
Time for Complete Settling (hr.)	24	24
Percent Solids in sludge (%)	1.6 ± 0.15	1.68 ± 0.29
Conc. of Mg in solution after neut. (ppm)	172	166

* limit of detection on atomic absorption spectrophotometer

experiment. This indicates that agitation conducted at 345 rpm provided slower contact between the neutralizing slurry and the acidic solution and therefore the rest of the experiments were performed at 645 rpm. As noted previously, in the discussion pertaining to mixing properties, when a mixing speed of 645 rpm was used, no dead volumes were identified and complete mixing was achieved rapidly (1-2 seconds).

4.1.3 Summary

Through the above process of selecting a reactor configuration, mixing rate and location for neutralizer addition, it was possible to minimize reaction time and obtain reproducible properties within the physical constraints of the bench scale reactor system used in this study. Having set these reactor hydrodynamic parameters, the effect of other variables upon the process could then be examined.

4.2 Effect of Iron Ions on Titration using $Mg(OH)_2$

Magnesium hydroxide was used to titrate a 525 cm^3 acidic solution with a starting pH of 2.0 as well as an acidic solution with the same starting pH and volume but containing 23.3 ppm of iron. It is shown in Figure 4.3 that the usual trends in titration are observed for both curves.

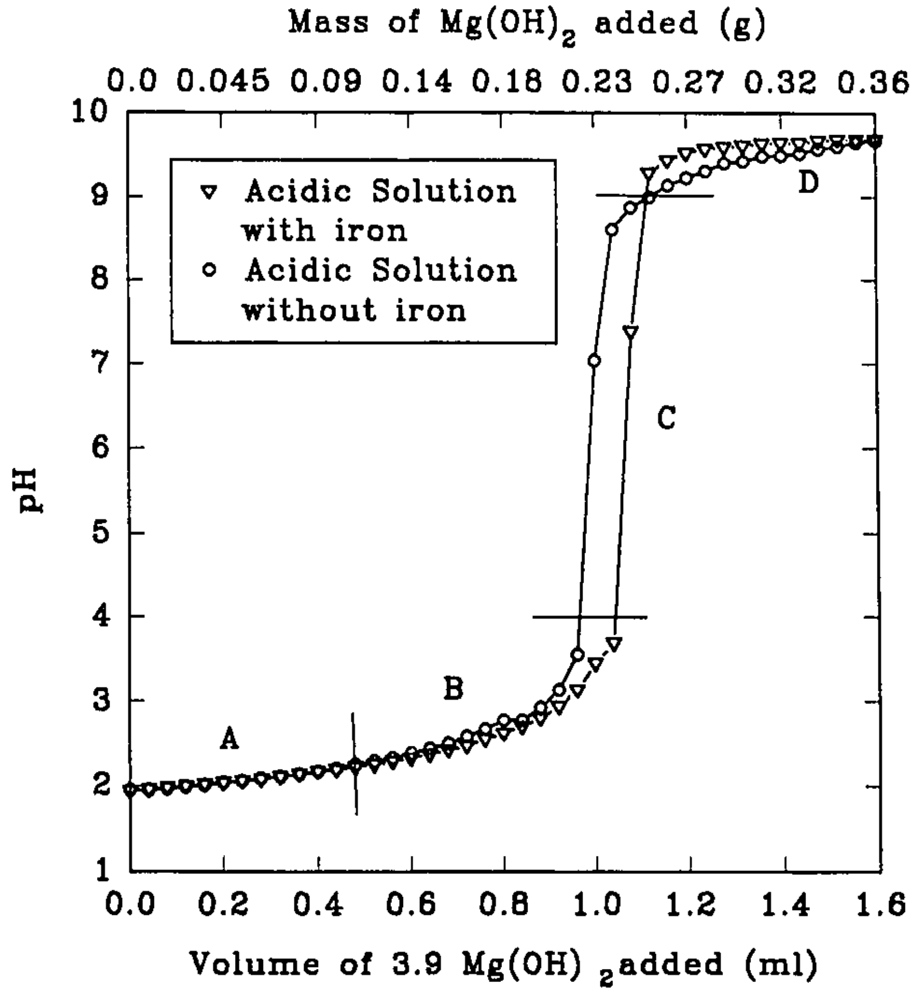

Figure 4.3 Titration curves for acidic solutions with and without iron using $Mg(OH)_2$

Neutralization using magnesium hydroxide is considered a two-step reaction (Teringo, 1986). Since magnesium hydroxide is sparingly soluble, it achieves an equilibrium with water where only a limited amount of magnesium and hydroxyl ions are present. Acid must consume the hydroxyl ions before more magnesium hydroxide can dissolve to release additional hydroxyl and magnesium ions.

The titration curves can be sectioned into four regions (A, B, C and D). Region A illustrates that the presence of iron in the acidic solution does not affect the pH of the solution as titration occurs until a pH of 2.2 is reached. After a pH of 2.2 is surpassed, the two titration curves in Figure 4.3 separate and this is attributed to the beginning of the crystallization process of iron hydroxide precipitates (Region B). Nucleation is defined as the process whereby molecules in solution randomly approach each other and form small aggregates (Harris, 1991). Metal precipitation continues until the iron ions are depleted at a pH of approximately 4. This is confirmed by Environment Canada (1987) which determined that ferric hydroxide is almost completely insoluble at a pH of 4.3. In region C, the titration curve for the solution that had contained iron ions then increases sharply with addition of more $Mg(OH)_2$, similar to the behaviour of the titration curve for the solution without iron ions.

In region C, at which the equivalence points of both reactions are located, the difference in the equivalence points is explained by iron hydroxide precipitation. It should also be noted that in both cases (with or without iron) more $Mg(OH)_2$ was required than theoretically predicted by F*A*C*T, a thermodynamics program based on free energy minimization (Thompson et al.,1985). Through atomic absorption analysis for Mg in solution, it was determined that approximately 58% of the magnesium hydroxide was dissociated at the equivalence point during the titration of both solutions.

Magnesium hydroxide is known to exhibit a buffering effect, and thus it was expected that the two titration curves would converge to a pH of about 9 to 9.5. Region D of Figure 4.3 demonstrates this effect.

As stated in the introduction, the buffering behaviour is a major advantage in the use of magnesium hydroxide as a precipitating and neutralizing agent for acidic effluents because any overdosing during neutralization would not be detrimental since a final pH of approximately 9 would always be obtained. This pH coincides with the upper discharge limit of the Clean Water Act (Teringo, 1990).

Figure 4.3 can also be used to determine the approximate amount of magnesium hydroxide required for neutralization to a pH of 7. This was calculated to be approximately 0.245 ± 0.002 g of magnesium hydroxide for the specific case tested. An excess of magnesium hydroxide was used in all subsequent experiments in order to ensure complete precipitation of the iron in solution and to have a slightly higher pH to ensure pH stability when the neutralized solution is discharged. Excess amounts of up to 0.445 g of magnesium hydroxide per 500 cm^3 of effluent were tested in experiments described later.

4.3 Neutralizer Concentration Results

Two sets of experiments were conducted in order to determine the effect of neutralizing agent concentration on the neutralization of an acidic effluent containing iron ions. The initial iron content in the acidic solution was 23.3 ± 1.25 ppm and the reactions were performed at 20°C for both sets of experiments. The first set of experiments was performed with various weight percentages of magnesium hydroxide in the slurries but the total slurry mass was held constant. The second set of experiments involved varying the percentage of the magnesium hydroxide in the slurry once again, however, the mass of magnesium hydroxide in the slurry was held constant.

4.3.1 Effect of Increased $Mg(OH)_2$ Concentration at Constant Slurry Mass

Experiments were conducted at constant total slurry mass at the three concentrations of $Mg(OH)_2$ of 10%, 20%, and 30% by weight (Table 4.3). The magnesium hydroxide weights tested were 0.230 g, 0.460 g, and 0.690 g respectively. The quantity of magnesium hydroxide gives an indication of the degree of neutralization capacity of the neutralizing agent.

