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**Acid Mine Drainage: Sludge Dewatering, Metal Recovery and Synthesis of
Magnetite Nanoparticles**

Xinchao Wei

**Dissertation submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
In
Civil and Environmental Engineering**

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Department of Civil and Environmental Engineering

**Morgantown, West Virginia
2005**

**Keywords: Acid Mine Drainage, Sludge Treatment, Dewaterability,
Selective Precipitation, Magnetite Nanoparticles
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ABSTRACT

Acid Mine Drainage: Sludge Dewatering, Metal Recovery and Synthesis of Magnetite Nanoparticles

Xinchao Wei

Acid mine drainage (AMD) is one of the significant environmental challenges for the coal and hard-rock mining industry. Traditional AMD treatment generates large volumes of sludge with low solids which are difficult to dewater. In this study, a systematic investigation was carried out on the characteristics and dewaterability of AMD sludge produced from an ammonia neutralization operation, and the dewatering performance of different treatment options. In order to mitigate the AMD sludge problem, a selective precipitation process was developed to recover Fe and Al while AMD was treated simultaneously. In conjunction, a low-cost synthesis approach was examined to prepare magnetite nanoparticles with the recovered iron from AMD, and its implication in environmental engineering was discussed.

The AMD sludge from ammonia neutralization was characterized by high pH and alkalinity, high total Fe and Al, elevated sulfate, and low solids ($0.72 \pm 0.24\%$). Compared to other AMD sludges and metal hydroxide sludges, ammonia-treated AMD sludge demonstrated relatively good dewaterability in terms of specific resistance to filtration. Coagulation and flocculation treatment did not effectively reduce the final volume of the settled sludge. Sludge cakes with 6.2% solids and a filter yield of $3.04 \text{ kg/m}^2\text{h}$ were achieved by vacuum filtration. Additionally, a belt filter press showed a good performance in improving solids content of the sludge cake.

Simultaneous metal recovery and AMD treatment were achieved using a selective precipitation process based on solubility characteristics of the major and minor metals in the AMD. Separate iron and aluminum hydroxide products with relatively high purity were successfully recovered via iron precipitation at pH 3.5-4.0 followed by aluminum precipitation at pH 6.0-7.0, while simultaneously meeting the NPDES effluent discharge standards. The proposed metal recovery process was relatively easy to implement in the field.

An approach to synthesize low-cost magnetite nanoparticles via coprecipitation was developed with the recovered ferric iron from AMD as the iron source. Through scanning and transmission electron microscopic studies, it was demonstrated that most of the magnetite nanoparticles ranged from 10 to 15 nm and were spheroidal or cubic in shape. Consequently, the recovered ferric iron from AMD could be used as a low-cost substitute feedstock for reagent-grade chemical for magnetite nanoparticle preparation, which provided great opportunity for the application of magnetite nanoparticles in environmental engineering.

DEDICATION

*To my parents
for
Their love to my brother, sisters and me*

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1. INTRODUCTION

1.1 BACKGROUND

Acid mine drainage (AMD), formed during present mining activities or at abandoned mine sites, causes environmental problems that can negatively impact ecosystems and human health, due to its low pH, high acidity, elevated concentrations of metals or metalloids, and high sulfate content. The origin of AMD is the result of the accelerated chemical or biochemical oxidation of sulphide minerals, typically pyrite, due to the exposure of these minerals to both water and oxygen. The chemical reactions involved in AMD formation are as follows:

Globally, AMD is one of the most significant environmental challenges facing the coal and hard-rock mining industries, although the true scale of AMD damage to the environment is difficult to estimate accurately (Johnson and Hallberg, 2005; Kuyucak, 2002). In West Virginia alone, AMD has impacted about 3,200 km (~2,000 mi) of streams (Demchik and Garbutt, 1999). Although prevention of AMD is technically the most desirable option, cost-effective prevention approaches are not yet available (Kuyucak, 2002). Consequently, various active and passive treatment processes have been implemented to increase alkalinity of AMD waters and subsequently precipitate metal ions, in order to minimize the adverse impacts of AMD and to meet the more stringent discharge limits imposed by environmental management agencies.

Active treatment involves the continuous addition of neutralizing agents, such as hydrated lime, sodium hydroxide, limestone, ammonia, or soda ash, to AMD waters to raise the pH and precipitate metals (Johnson and Hallberg, 2005; Skousen *et al.*, 1998; Kuyucak, 1998). A major challenge in AMD treatment is management of large volumes of loose sludge, typically containing 1-5% solids, generated through neutralization (Kuyucak, 1998; Ackman, 1982). The volume of AMD sludge produced varies widely and can be as much as 10 to 30% of the incoming AMD flow (Ackman, 1982; Keefer, 1979). It has been repeatedly reported that the voluminous AMD sludge can be very difficult to dewater. After settling in ponds or lagoons at the treatment sites, AMD sludge is transported by pipeline and/or truck, and is typically disposed of via the following methods: deep mine disposal, retained-in-pond disposal, and disposal at coal refuse areas (Ackman, 1982). The very low solids concentration makes the transportation and disposal of AMD sludge very costly. Consequently, sludge volume reduction is desired at every AMD treatment site. However, very limited information is available in the literature related to the detailed AMD sludge characterization and dewaterability evaluation.