Firstly, the criteria of complete neutralization resulting in a final pH of 7 or higher, was not obtained in the concentration experiment using a slurry concentration of 10% $Mg(OH)_2$. A pH of 3.38 was achieved when 0.230 ± 0.001 g of $Mg(OH)_2$ was injected into the acidic solution. One third of the iron that was in the initial acidic solution was removed because the start of ferric hydroxide precipitation occurs at a pH of approximately 2.2 as mentioned above (c.f. section 4.2). Because ferric hydroxide particulates have a characteristic colour of red-brown (Pourbaix, 1974). It was physically apparent during experimentation that some metal precipitation had occurred since the solution had turned a light rust-orange colour. In addition, it is also possible that some iron was removed from solution by magnesium hydroxide particles since magnesium hydroxide is known to have the capacity to directly remove metals through surface adsorption (Teringo, 1986).

Table 4.3

Experimental Results of Various $Mg(OH)_2$ Concentrations at Constant Slurry Mass

	10% $Mg(OH)_2$	20% $Mg(OH)_2$	30% $Mg(OH)_2$
Initial Fe Concentration (ppm)	24	24	23
Reaction Temperature (°C)	19.9	20.0	20.0
Mass of $Mg(OH)_2$ in Slurry (±0.001g)	0.230	0.460	0.690
Mass of Slurry (±0.001g)	2.301	2.300	2.300
Final pH (±0.01)	3.38	9.33	9.56
Reaction Time (minutes)	∞	1.4 ± 0.15	0.93 ± 0.03
Fe Conc. after Neut. (ppm)	16.0	<0.4 *	<0.4 *
Neutraliz. Capacity (%)	33.3	98.3	98.3
Time for Complete Settling (hr)	24	1	1
Percent Solids in sludge (%)	1.97 ± 0.37	5.34 ± 0.08	7.36 ± 0.07
Conc. of Mg in solution after neut. (ppm)	206	191	188

* limit of detection on atomic absorption spectrophotometer

The remaining concentration experiments did achieve neutralization capacities of greater than 98.3% removal of the initial iron present in solution. The quality of the treated effluent of the 20% and 30% $Mg(OH)_2$ experiments with respect to the concentration of iron was well below the water discharge standard of 1 ppm.

In comparing the reaction times, the neutralization reaction utilizing 10% $Mg(OH)_2$ never reached a pH of 7 and thus by the definition of reaction time in section 3.2, an infinite amount of time was required. The reaction using 30% $Mg(OH)_2$ had a faster reaction time at 0.93 minutes as compared to 1.4 minutes for the reaction using 20% $Mg(OH)_2$. This response is explained by the fact that 1.5 times the amount of magnesium hydroxide was present in the 30% $Mg(OH)_2$ neutralizing agent as compared to that in the 20% $Mg(OH)_2$ (Figure 4.4).

Since the reaction using 10% $Mg(OH)_2$ did not have sufficient alkaline capacity for complete metal precipitation, the agglomerated ferric hydroxide particles that were formed were visibly smaller due to the reduced crystal growth stage of metal precipitation and required 24 hours for complete settling.

In the cases where neutralization was performed using 20% and 30% $Mg(OH)_2$, the final pH values obtained were 9.33

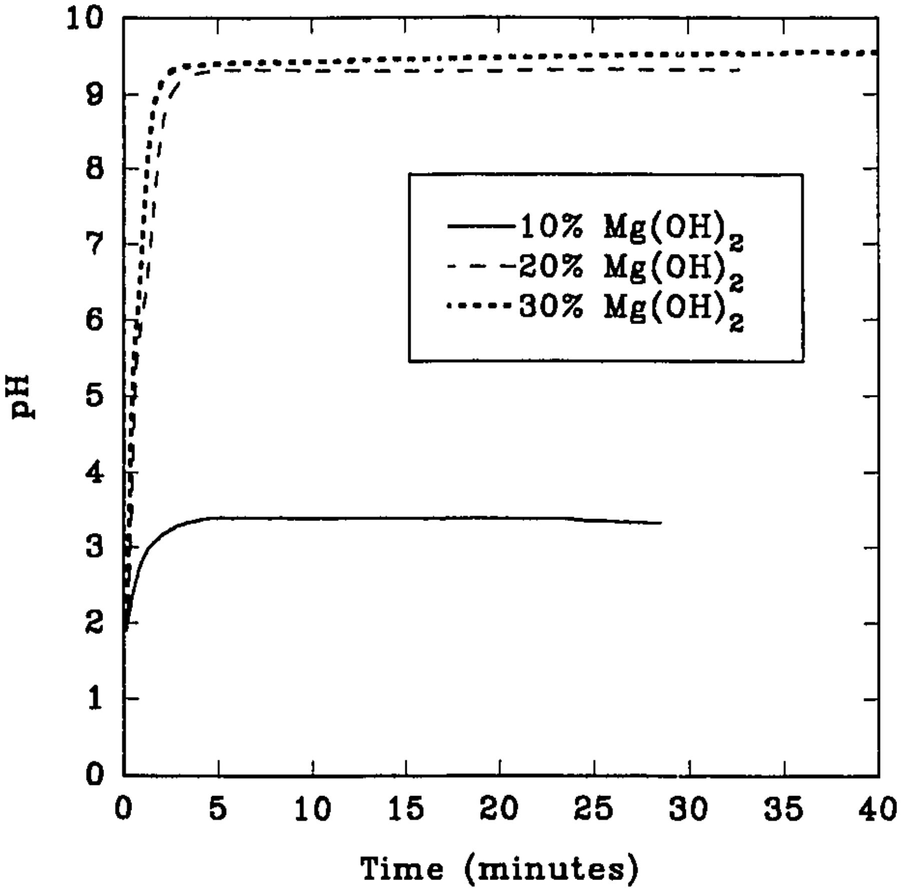

Figure 4.4 Effect of slurry concentration on time of reaction at constant total slurry mass

and 9.56, respectively. Ferrous hydroxide begins to form at approximately a pH of 9 and this was physically demonstrated by the fact that white precipitates were present in the reactor after neutralization. Ferrous hydroxide is characteristically white in contrast to ferric hydroxide which forms as a red-brown precipitate as noted above. In fact, at the final pH after neutralization using the 20% $Mg(OH)_2$, a faint trace of rust-orange precipitate was still visible in the sludge produced, but after a period of 16 hours, the particulates were entirely white. By observation of the precipitate colour, this demonstrated that reduction of ferric ions to ferrous ions continued at a very slow rate even after the pH had reached a constant value. After the reduction reaction was completed, the final pH had decreased by 0.18. An alternative expanation for the presence of white precipitates could be due to the excess magnesium hydroxide particles and the surface attraction between $Fe(OH)_3$ and $Mg(OH)_2$.

The difference in colour between the orange-brown ferric hydroxide (from the 10% $Mg(OH)_2$ neutralization) and the lighter coloured ferrous hydroxide (from the 20% $Mg(OH)_2$ neutralization) precipitates obtained in these experiments can be seen in Plates 4.1 and 4.2. These amorphous precipitates which have agglomerated, are shown enlarged 1000 times by using an optical microscope.

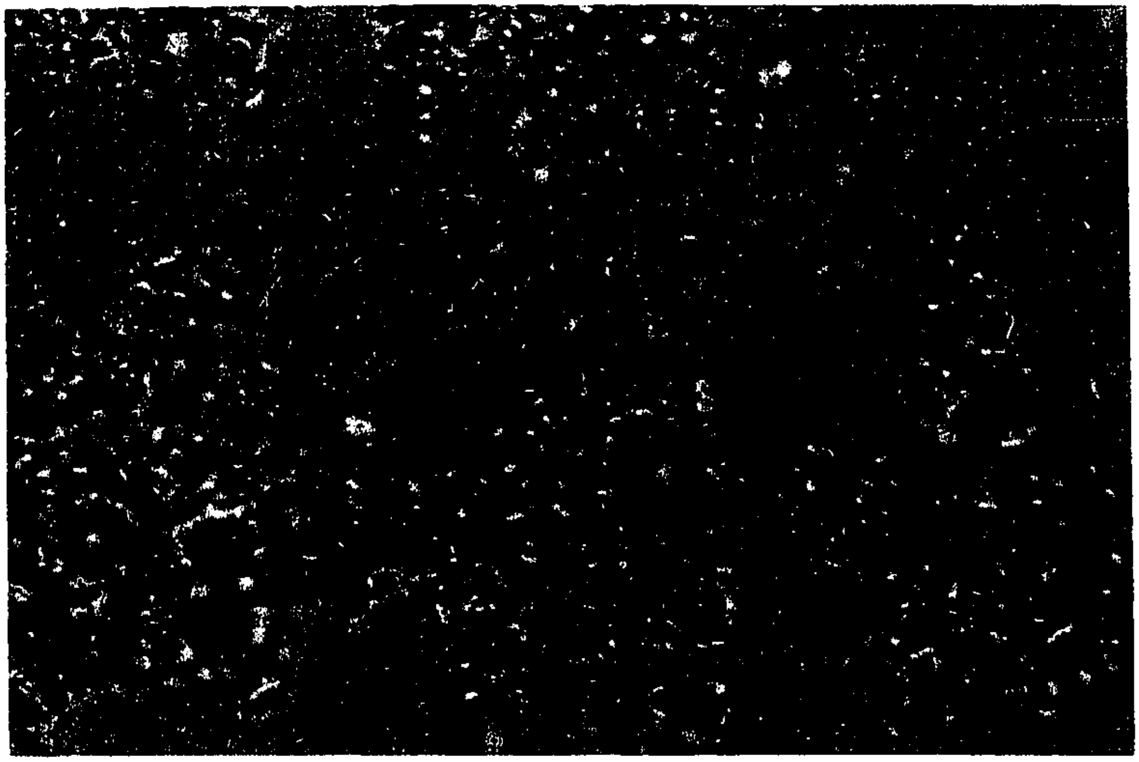

Plate 4.1 Ferric hydroxide formed during neutralization using 10% $Mg(OH)_2$ (magnification=1000 X)

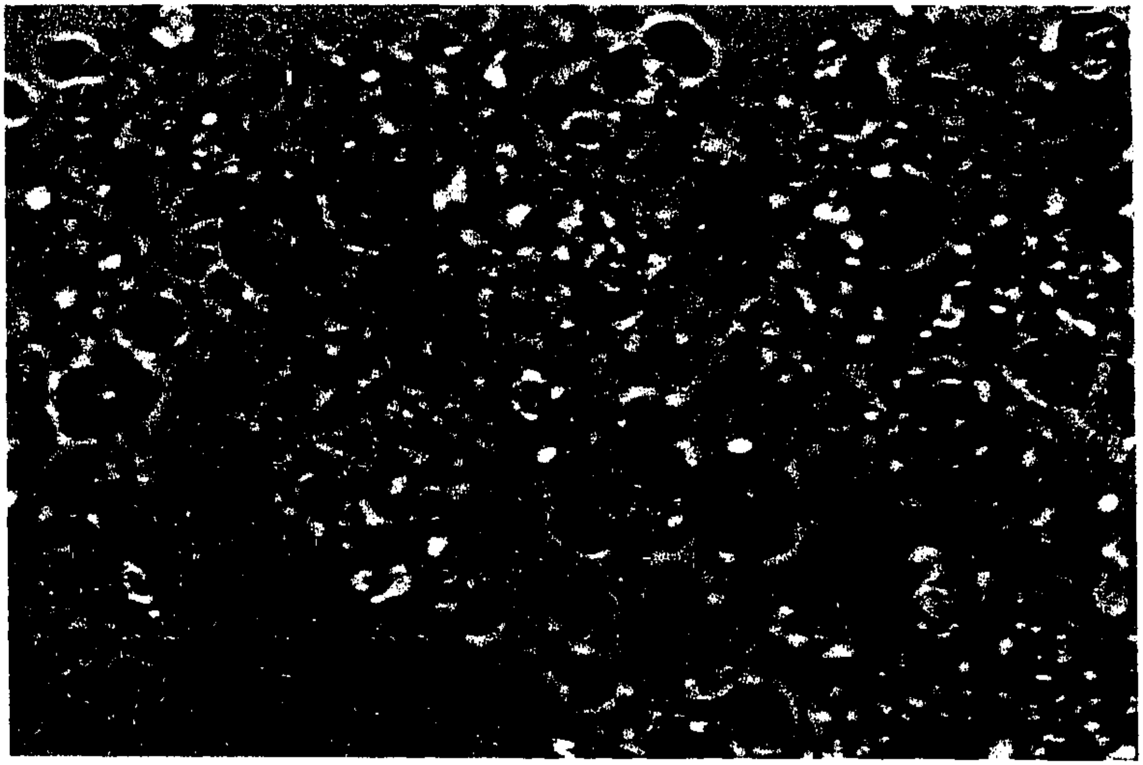

Plate 4.2 Ferrous hydroxide formed during neutralization using 20% $Mg(OH)_2$ (magnification=1000 X)

The excess magnesium hydroxide particles present in experiments using 20% and 30% $Mg(OH)_2$ showed the following results. Firstly, the percent solids of the experiment using 30% $Mg(OH)_2$ was approximately 1.4 times more than that found for the experiment using 20% $Mg(OH)_2$, which was consistent with the excess magnesium hydroxide weight added in the neutralizing agent in comparing the two cases. In addition to the white colour of the sludges, the sludges for both the 20% and 30% $Mg(OH)_2$ were also found to settle within 1 hour, significantly faster than when 10% $Mg(OH)_2$ was used. It is proposed that excess $Mg(OH)_2$ acts as seeds for larger crystal growth resulting in a faster settling sludge. This could be confirmed by testing the precipitates for heterogeneity.

4.3.2 Effect of Slurry Concentration at Constant $Mg(OH)_2$ Mass

In the second group of experiments, the concentration of total magnesium hydroxide slurry was varied (10%, 20%, and 30% $Mg(OH)_2$ slurry) but all neutralization reactions using these concentrations had a constant $Mg(OH)_2$ mass of 0.260 ± 0.001g when added to the iron-containing acidic solution. This quantity of magnesium hydroxide was in excess of the amount required for neutralization to a pH of 7 because final pH readings ranged from 8.81 to 9.04. Therefore, the resulting sludge in the neutralized solution contained some magnesium hydroxide particles. The results of these neutralizer concentration experiments are found in Table 4.4. Since all of these experiments were performed using a constant mass of $Mg(OH)_2$ in the neutralizer slurry, the effects seen from the experiments can be attributed to the different concentrations of the neutralizing agent added.

In all three cases (10%, 20%, and 30% $Mg(OH)_2$), the quality of the treated effluent was satisfactory in that the iron removal from the initial solution was greater than 98.2 ± 0.1 %.

It was expected that a higher concentration of neutralizing slurry would have a faster rate of neutralization. This hypothesis was partially verified since the reaction using 20% $Mg(OH)_2$ was twice as fast as the one using 10% $Mg(OH)_2$ (Figure 4.5). However, the same trend was not observed with the 30% $Mg(OH)_2$ neutralization in which case the observed reaction time was slower than the 20% $Mg(OH)_2$ reaction by a factor of 3. In order to investigate this observation, the neutralizing agent properties were examined as were the properties of the sludge product.