AMD sludge typically consists of various metal oxides/hydroxides (Kirby *et al.*, 1999), because the traditional AMD treatment precipitates the metals present in the water together in the sludge. Consequently, AMD sludge is of little to no practical value, making the ultimate disposal of sludge economically unfavorable. However, AMD is a potential metal source due to its high metal concentrations, and metals can be recovered from AMD through physical, chemical and biological processes (Jenke and Diebold, 1983; Matlock *et al.*, 2002; Tabak *et al.*, 2003). Metal recovery from AMD sludge is one potential way to extend the use of natural resources, while maintaining an economy of sustainable development. Chemical methods involve the addition of chemicals to the AMD water to selectively precipitate metals based on their solubility

differences, while the AMD is treated and the effluent meets the discharge limitations. Practical implementation of chemical methods to recover metals requires minimum manipulation to the current active AMD treatment processes.

The synthesis of magnetite nanoparticles has been the focus of numerous recent research efforts and the application of magnetite nanoparticles in environmental engineering as nano-sorbents for pollutants removal is promising (Hu *et al.*, 2004; Mak and Chen, 2004; Moeser *et al.*, 2002; Leun and SenGupta, 2000; Cumbal and SenGupta, 2005). However, all the previous research on magnetite nanoparticle synthesis utilized reagent-grade chemicals as the iron source. Hence, the chemical cost could limit the application of magnetite nanoparticles in water or wastewater treatment, since water or wastewater treatment usually deals with large volumes of flow with different pollutants. Among the metallic ion species in AMD, iron is the ubiquitous, staple metal due to the omnipresence of pyrite and its tendency to be oxidized (Johnson and Hallberg, 2005; Kim *et al.*, 2002). In fact, iron oxide/hydroxide is the dominant constituent (ranging from 20-70%) in AMD sludges from both passive and active treatment (Kirby *et al.*, 1999). In view of the great amount of AMD generated annually, the potential to recover iron from AMD is significant. The potential can be further magnified if value-added products are made from the recovered iron. Unfortunately, relative little research is found in the literature related to the value-added use of the metals recovered from AMD.

1.2 OBJECTIVES

By using AMD water and sludge samples, collected from a bond-forfeited coal mine site (Upper Freeport seam) in north central West Virginia, detailed experimental research was carried

out for sludge characterization, dewaterability evaluation, iron and aluminum recovery, and synthesis of magnetite nanoparticles, with the following objectives:

1. To establish the physical and chemical characteristics of AMD sludge produced through ammonia neutralization, to systematically evaluate sludge dewaterability, and to provide insight into the performance of various treatment options.
2. To evaluate the solubility of metals present in the AMD water, to develop a selective precipitation process to recover iron and aluminum from AMD, and to assess the effects of different neutralizing reagents on metal recovery and precipitate purity.
3. To develop an approach to synthesize low-cost magnetite nanoparticles with ferric iron recovered from AMD water, and to address its implications in environmental engineering.

1.3 DISSERTATION OVERVIEW

The second chapter addresses the need for sludge volume reduction at AMD treatment sites. It focuses on the determination of sludge characteristics, examination of sludge dewaterability, and evaluation of different treatment approaches to reduce sludge volume. It includes a review of the AMD sludge problem, sludge characterization, and past sludge dewatering work found in the literature, and points out the necessity for research on sludge volume reduction. It covers the detailed experimental protocol, results and discussion and summary of conclusions.

Chapter three covers the development of a selective precipitation process to recover Fe and Al from AMD water, so that the AMD treatment can be converted into a metal recovery

process and the sludge problem can be mitigated. It incorporates a review of the current research attempts to recover metals from AMD by physical, chemical and biological process. The experimental approach is described in detail, and the results of AMD water characteristics, metal solubility study, Fe and Al precipitation operations, neutralizing reagent evaluation, and iron oxidation are presented in this chapter. The discussion of the advantages and implementation of the proposed metal recovery process is included as well.

The fourth chapter presents the research approach taken to make use of the recovered Fe from AMD to fabricate value-added products, i.e. the synthesis of magnetite nanoparticles. It includes an overview of magnetite nanoparticles, the synthesis approaches, and their application in environmental engineering. It describes the coprecipitation method to synthesize low-cost magnetite nanoparticles with ferric iron recovered from AMD, presents the results of X-ray diffraction, scanning and transmission electron microscopic studies of synthesized nanoparticles, compared with those prepared from reagent-grade chemicals, and a discussion of its implication in environmental engineering is provided.

Chapter five provides the summary of conclusions drawn from the previous three chapters.