The pH readings and particle size of the magnesium hydroxide in each neutralizer slurry were investigated to

Table 4.4

Experimental Results of Various $Mg(OH)_2$ Concentrations at Constant $Mg(OH)_2$ Mass

	10 % $Mg(OH)_2$	20% $Mg(OH)_2$	30% $Mg(OH)_2$
Initial Fe Concentration (ppm)	24.5	22	24.5
Reaction Temperature (°C)	20.0	20.0	20.0
Mass of $Mg(OH)_2$ in Slurry (±0.001g)	0.260	0.260	0.261
Mass of Slurry (±0.001g)	2.604	1.302	0.868
Final pH (±0.01)	9.01	9.04	8.81
Reaction Time (minutes)	11.2 ± 0.8	5.7 ± 0.05	17.1 ± 0.55
Fe Conc. after Neut. (ppm)	<0.4 *	<0.4 *	<0.4 *
Neutraliz. Capacity (%)	98.4	98.2	98.4
Time for Complete Settling (hr)	2	2	4
Percent Solids in sludge (%)	0.87 ± 0.07	1.28 ± 0.07	0.97 ± 0.10
Conc. of Mg in solution after neut. (ppm)	185	176	185

* limit of detection on atomic absorption spectrophotometer

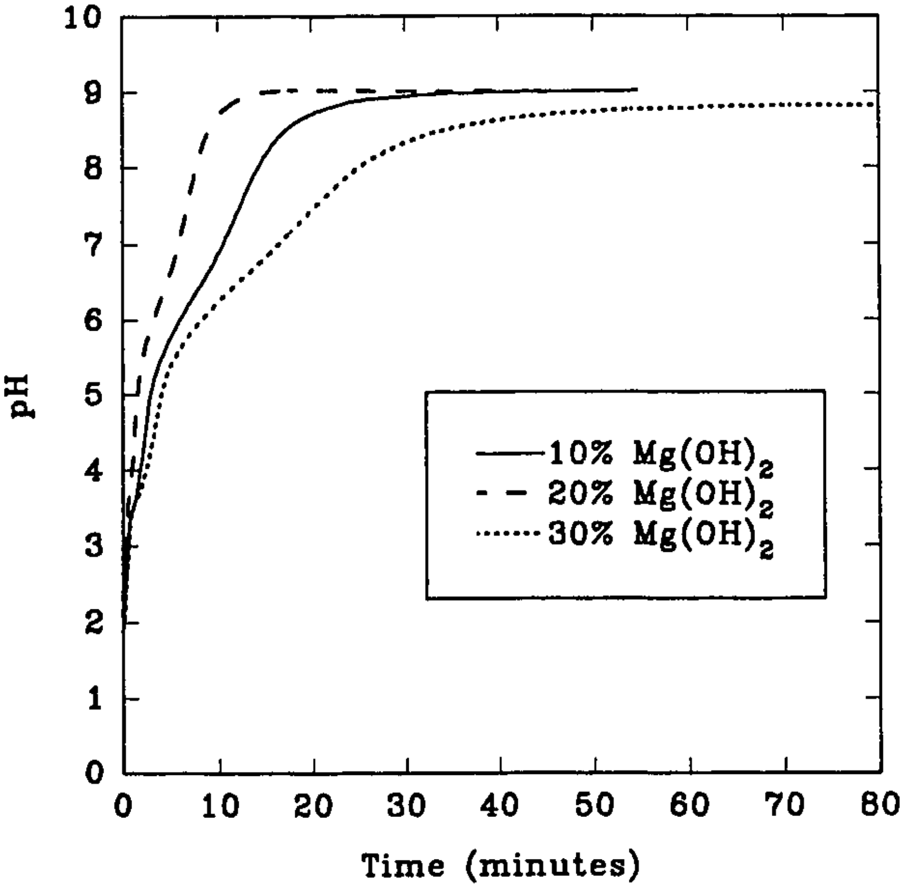

Figure 4.5 Effect of slurry concentration on time of reaction at constant $Mg(OH)_2$ mass

determine if these factors contributed to the different reaction times observed. It was found that the 10%, 20%, and 30% $Mg(OH)_2$ slurries had similar pH values of 9.73, 9.77 and 9.70 ± 0.01 respectively.

A comparison of the particle size distributions of neutralizing agent slurries as determined by the Malvern Particle Sizer 2600 series, are presented in Figure 4.6. In the 10% $Mg(OH)_2$ slurry, over 95% of the particles had sizes ranging from 1.9 to 17.7 µm with the median particle size at 8.0 µm, with a standard deviation (σ) = 4.4 µm. For the 20% $Mg(OH)_2$ slurry, over 99% of the particles had sizes ranging from 1.9 to 23.8 µm with the median particle size at 7.3 µm and $\sigma = 3.6$ µm. Finally, for the 30% $Mg(OH)_2$ slurry, over 99% of the particles had sizes ranging from 1.9 to 23.8 µm with the median particle size at 8.4 µm, and the $\sigma = 3.4$ µm. Since the median particle size of particles in the neutralizing agent slurries were all similar, mass transfer effects due to the dissolution of the particles of the magnesium hydroxide did not contribute to the difference in the reaction times between the experiments.

The resulting sludge from the 30% $Mg(OH)_2$ neutralization required 4 hours to settle in contrast to the 2 hours required for settling of the sludge produced from the 10% and 20% $Mg(OH)_2$ neutralizations. This suggests that the following reaction mechanism may have occurred.

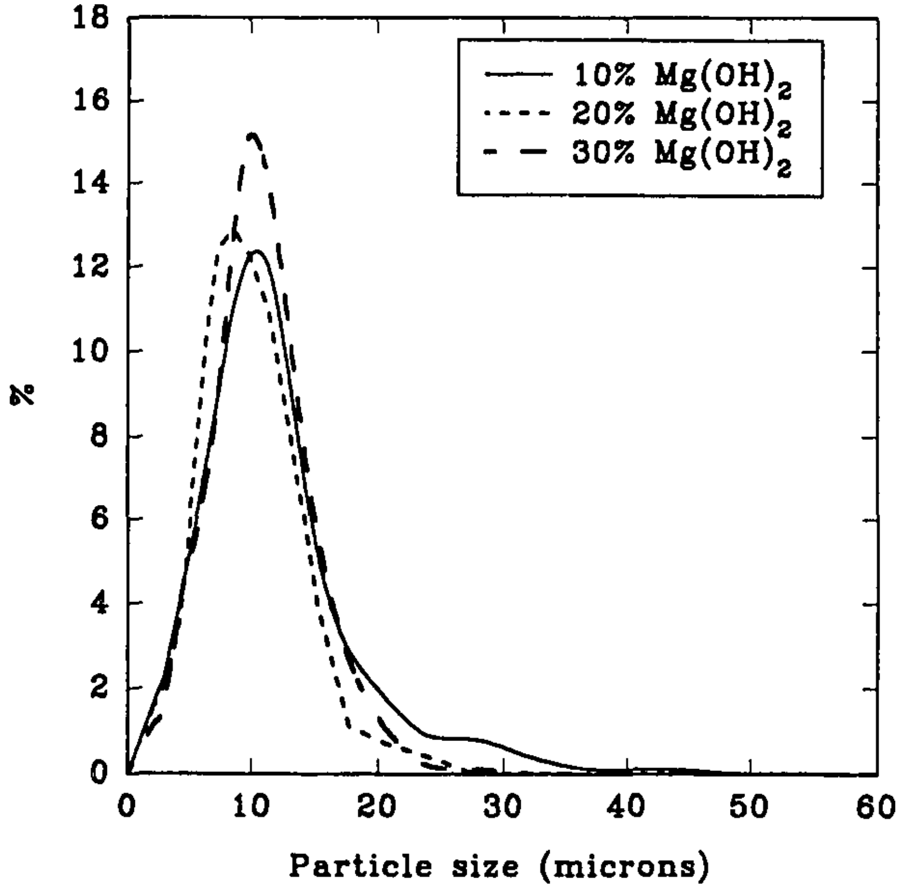

Figure 4.6 Effect of $Mg(OH)_2$ concentration on particle size distribution of the slurry

At the instant that 30% $Mg(OH)_2$ contacted the acidic solution, the pH surrounding the slurry particles may have been increased enough to precipitate ferrous hydroxide at the interface of the acidic solution and the slurry particle surface encapsulating the $Mg(OH)_2$, and rendering it temporarily ineffective for neutralization or iron precipitation. As mixing in the reactor system distributed the neutralizing agent, the pH conditions surrounding the particles became more acidic and the ferrous hydroxide was reconverted to its constituents due to the solubility of ferrous hydroxide in an acidic solution. This process would cause a delay in the nuclei formation and crystal growth phases of ferric hydroxide precipitation when compared to the neutralization using 20% $Mg(OH)_2$ resulting in the formation of smaller ferric hydroxide particles which would take longer to settle.

Therefore, the 30% $Mg(OH)_2$ slurry would not be recommended since the reaction time is slow; sludge quality is poor and there would be more difficulty in pumping this concentration of $Mg(OH)_2$ slurry than the 10% or 20% $Mg(OH)_2$ in an industrial process. The optimum slurry concentration for a given effluent would have to be determined by testing a range of values. In this study however, the 20% $Mg(OH)_2$ was found to be the best concentration tested according to the criteria and hence was used in all subsequent experiments.

4.4 Reaction Temperature Effect

Four reaction temperatures of 10°C, 15°C, 20°C, and 25°C were investigated in neutralizing an acidic solution using 20% $Mg(OH)_2$. The results (Table 4.5) indicated that there was no significant difference between the results with respect to either the settling rate of the sludge (within 2 hours) or the treated effluent quality (<0.4 ppm of iron).

The rate of neutralization is affected kinetically by temperature as shown in Figure 4.7. As the reaction temperature was increased by 10°C, the reaction time required for neutralization was approximately halved. For example, reaction time required for neutralization at 25°C is 3.9 minutes while the reaction time required for neutralization at 15°C was 7.5 minutes.

An increase in the reaction temperature had a mild effect on the sludge properties of the iron hydroxide sludge. A 10°C increase in the reaction temperature, increased the percentage of solids in the sludge from 1.10% to 1.28%. Using percent solids as a measure of the density of the sludge, the density of the iron hydroxide sludges produced increased slightly with increased temperature.

The particle size distributions of the iron hydroxide sludges, were not significantly affected by reaction

Table 4.5

Experimental Results of Various Reaction Temperatures Using 20% $Mg(OH)_2$ Slurry Additions

	10°C	15°C	20°C	25°C
Initial Fe Conc. (ppm)	25	24.5	22	25
Reaction Temp. (°C)	10.1	15.1	20.0	25.0
Mass of $Mg(OH)_2$ in slurry (±0.001g)	0.260	0.260	0.260	0.260
Mass of slurry (±0.001g)	1.302	1.302	1.302	1.301
Final pH (±0.01)	9.0	9.03	9.04	9.13
Reaction Time (minutes)	10.8 ± 1.75	7.5 ± 0.25	5.7 ± 0.05	3.91 ± 0.09
Fe Conc. after Neut. (ppm)	<0.4 *	<0.4 *	<0.4 *	<0.4 *
Neutral. Capacity (%)	98.4	98.4	98.2	98.4
Time for Complete Settling (hr)	2	2	2	2
Percent Solids in sludge (%)	1.10 ±0.07	1.12 ±0.07	1.28 ±0.07	1.26 ±0.06
Conc. of Mg in sol. after neut. (ppm)	176	192	176	200

* limit of detection on atomic absorption spectrophotometer

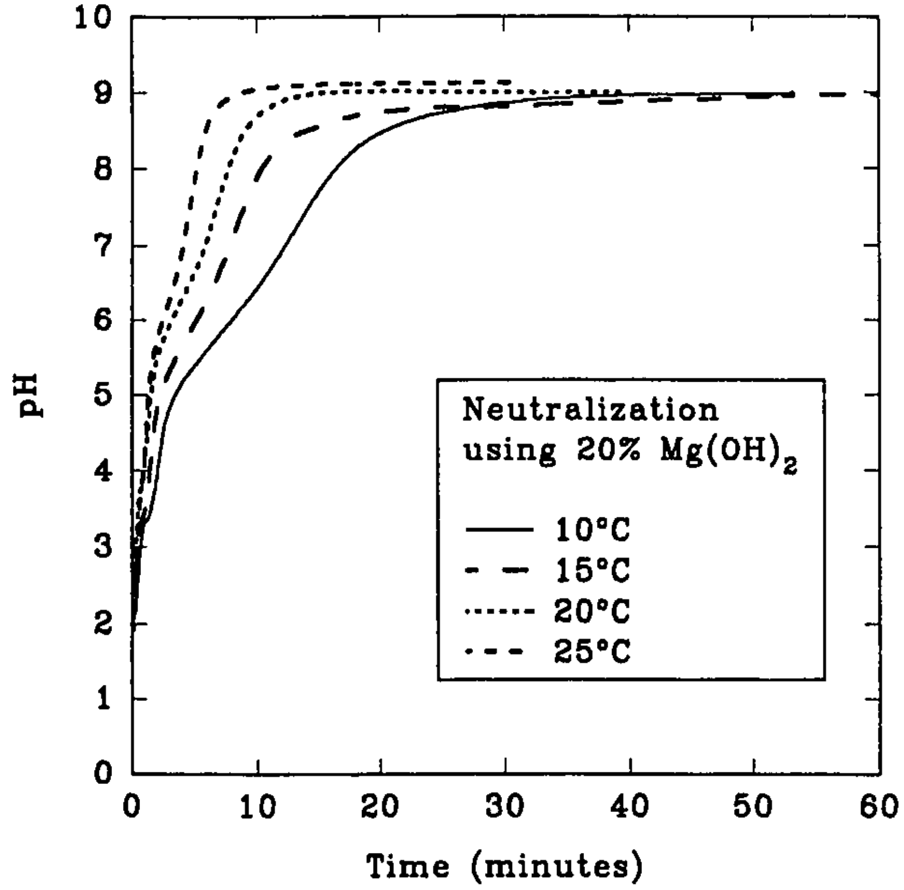

Figure 4.7 Effect of reaction temperature on time of reaction using 20% $Mg(OH)_2$

temperature. The Malvern Particle Sizer 2600 series was used to analyze the neutralized solutions approximately six hours after neutralization. A comparison of the particle size distributions of neutralizations occurring at 10°C and 20°C are presented in Figure 4.8. When neutralization was performed at a temperature of 10°C, over 99% of the particles had sizes ranging from 2.2 to 20.1 µm with the median particle size at 7.4 µm, with a standard deviation (σ) = 3.0 µm. For the 20°C neutralization experiment, over 99% of the particles had particles ranging from 1.9 to 23.8 µm with the median particle size at 6.8 µm with σ = 1.8 µm. Therefore, reaction temperature had a minimal effect on particle size. In summary, increasing reaction temperature from 10°C to 25°C resulted in a decrease in reaction time but had no other significant effects on sludge production or characteristics.

4.5 Rate of $Mg(OH)_2$ Addition Results

The rate at which magnesium hydroxide slurry is added to the iron-containing acidic solution, affected the resulting properties of the metal hydroxide sludge. Table 4.6 presents a comparison between a neutralization performed by a single injection and one added dropwise every 30 seconds for 11 minutes, with both reactions conducted at 25°C. The results showed that the reaction time was faster for the single injection. This is because the dropwise

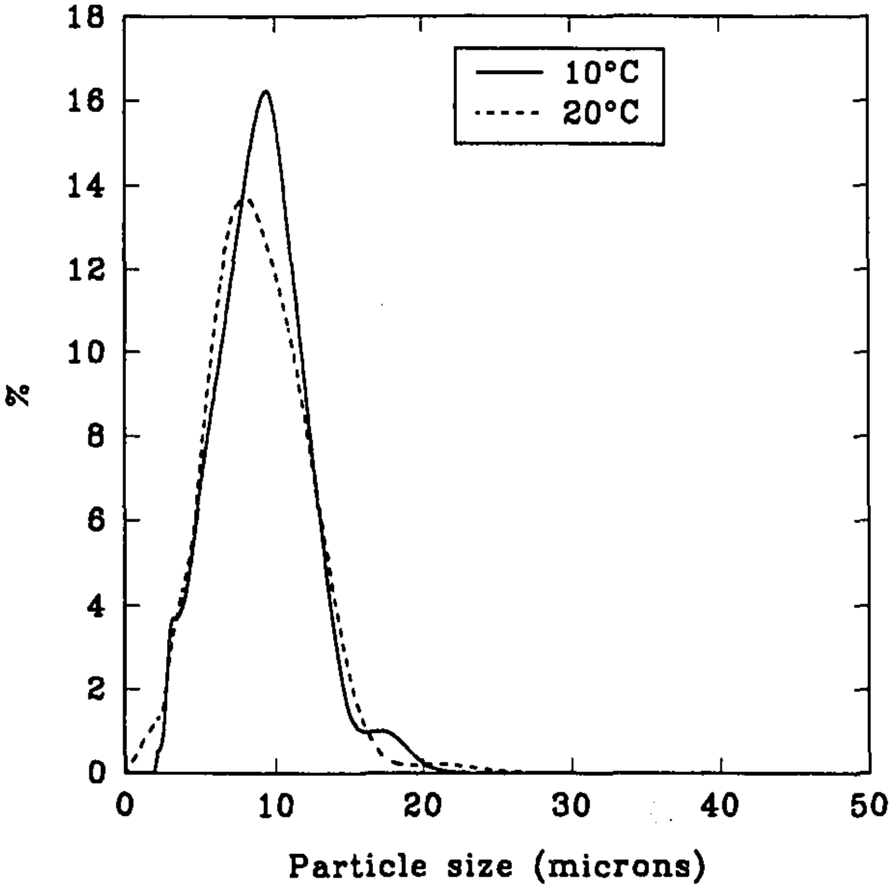

Figure 4.8 Effect of reaction temperature on particle size distribution of the sludge