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2 CHARACTERIZATION AND DEWATERING EVALUATION OF ACID MINE DRAINAGE SLUDGE FROM AMMONIA NEUTRALIZATION*

ABSTRACT

A major problem in the active treatment of acid mine drainage (AMD) is the generation of large volumes of sludge through pH neutralization and subsequent metal precipitation. The sludge typically contains a low concentration of solids, resulting in associated handling and disposal difficulties. Anhydrous ammonia is one reagent commonly used to neutralize AMD due to its quick reaction rate, easy implementation, and relatively low chemical and operational costs. However, very limited information is available in the literature related to the detailed characterization and dewaterability of ammonia-treated AMD sludge. In this study, sludge was collected from an AMD treatment facility where ammonia neutralization was used. The sludge characteristics included high pH and alkalinity, high total Fe and Al, elevated sulfate, and low solids content (0.72 ± 0.24 %). Coagulants and flocculants were not effective in reducing the settled sludge volume. Based on filtration tests, ammonia-treated AMD sludge demonstrated relatively good dewaterability in terms of specific resistance to filtration (*SRF*). Sludge cake containing 4.5-6.3% solids were obtained using vacuum filtration at a vacuum of 50.8 kPa (15-inch Hg). The appropriate immersion time was 60 seconds for a vacuum filter, and sludge cakes of 6.2% solids and a yield of $3.04 \text{ kg/m}^2\text{h}$ were achieved. Overall, the belt filter press showed the best performance in improving total solids content in the sludge cakes, where concentrations of ~10% solids were achieved.

Key Words: acid mine drainage sludge, characterization, dewaterability, specific resistance to filtration, vacuum filtration.

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2.1 INTRODUCTION

The formation of acid mine drainage (AMD) has been an environmental problem for decades in coal mining areas such as the *Mid Appalachian* region and the western United States. In West Virginia alone, AMD has impacted about 3,200 km (~2,000 mi) of streams (Demchik and Garbutt, 1999). Problems associated with AMD include acidic water with elevated concentrations of dissolved metal ions, which can be toxic to aquatic organisms, corrode infrastructure, damage benthic habitats, and affect the overall aesthetics of receiving streams (Tabak *et al.*, 2003; DeNicola and Stapleton, 2002; Soucek *et al.*, 2000). In order to minimize the negative impacts of AMD, various active and passive treatment processes have been implemented to increase alkalinity of AMD waters and subsequently precipitate metal ions (Hammarstrom *et al.*, 2003; Dempsey and Jeon, 2001; Zinck and Aube, 2000; Gazea *et al.*, 1996). Active treatment involves the continuous addition of neutralizing agents to AMD waters. Ammonia, along with hydrated lime, sodium hydroxide, limestone and soda ash, is commonly used in active AMD treatment (Johnson and Hallberg, 2005). Among these reagents, ammonia is used to effectively raise the pH of AMD waters up to 9.2 (Skousen *et al.*, 1998). The advantages of ammonia neutralization are the quick reaction rate, easy implementation in the field and relatively low chemical and operational costs.

A major challenge in AMD treatment is management of large volumes of loose sludge generated through neutralization (Kuyucak, 1998; Ackman, 1982; Yeh and Jenkins, 1971). In general, AMD sludge contains a mixture of various metal hydroxides and/or oxides (Kirby, *et al.*, 1999), where the ultimate chemical composition is a function of the AMD water characteristics and treatment method. The total solids content of AMD sludge reported in the literature varies from 1 to 20%, with a typical value of 1 to 5% (Johnson and Hallberg, 2005;

Kuyucak, 1998; Ackman, 1982; Keefer, 1979). According to Dempsey and Jeon (2001) and Brown *et al.* (1993), AMD sludge generated in neutralization with calcium hydroxide, ammonium hydroxide, sodium carbonate and sodium hydroxide contained only 0.5 to 1.5% solids. However, limited information is available in the literature related to the detailed characterization of AMD sludge – particularly for sludge generated through anhydrous ammonia treatment.

The volume of AMD sludge produced varies widely and can be as much as 10 to 30% of the incoming AMD flow (Ackman, 1982; Keefer, 1979). The volume alone poses a great challenge for dewatering operations, since AMD is generated in large amounts worldwide, although the true scale of the volume is difficult to assess accurately. It has been repeatedly reported that the voluminous AMD sludge can be very difficult to dewater (Dempsey and Jeon, 2001; Jenke, and Diebold, 1983; Ackman, 1982; Judkins and Parsons, 1969).

Specific resistance to filtration (*SRF*) is extensively used to characterize the dewaterability of sludges, and a smaller value of *SRF* indicates better dewaterability (Eckenfelder, 2000; Agerbaek and Keiding, 1993). Dempsey and Jeon (2001) determined the *SRF* of AMD sludge generated through sodium hydroxide neutralization, ranging from 2.6 to 12.5×10^{11} m/kg, which was apparently greater than the *SRF* of AMD sludge produced from passive treatment, thus demonstrating that the AMD sludge from sodium hydroxide treatment was more difficult to dewater. Sibrell and Watten (2003) compared the dewatering performance of AMD sludge produced by sodium hydroxide, hydrated lime, and limestone from a pulsed limestone bed (PLB), and found that *SRF* was 10.4, 7.3 and 3.1×10^{12} m/kg respectively, which indicated sludge generated from limestone neutralization had the best filterability. The effect of crystal seeding on sludge filterability was studied by Judkins and Parsons (1969) and the *SRF* for lime-treated

AMD sludge was determined to be approximately $2.5 \times 10^6 \text{ sec}^2/\text{g}$ (equivalent to $2.5 \times 10^{10} \text{ m/kg}$). Their results pointed out that a return sludge seeding process improved sludge dewaterability. Further, the Coal Research Bureau (1971) reported that vacuum filtration resulted in filter cakes with an average solids concentration of $\sim 23\%$, as compared to the original 0.6% solids, in a system with a 3.2 m^2 filter surface area when filtering lime-treated coal mine drainage sludge at a vacuum of 0.6 atm . No studies on dewaterability of AMD sludge from ammonia neutralization were found in the literature.