Table 4.6

Comparison Between Rate of Addition Experiments
Using 20% $Mg(OH)_2$

	Single Addition	Dropwise Addition
Initial Fe Concentration (ppm)	25	25
Reaction Temperature (°C)	25.0	25.0
Mass of $Mg(OH)_2$ in Slurry (±0.001g)	0.260	0.260
Mass of Slurry (±0.001g)	1.301	1.301
Final pH (±0.01)	9.13	9.14
Reaction Time (minutes)	3.91 ± 0.09	12.5 ± 0.25
Fe Concentration after Neut. (ppm)	<0.4 *	<0.4 *
Neutralization Capacity (%)	98.4	98.4
Time for Complete Settling (hr.)	2	2
Percent Solids in sludge (%)	1.26 ± 0.06	1.56 ± 0.06
Conc. of Mg in solution after neut. (ppm)	200	186

* limit of detection on atomic absorption spectrophotometer

method required more time for the level of magnesium hydroxide to accumulate in the acidic solution until adequate neutralization capacity was present to neutralize the acidic solution (Figure 4.9).

For both types of addition, there were no differences found in the final pH readings, the treated effluent qualities and the settling rates. However, the sludge density as measured by the percentage of solids in the settled material, formed from the dropwise addition was higher at 1.56% than the single addition experiment which was measured to be 1.26%. A potential explanation for the relationship between sludge density and method of neutralizer addition could be as described below.

In the process of crystallization (Nielsen, 1964), two phases occur: nucleation and particle growth, where particle growth involves the addition of more molecules to the nucleus to form a crystal. The rate of these two phases is found to be dependent on the degree of supersaturation of the solute in solution. The more substance that is dissolved, the greater the supersaturation. A highly supersaturated solution promotes a faster nucleation rate which results in a suspension of very tiny particles which is undesirable in this application. In contrast, a decrease in supersaturation promotes particle growth. It is known that a rapid addition of the neutralizing agent into the

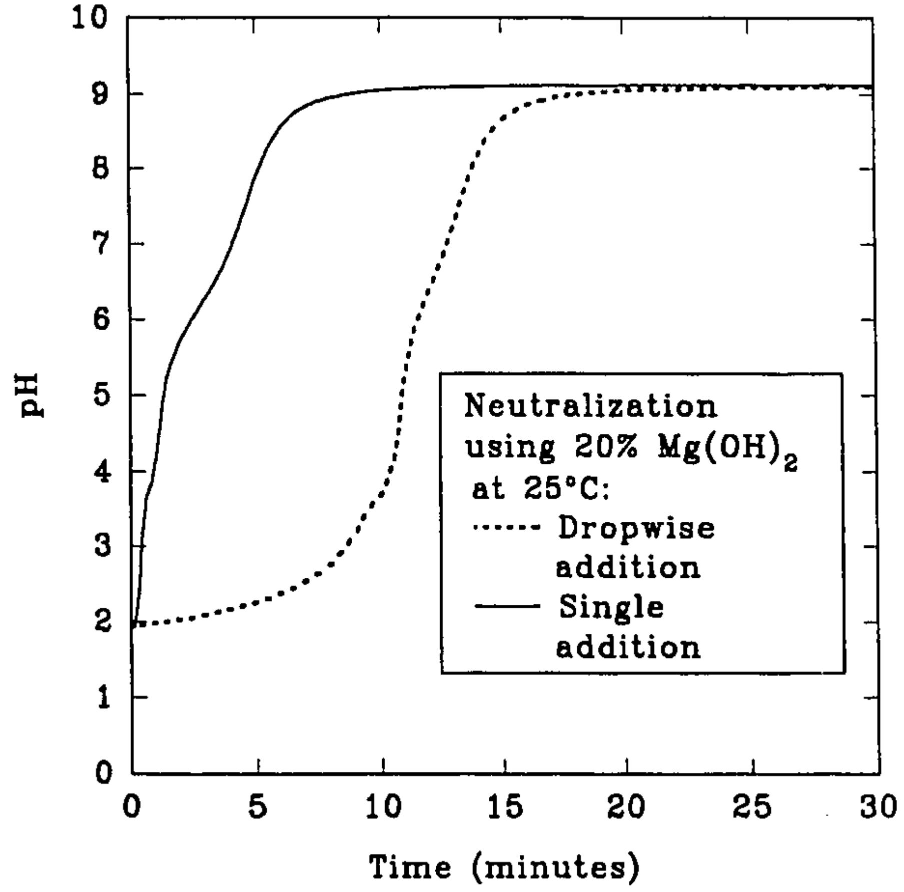

Figure 4.9 Effect of rate of addition of neutralizing agent on the time of reaction

solution causes a highly supersaturated condition locally at the point of contact between the solution and the neutralizing agent which is not conducive to particle growth. Slow addition of the $Mg(OH)_2$ slurry with vigorous mixing decreases the supersaturation in the solution and promotes particle growth.

Additional experiments were done to further investigate the effect of rate of neutralization on the metal hydroxide sludge properties. This experiment involved repeating the above single addition using the same conditions, however, the neutralizing agent to be injected was divided into two equal portions. After adding half of the neutralizing agent to the iron-containing acidic solution, the pH was allowed to stabilize before the remainder of the neutralizing agent was added (Figure 4.10). A pH of 2.31 was obtained. The second portion of neutralizing agent was then injected. The quality of the treated effluent in both cases of one addition or two additions of neutralizing agent, were within the regulatory standards and the time periods required for sludge settling were also similar.

However, the particle size distributions of the sludge particles from the two cases were different. It was expected that by adding half the neutralizer separately, nuclei of ferric hydroxide would form and would become the seeds for further particle growth. This was in fact the