Recognizing ammonia as a common neutralizing reagent in AMD treatment and the corresponding need to reduce AMD sludge volumes, the objective of this study was to establish the physical and chemical characteristics of AMD sludge produced through ammonia neutralization system, to systematically evaluate sludge dewaterability, and to provide insights into the performance of various treatment options.

2.2 EXPERIMENTAL PROTOCOLS

2.2.1 Site description and sludge sample collection

Sludge produced through AMD treatment at a bond-forfeited coal mine, cutting through Upper Freeport coal seams in north central West Virginia, was used in this study. The water originated in underground pools and was pumped to the surface where it was treated with hydrogen peroxide to oxidize Fe^{2+} to Fe^{3+} and anhydrous ammonia was added to raise the pH from ~ 2.6 to above 8 to facilitate metal precipitation. The supernatant was then siphoned into a clarifying pond and discharged into a local receiving stream. Approximately $\sim 30,000 \text{ m}^3$ of settled sludge with a solids concentration ranging from 0.5 to 1% was produced annually.

AMD sludge samples were collected from the settling pond at the AMD treatment facility. Sludge was stored in closed five-gallon buckets and kept at 4°C after each collection. The sludge was brought to room temperature and completely mixed before subsequent testing. Multiple sludge collections were made during this study to assess variations in AMD sludge characteristics. Sludge from the same collection was used for coagulation/flocculation tests and for filtration parameter evaluation in order to minimize the effect of variation in sludge characteristics on process performance.

2.2.2 Sludge characterization

AMD sludge characteristics, including specific gravity, total solids, dissolved solids, alkalinity and sulfate, were determined according to corresponding standard methods (APHA, 1998). Calculation of % solids was based on the total solids. pH, specific conductance and temperature were measured with a YSI meter (Model 63). The metals (Fe, Al, Ca, Mg and Mn) were analyzed according to Standard Method 3111 (APHA, 1998) using an atomic absorption spectrometer (*Perkin Elmer* 3100). Total ammonia nitrogen, nitrate, nitrite and total phosphorus were determined according to EPA Methods 350.1, 353.2, 353.2 and 200.7, respectively. The particle size distribution of the sludge was determined using a *Coulter LS* 230 particle size analyzer, capable of measuring particles in the range of 0.25 to 250 µm. Sludge viscosity was measured using a *Brookfield DV-III* programmable rheometer.

2.2.3 Sludge dewaterability

Specific resistance to filtration (*SRF*) was used to characterize the dewaterability of ammonia-treated AMD sludge. The apparatus and procedures to determine *SRF* were described by Christensen and Dick (1985) and Eckenfelder (2000). Whatman No. 2 filter paper (Φ70mm)

with effective filtering area of 32.15 cm² was used. For each *SRF* test, 180-mL of AMD sludge was used. A vacuum of 50.8 kPa was applied to determine *SRF* of the AMD sludge, and vacuum ranging from 44.0 to 74.5 kPa was used to examine the sludge compressibility and effect of vacuum on total solids content of the filter cakes. All *SRF* tests were conducted in triplicate at least. Calculation of *SRF* was based on the plot of the inverse filtration rate (dt/dV) versus the accumulated filtrate volume (V), from which the slope (b) of the straight line was obtained. The equation for *SRF* calculation, developed by Eckenfelder (2000), was the following:

$$SRF = \frac{2bPA^2}{\mu \cdot c} \quad \text{-----}(1)$$

where, *SRF* = specific resistance to filtration (*SRF*), m/kg;

P = vacuum, Pascal;

b = slope of the plot (t/V versus V), sec/m⁶;

A = filter area, m²;

μ = viscosity, Pascal·sec;

c = weight of solids/unit volume of filtrate, kg/L;

$$c = \frac{1}{C_i / (100 - C_i) - C_f / (100 - C_f)} \quad \text{-----}(2)$$

C_i = initial moisture content, %;

C_f = final moisture content, %.

2.2.4 Coagulation/flocculation tests

Based on literature review, thirteen polymeric flocculants and coagulants were selected, including seven anionic and four cationic flocculants, and two coagulants of different polymer types, molecular weights, and charge. The polymeric flocculants and coagulants used in this

study and their corresponding codes in the text below are listed in Table 2.1. Four traditional inorganic coagulants (iron and aluminum sulfate/chloride salts, reagent grade) were obtained from *Fisher Scientific*. In addition, bentonite clay, starch and alginic acid (salt sodium powder) were also acquired from *Fisher Scientific* to test their performance in reducing sludge volume. Polymer stock solutions of 0.1% were prepared according to the procedures suggested by the suppliers. All stock solutions were aged for at least a half hour before applied and no solutions over 24-hr old were used. Solutions of 0.5% wt. were prepared for iron and aluminum coagulants. The tested dosage ranged from 10-150 ppm. Bentonite clay (dose of 100-1500 mg/L) and starch (dose of 10-150 mg/L) were applied as powders and wetted for half an hour before addition.