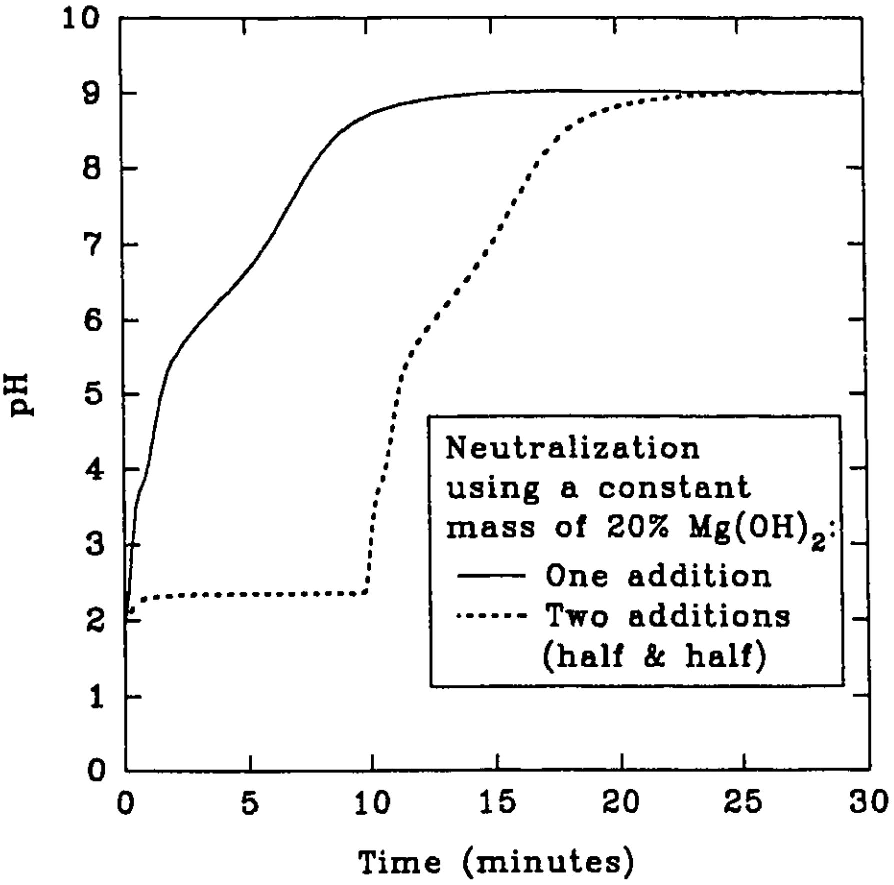

Figure 4.10 Effect of method of neutralizer addition on time of reaction

case as illustrated in Figure 4.11 by the increase in the number of larger particles. This is also confirmed by the results from the decanted sludge properties where 1.41% solids formed in the two step neutralization as compared to the 1.28% solids formed in the single addition.

4.6 Recycle Results

In order to investigate the effect of recycle in the neutralization reaction, the metal hydroxide sludge that was produced from the reaction described in section 4.5 using a single injection of 0.260 g of $Mg(OH)_2$ was used as the recycle. Two recycle experiments were performed: Case 1) recycle particles were added immediately after the $Mg(OH)_2$ slurry was added to the iron-containing acidic solution, and Case 2) recycle particles were added before the neutralizing agent was added. The results are tabulated in Table 4.7.

In comparing the recycle experiments to the experiment with no recycle, it was noted that all three treatments produced effluents that contained iron in solution at concentrations below 0.4 ppm. The reaction times required for the experiments of no recycle, recycle immediately after neutralizing agent addition, and recycle before neutralizing agent addition, were 5.76, 5.29 and 4.9 minutes respectively (Figure 4.12). It should be noted that in the case of recycle addition before the neutralizing agent addition, the

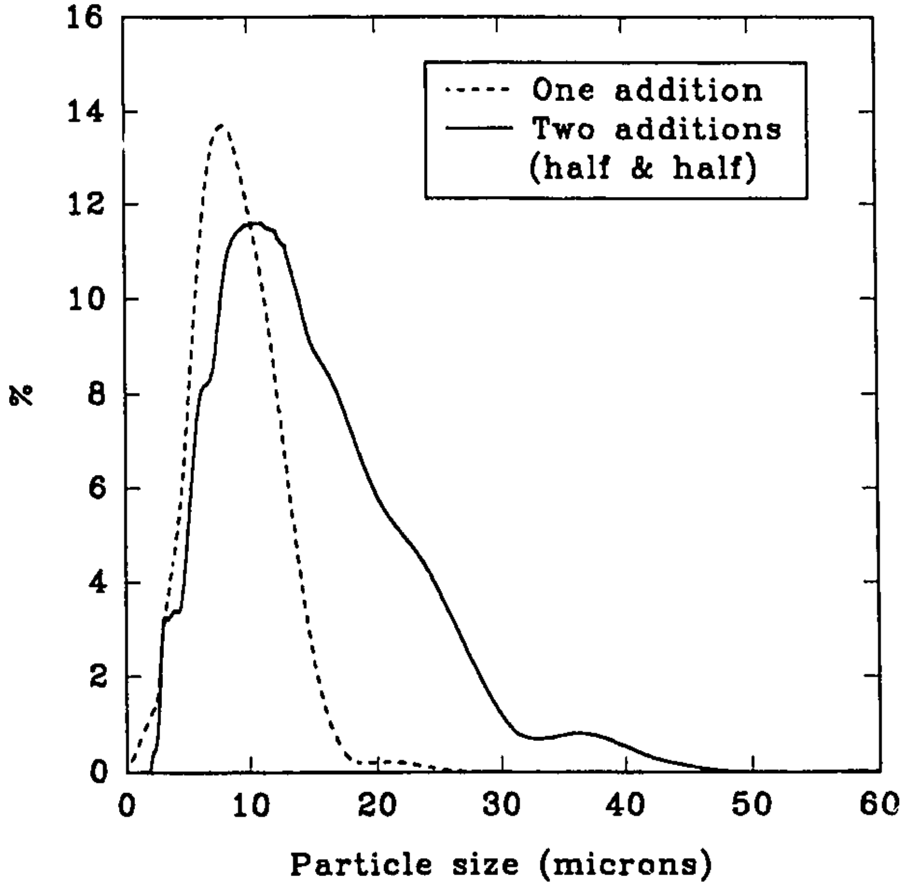

Figure 4.11 Effect of method of neutralizer addition on particle size distribution

Table 4.7

Experimental Results of Recycle Tests
Using 20% $Mg(OH)_2$

	No Recycle	Recycle After Neut. Agent Addition	Recycle Before Neut. Agent Addition
Initial Fe Concentration (ppm)	22	25	25
Reaction Temperature (°C)	20.0	20.0	20.0
Mass of $Mg(OH)_2$ in Slurry (±0.001g)	0.260	0.261	0.260
Mass of Slurry (±0.001g)	1.302	1.303	1.301
Final pH (±0.01)	9.04	9.06	8.97
Reaction Time (minutes)	5.7 ± 0.05	4.9 ± 0.2	5.2 ± 0.2
Fe Conc. after Neut. (ppm)	<0.4 *	<0.4 *	<0.4 *
Neutraliz. Capacity (%)	98.2	98.4	98.4
Time for Complete Settling (hr)	2	2	2
Percent Solids in sludge (%)	1.28 ± 0.07	1.78 ± 0.11	1.54 ± 0.11
Conc. of Mg in solution after neut. (ppm)	176	195	186

* limit of detection on atomic absorption spectrophotometer

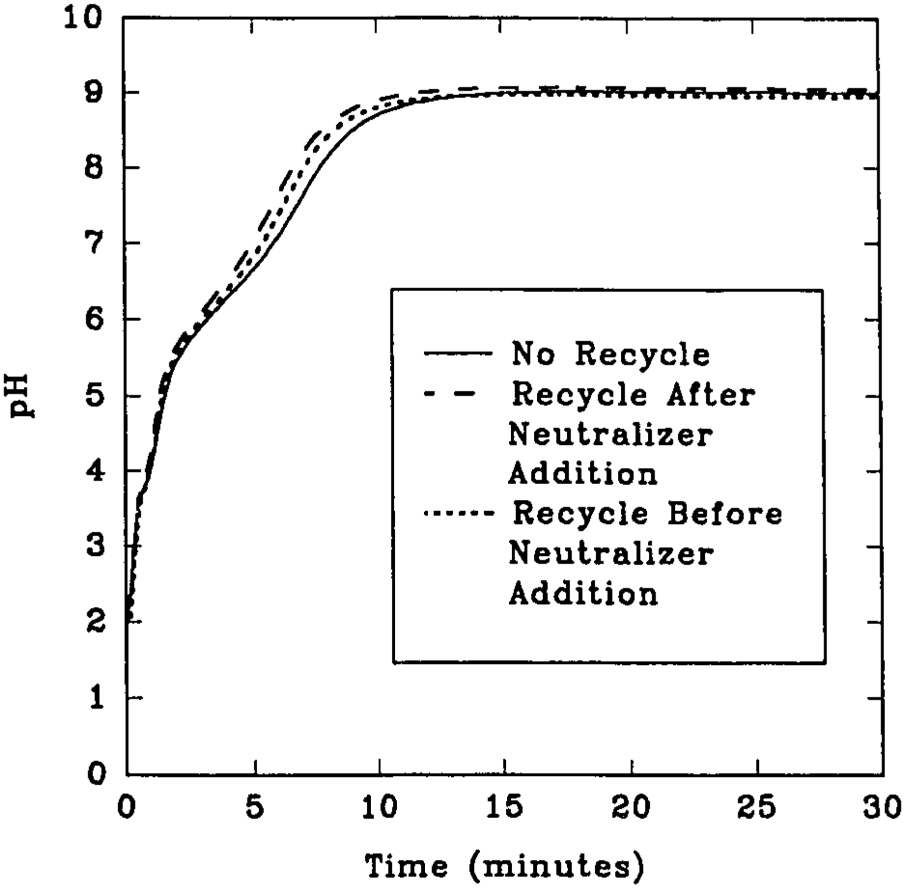

Figure 4.12 Effect of recycle on time of reaction

starting pH value of 2 did not change after the recycle particles were added into the acidic solution. Thus, in Figure 4.12 time t=0 corresponded to the time at which the neutralizing agent was added.