Jar tests were used to determine the effects of coagulants/flocculants on sludge settling. Since the objective was to reduce sludge volume by coagulation/flocculation, percent settled sludge (P_{ss}) was used as the criteria to judge the sludge settling performance:

$$P_{ss} = \frac{V_{ss}}{V_T} \times 100\% \quad \text{-----}(3)$$

where V_{ss} = settled sludge volume and , V_T = total sludge volume. Lower P_{ss} values indicated better coagulant/flocculent performance because a more dense sludge was generated. Jar tests were carried out in 600-mL beakers using a *Phipps and Bird* stirrer. In each jar settling test, 500 mL sludge was rapidly mixed for 2 minutes to achieve homogeneity. Stock solutions of flocculants or coagulants were then added to reach the appropriate concentration and the sample was mixed for 2 minutes at 100 rpm to disperse and ensure sufficient contact with sludge particles. The samples were then slowly mixed for 30 seconds at 25 rpm to allow for floc formation. The time for rapid mixing and slow mixing was determined by the results of preliminary tests. After slow mixing, the sludge was allowed to settle for 24 hrs.

Table 2.1. Polymeric flocculants and coagulants used in this study.

	Code	Chemical Type	Vendor
	Floc-A	Anionic proprietary polymer, high charge	Vulcan
	Floc-B	Anionic, modified polyacrylamide, high charge	CYTEC
	Floc-C	Anionic, ammonium polyacrylate, high charge	CYTEC
	Floc-D	Anionic, high molecular weight polyacrylamide, high charge	Hychem
	Floc-E	Anionic, very high molecular weight polyacrylamide, medium charge	Hychem
<i>Flocculants</i>	Floc-F	Anionic acrylamide copolymer	CYTEC
	Floc-G	Anionic acrylic emulsion copolymer	CYTEC
	Floc-H	Cationic polyacrylamide copolymer, high charge	Vulcan
	Floc-I	Cationic polyacrylamide copolymer, low charge	Vulcan
	Floc-J	Cationic acrylic copolymer, synthetic polymeric demulsifier	Alco
	Floc-K	Cationic acrylic copolymer, synthetic polymeric flocculant	Alco
	Coag-A	Cationic, medium molecular weight polyDADMAC, high charge	Hychem
<i>Coagulants</i>	Coag-B	Cationic, high molecular weight polyDADMAC, high charge	Hychem

2.2.5 Filtration tests

Vacuum filtration tests were conducted using a Buchner funnel setup and a filter leaf. The same apparatus described previously for *SRF* testing was used in Buchner funnel tests. Vacuum filtration in an industrial setting is a continuous process, consisting of a cycle of submerged operation, drying, and cake removal. The filter leaf is a bench-scale model of a prototype filter, which can be used to simulate such a cycle and provide a direct indication of the performance of industrial vacuum filters (Vesilind, 1979; Martel, 1994). Filter leaf tests were carried out with the setup described by Vesilind (1979), which included a round disk (43 mm effective diameter) with a corrugated surface to facilitate the outflow of filtrate. Whatman No. 2 paper was used as the filter medium. The disk was connected to a vacuum source through a flask, where the filtrate was collected. The cycle of a filter leaf test consisted of submerged operation for 30 to 120 seconds followed by 60 seconds for cake drying and subsequent cake removal. The total solids content of the filter cake was then determined and used to calculate the filter yield based on the effective filter area and a filter cycle.

Belt filter press tests were conducted by the filter manufacturer (PHOENIX Process Equipment Co., Louisville, KY), using a bench-scale belt filter press, comparable to PHOENIX Model LC-800L Trailer-Mounted belt filter press. The filter process consisted of sludge conditioning, gravity drainage, and mechanically applied forces to remove water from the sludge. Shearing and compression forces were generated from the configuration of the belt. The system was able to capture 95% of the suspended solids. The AMD sludge with ~0.4% solids was used as feed for the belt press tests.

2.3 RESULTS AND DISCUSSION

2.3.1 Characterization of ammonia-treated AMD sludge

A summary of the physical and chemical characteristics of AMD sludge generated through ammonia neutralization is presented in Table 2.2. From the standard deviations of the measured parameters, it can be seen that sludge characteristics varied from collection to collection, which was likely due to variation in AMD influent characteristics (pH, metals, acidity, flow rate, *etc.*), weather conditions, and/or insufficient real-time adjustment of chemical addition during AMD treatment operation. Notable sludge characteristics included high pH and alkalinity, high total Fe and total Al, elevated sulfate concentration, low nitrate concentration, and low solids concentration. In particular, a notable impact of the low total solids content (0.72 ± 0.24 %) was the production of large annual quantities of AMD sludge at the treatment site (c.a. 30,000 m³/yr). Based on chemical analyses, Fe and Al were the dominant metal species in the ammonia-treated AMD sludge while Ca, Mg and Mn concentrations were low. Consequently, ammonia neutralization produced a relatively pure sludge in terms of Fe and Al hydroxide contents. In contrast, AMD sludge from lime treatment is typically high in Ca due to the presence of gypsum or unreacted lime (up to 40% dry base, Coal Research Bureau, 1971). Consequently, ammonia-treated AMD sludge may have some potential for value-added use due to its relatively high Fe and Al hydroxide contents. For example, AMD sludge might be used as a raw material in the manufacture of pigments or coagulants (Hedin, 2003; Kirby *et al.*, 1999; Rao *et al.*, 1992).

Table 2.2. Physical and chemical characteristics of AMD sludge samples from ammonia neutralization.*

Physical Characteristics		Chemical Characteristics (mg/L)	
pH	8.54 ± 0.67	Alkalinity (as CaCO ₃)	1983 ± 995
Specific Conductance	3572 ± 450	Total Fe	1401 ± 692
(μS/cm)		Total Al	380 ± 172
Temperature (°C)	18.1 ± 6.3	Total Mn	13.3 ± 4.5
Density (g/mL)	1.008 ± 0.011	Total Ca	68.5 ± 33.0
% Solids (g/g)	0.72 ± 0.24	Total Mg	60.3 ± 10.3
Total Solids (g/L)	7.31 ± 2.53	Sulfate, SO ₄ ²⁻	1294 ± 145
Dissolved Solids (g/L)	2.1 ± 0.49	TAN**	429.7 ± 95.9
Mean particle	12.1 ± 1.5	Nitrate, NO ₃ ⁻	0.78 ± 0.14
size(μm)		Nitrite, NO ₂ ⁻	BDL***
Viscosity (cP)	11.8 ± 1.1	Total Phosphorus	0.23±0.14

*Data presented are average ± standard deviation (seven samples from different sludge collections at the AMD site); **Total Ammonia Nitrogen; ***Below detection limit.

The elevated total ammonia nitrogen (TAN) was due to the addition of ammonia for AMD neutralization. Based on the very low nitrate content, little ammonia was oxidized to nitrate, probably due to the high pH, which did not favor the nitrification reaction (EPA, 1993).

The mean particle size of the AMD sludge was $12 \pm 1.5 \mu\text{m}$, which was finer than the precipitated cupric hydroxide sludge (mean diameter ranging from 35 to 69 μm) and chromium hydroxide sludge (mean diameter ranging from 17 to 52 μm) reported in the literature (Knocke, 1980). Particle size was reported as having the greatest effect on the filterability of metal hydroxide sludge (Eckenfelder, 2000; Knocke, 1980), where a decrease in sludge particle size significantly increased the resistance to filtration. As a result, ammonia-treated AMD sludge could be difficult to dewater. The particle size distribution of ammonia-treated AMD sludge followed the *Rosin-Rammler* distribution, which was different from that of other wastewater sludges, since they were usually characterized by a power law distribution (Lawler, 1997; Kaminski, 1997).

2.3.2 Coagulation/flocculation of ammonia-treated AMD sludge

Based on the sludge characterization, the ammonia-treated AMD sludge was very low in solids ($0.72 \pm 0.24 \%$). Since coagulants and flocculants have proven to be effective in enhancing the sludge settling process and in producing dense sludge flocs (Vesilind, 1979; Ruehl, 2001), an increase in solids concentration and a reduction in sludge volume were expected through coagulation/flocculation treatment. In addition, treatment with coagulants/flocculants could be easily applied in the field without major modifications to the existing AMD treatment operations.

Settling results for anionic polymers applied at different concentrations are shown in Figure 2.1. With the exception of Floc-F, none of the anionic polymers resulted in a reduced sludge volume. In fact, an increase in P_{ss} was recorded for the other anionic polymers at high polymer concentrations. Floc-F reduced sludge volume at high applied concentrations (≥ 60 ppm). However, the volume reduction was less than 3% when compared to controls – even at the highest applied concentration of 150 ppm. Therefore, it was concluded that none of anionic polymers effectively reduced sludge volume. However, based on visual observations made during testing, the addition of most anionic polymers resulted in large flocs during slow mixing and the sludge settled much more rapidly than sludge in which floc formation was not visible. Consequently, the anionic polymers did not reduce the sludge volume, though the sludge settling rate had been enhanced.

Results of settling tests performed using four cationic polymers are presented in Figure 2.2. Floc-I, a low charge cationic polyacrylamide copolymer, resulted in sludge volume reduction of 9% at concentrations ≥ 60 ppm, when compared with controls. None of the other cationic polymers produced meaningful sludge volume reduction.

Since one mechanism of polymer flocculants is interparticle bridging (Metcalf & Eddy, 2003), the floc structure within the AMD sludge might actually have been enhanced by flocculants, making the sludge difficult to compress by settling alone. Consequently, it was believed that a more effective sludge volume reduction might be achieved through the addition of coagulants, which exploited mechanisms different from polymeric flocculants (*e.g.*, electric double layer compression, charge neutralization, and precipitate enmeshment).

Figure 2.1. Percent settled sludge at different concentrations of anionic polymers.

Figure 2.2. Percent settled sludge at different concentrations of cationic polymers.

Results of settling tests performed using coagulants are presented in Figure 2.3. Neither iron nor aluminum coagulants resulted in meaningful sludge volume reductions over the range of concentrations studied. The polymer coagulants (Coag-A and Coag-B) led to large sludge volumes with increasing dose. Further, the addition of bentonite clay, starch and alginic acid (salt sodium powder) did not produce meaningful decreases in P_{ss} . Consequently, the volume of ammonia-treated AMD sludge was not successfully reduced by addition of either coagulants or flocculants.