Although the sludges produced in all three experiments settled within two hours, the percentage of solids in the sludge was affected by the recycled sludge material. In both of the recycle cases, the sludges produced were denser; a solids content of 1.78% was found for the case where the recycle was added after the neutralizer and 1.54% solids was found for the case where recycle was added before the neutralizing agent was added. These sludges are both significantly denser than the 1.28% solids that was found for sludges with no recycle.

Results from the particle size distribution analysis (Figure 4.13) show that when recycle particles are added before or immediately after the neutralizing agent, the size distribution of the particles produced is not significantly affected as long as the same quantity of seeds are present for the promotion of crystal growth. Figure 4.13 also shows that recycle experiments produced sludges with larger particle sizes when compared to the case with no recycle. Therefore, recycling of the sludge produced during neutralization is beneficial in that larger particles are produced and excess magnesium hydroxide is not required;

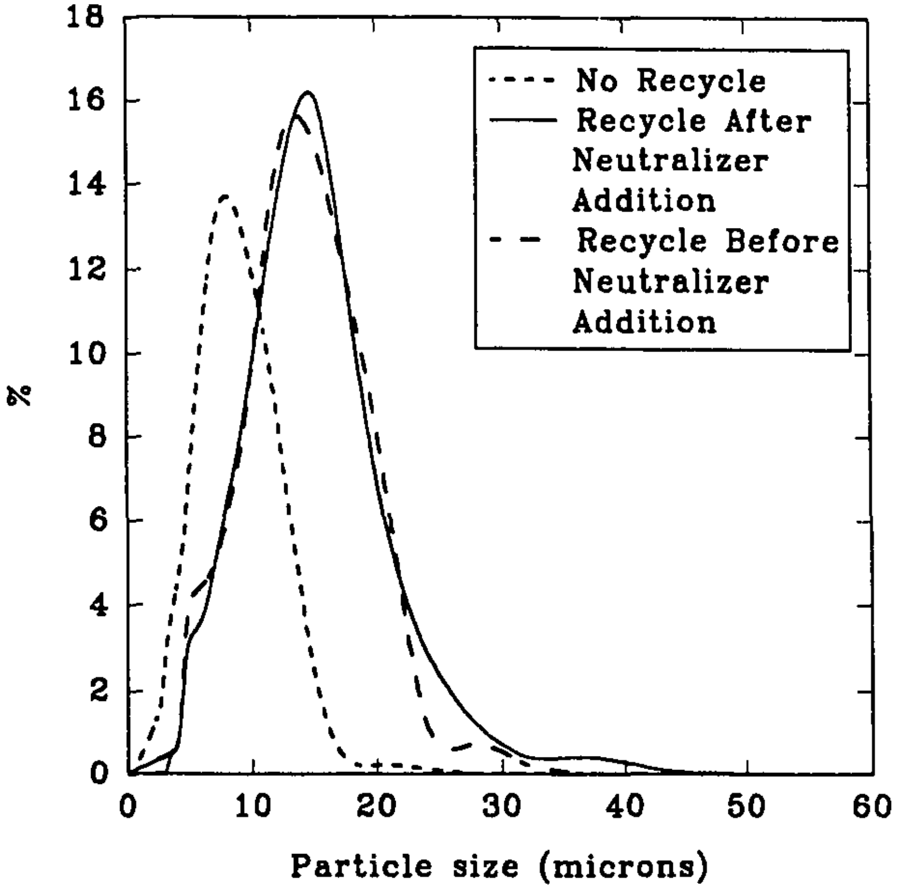

Figure 4.13 Effect of recycle on particle size distribution of sludge

thereby reducing the cost of neutralization and reducing the concentration of magnesium that is discharged into the environment.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The primary objective of this research was to evaluate the effectiveness of magnesium hydroxide as a neutralizing and metal precipitating agent for a simulated iron-containing acidic solution. Several process variables were studied including, $Mg(OH)_2$ slurry concentration and dosage, reaction temperature, rate of $Mg(OH)_2$ addition and recycle. The results of the neutralization experiments were compared on the basis of $Mg(OH)_2$ slurry neutralizing capacity neutralization time, resulting sludge settling rate and percent solids content and quality of the treated effluent.

5.1 Conclusions

1. Magnesium hydroxide was found to be an effective neutralizing agent in all concentrations tested (10%, 20%, and 30% $Mg(OH)_2$) for the removal of iron in an acidic solution as long as the resulting effluent pH was greater than 8.8. Greater than 98.3% iron removal was achieved in all such cases.

2. Increasing magnesium hydroxide slurry concentration decreases the neutralization time required. However, beyond a threshold magnesium hydroxide slurry concentration, a ferric hydroxide-ferrous hydroxide precipitation mechanism

has an inhibiting effect on the neutralization time and the sludge production and properties.

3. By comparing the titrations using a $Mg(OH)_2$ slurry of an iron-containing acidic solution with that of an acidic solution containing no iron, it was determined that the onset of iron hydroxide crystallization occurs at a pH of approximately 2.2.

4. At lower pH values (2.2 to 4.3) the sludge consists primarily of reddish brown hydroxide while at higher pH values (9.3 to 9.7) the sludge consists primarily of ferrous hydroxide.

5. Magnesium hydroxide exhibits a buffering effect which stabilizes the pH between 8.8 to 9.7, even with overtreatment of an iron-containing acidic solution.

6. Increasing reaction temperature from 10°C to 25°C results in decreased reaction time but has no significant effects on sludge production or characteristics.

7. In general, process conditions which promote larger sludge particle formation result in a denser, faster settling sludge.

8. In comparison with a single addition of $Mg(OH)_2$ to an acidic solution, dropwise addition or segmented addition promotes larger particle growth of the iron hydroxide sludge particles.

9. Recycling of sludge particles to a neutralization process improves the crystallization process of iron hydroxide by providing nuclei for crystal growth. Recycling of sludge particles is advantageous because larger particles are produced resulting in a denser sludge and excess magnesium hydroxide is not required, thereby reducing the cost of neutralization and reducing the concentration of magnesium discharged to the environment.

5.2 Recommendations

Further analysis of the resultant precipitates obtained after magnesium hydroxide treatment for heterogeneity and exact chemical composition would provide a better indication of the mechanism of the neutralization and metal precipitation reactions.

Although the reaction temperature experiments (10°C - 25°C) did not show significant advantages in terms of the sludge properties, further investigation should be done at temperatures below 10°C to determine if sludge properties are affected at these temperatures since they occur in the Canadian climate.

Optimization of the concentration of $Mg(OH)_2$ slurry to be used for neutralization must be performed to ensure that sludge properties are optimal and that pumping of the slurry is viable.

An optimization of the recycle process used in the project should be performed and compared to results from a High Density Slurry (HDS) process using magnesium hydroxide.

In order to better approximate an industrial process, the neutralization processes with either recycle or a slow rate of neutralizer addition should be further examined in a continuous process. Larger sludge particles are expected.

Aging of the resultant sludge particles should also be investigated to predict what transformations or reactions occur in the sludge particles in landfill. Further approximations to an industrial process would be to test acidic solutions containing a combination of metals or to test actual industrial effluent samples.

Experiments should be conducted to determine the kinetics of the neutralization process using magnesium hydroxide. A rate expression would then be developed so that a successful industrial process based on the use of magnesium hydroxide could then be designed.

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