Several factors related to the properties of the ammonia-treated AMD sludge likely played important roles in the sludge coagulation/flocculation tests, which might help explain the inefficacy of coagulants and flocculants in reducing sludge volume. For instance, the high ionic strength of the sludge (as indicated from the specific conductance of $3,572 \pm 450 \mu\text{S}/\text{cm}$ in Table 2.2) might be one reason why coagulants were ineffective. Since the ionic strength was high, the double layer was likely well compressed before coagulants were added. In this case, the addition of coagulants had only a minor effect on the ionic strength of the sludge suspension. Thus, there was little likelihood that coagulants would be able to compress the double layer around colloidal particles and achieve meaningful reduction in sludge volume. Further, according to Bratby (1980), polymer chains and the overall range of extension of polymer loops were shorter under conditions of elevated ionic strength. As a consequence, the high ionic strength in ammonia-treated AMD sludge would result in a decrease in the flocculation performance of the polymeric flocculants.

Figure 2.3. Percent settled sludge at different concentrations of coagulants.

2.3.3 Dewaterability of ammonia-treated AMD sludge

Specific resistance to filtration (SRF)

Since coagulation/flocculation treatment was not effective in reducing sludge volume, mechanical dewatering was considered as a viable treatment alternative, provided sufficient space existed at the layout of a series of drying lagoons at the AMD treatment site. For mechanical dewatering, it is necessary to evaluate the sludge dewaterability in order to achieve efficient operation, and *SRF* is a good measure to characterize sludge dewaterability (Christensen and Dick, 1985; Murthy and Novak, 1999; Sanin and Vesilind, 1999). The *SRF* values of the ammonia-treated AMD sludge in this study were determined at $1.31 \pm 0.32 \times 10^{11}$ m/kg. The measured *SRF* of ammonia-treated AMD sludge was comparable to the *SRF* values of NaOH-treated AMD sludge determined by Dempsey and Jeon (2001). However, it was much lower than the *SRF* values for AMD sludge produced through sodium hydroxide, hydrated lime, and limestone neutralization, reported by Sibrell and Watten (2003). In contrast, *SRF* values for nickel hydroxide, chromium hydroxide and electroplating sludges ranged from 8 to 200×10^{11} m/kg, 5 to 50×10^{11} m/kg, and 130 to 145×10^{11} m/kg, respectively (Knocke *et al.*, 1980). Consequently, ammonia-treated AMD sludge demonstrated relatively good dewaterability in terms of *SRF* values, when compared to other metal hydroxide sludges.

The addition of polymers altered the *SRF* of ammonia-treated AMD sludge (Figure 2.4). The polymers were selected based on the good floc formation observed in previous jar settling tests. Floc-G (anionic polymer), Floc-I (cationic polymer) and Floc-D (anionic polymer) reduced the *SRF* of the AMD sludge, among which Floc-G decreased the *SRF* by about two-thirds, from

1.7×10^{11} m/kg to 0.6×10^{11} m/kg. Other polymer flocculants did not lead to a reduction in *SRF*. In the meanwhile, the best floc formation was observed when Floc-G was applied. Thus, despite the general poor improvement in sludge volume reduction by settling, as demonstrated previously, the addition of appropriate polymers did improve the filterability of AMD.

AMD sludge compressibility

The compressible properties of sludges during filtration are generally characterized by the compressibility coefficient (*S*) (Eckenfelder, 2000; Lotito *et al.*, 1990). A greater *S* value is indicative of a sludge that is easier to compress. When the sludge cake is compressed, the resistance to filtration rises (Eckenfelder, 2000). Determination of the sludge compressibility coefficient is based on the correlation between sludge *SRF* and applied vacuum (Eckenfelder, 2000). One such relationship between *SRF* and the applied vacuum for the ammonia-treated AMD sludge is presented in Figure 2.5. *SRF* increased linearly with increasing applied vacuum on log-log scale. *S*, the slope of the regression line, for the ammonia-treated AMD sludge was 1.07. Dempsey and Jeon (2001) examined the compressibility of AMD sludge and determined an *S* of 0.86 for NaOH-treated sludge, and *S* ranged from 0.3 to 0.6 for sludge generated from passive treatment systems (anoxic limestone drain). In contrast, the *S* value of 1.07 was very close to that of ferric hydroxide (~1) reported by Dahlstrom (1985). The relatively high *S* value indicated that ammonia-treated AMD sludge was more compressible than other sludges. Consequently, in practice, the increase in applied vacuum would not necessarily increase the vacuum filter throughput due to the simultaneous increase in the *SRF*, caused by the compressible nature of ammonia-treated AMD sludge.

Figure 2.4. Effect of polymer addition on *SRF* of AMD sludge.*

*The applied vacuum was 50.8 kPa and polymer concentration was 100 ppm.

Figure 2.5. Relationship between SRF and applied vacuum.*

* P : applied vacuum in kPa; SRF : specific resistance to filtration in m/kg.

2.3.4 Vacuum filtration performance

Buchner funnel tests

The total solids content in the sludge cakes increased slightly as the applied vacuum was raised from 44.0 to 74.5 kPa. The highest solids content of 5.1% achieved at 74.5 kPa in this study was far below the 23% for the vacuum filtration of a lime-treated AMD sludge reported by Coal Research Bureau (1971). The addition of either anionic or cationic polymers did not improve the solids content in the filter cakes of ammonia-treated AMD sludge, although *SRF* values were affected by the polymers (Figure 2.4). The low solids content obtained from vacuum filtration was likely due to the composition and small particle size of ammonia-treated AMD sludge. For example, gypsum and unreacted lime were the main solids constituents in lime-treated sludge (Coal Research Bureau, 1971). In contrast, iron and aluminum hydroxides were the major solids in the ammonia-treated AMD sludge, as indicated in Table 2.2. Further, the fine particles in the ammonia-treated AMD sludge provided a large hydrophilic surface area for adsorption and attachment of moisture, which was difficult to remove by vacuum filtration.

Filter leaf tests

The effect of applied vacuum on the total solids content of the filter cake and the filter yield is presented in Figure 2.6. At a vacuum ranging from 44.0 to 74.5 kPa, the filter yields were maintained at 2.8 to 3.0 kg/m²h and the total solids contents of the filter cake ranged from 5.9 to 6.3%, which was slightly higher than that of the sludge cake from the Buchner funnel tests. Clearly, the increase in applied vacuum had no significant effect on solids content in the sludge cake or the filter yields when the vacuum was above 50.8 kPa, which could be due to the increase in *SFR* with increasing vacuum, as presented previously in Figure 2.5. Due to the

technical difficulty of maintaining high vacuum and the associated energy consumption, a vacuum of 50.8 kPa (15-inch Hg) was considered appropriate for full-scale vacuum filters to dewater the ammonia-treated AMD sludge.

Sufficient immersion time is necessary for the sludge to form a stable cake of good texture to ensure the pathway of clear filtrate with the appropriate filter resistance. However, a long immersion time requires a long filter cycle, which can reduce filter yield and handling capacity. Additionally, a thick cake results in an increased resistance to filtrate flow. The effect of immersion time on the solids in the sludge cake and the filter yield is illustrated in Figure 2.7. Lower solids content in the sludge cake was observed for longer immersion time. The filter yield initially increased with increasing immersion time. However, when the immersion time exceeded 90 seconds in one filter cycle, the filter yield dropped. This was attributed to the increase in *SRF* due to the increasing cake thickness with sludge buildup. Based on the results of total solids content and filter yield, an immersion time of 60 seconds was considered appropriate for vacuum filter operation, where a total solids content of 6.2% and a filter yield of 3.04 kg/m²h were achieved.

2.3.5 Bench-scale belt filter press

Based on preliminary trials, sludge of ~16.1% solids was achieved by hand squeezing the filter cake contained in a cotton bag, indicating the water was easily squeezed out under mechanical shear or compressive forces. On an industrial scale, this process is most closely approximated by a belt filter press process (Bullard and Barber, 1996; Day, 2002), which has been proven to be effective for the treatment of various kinds of municipal wastewater sludge and biosolids (Metcalf & Eddy, 2003).

Figure 2.6. Effect of applied vacuum on total solids content of filter cake and filter yield.*

*Experimental conditions were 60 sec. for immersion, 60 sec. for drying and 30 sec. for cake removal.

Figure 2.7. Effect of immersion time on total solids content of filter cake and filter yield.*

*The applied vacuum was 50.8 kPa with 60 sec. for drying and 30 sec. for cake removal.

Belt filtration tests were conducted using a bench-scale belt filter press to dewater the ammonia-treated AMD sludge in this study. The initial total solids content of the sludge was ~0.4% solids. Ultimately, a sludge cake of ~10% solids was achieved, which was a conveyable, stackable material. Since the total solids content was very low (~0.4%) in the feed sludge, the performance of the belt filter press was expected to improve if the total solids content of the feed could be raised to ~1%. Consequently, a combination of processes may be used for maximum dewatering efficiency.

2.4 SUMMARY

The AMD sludge from ammonia neutralization was characterized by high pH and alkalinity, high total Fe and Al, elevated sulfate, and low solids ($0.72 \pm 0.24\%$). The particles in the sludge were fine, with a mean of $12 \pm 1.5\mu\text{m}$, which fitted the *Rosin-Rammler* distribution. Compared with lime-treated AMD sludge, this sludge was relatively pure in composition with the iron and aluminum hydroxides as the main solids constituents. Consequently, potential value-added uses of sludge from ammonia-treated AMD existed. Coagulation and flocculation treatment did not effectively reduce the final volume of the settled sludge. Poor performances of coagulation and flocculation might be caused by the high ionic strength of the sludge suspension.

The *SRF* values were $1.31 \pm 0.32 \times 10^{11}$ m/kg for ammonia-treated AMD sludge. Compared to other AMD sludges and metal hydroxide sludges, ammonia-treated AMD sludge demonstrated relatively good dewaterability in terms of *SRF* values. Further, filterability could be improved considerably through the addition of appropriate polymeric flocculants. The compressibility coefficient (1.07) demonstrated the ammonia-treated AMD sludge was compressible.

The total solids content in the sludge cakes obtained from vacuum filtration tests with Buchner funnel and filter leaf ranged from 4.5 to 6.3% for ammonia-treated AMD sludge, which was not improved by polymer addition. A vacuum of 50.8 kPa was the appropriate level for vacuum filtration. The appropriate immersion time was 60 seconds for a vacuum filter, and a total solids content of 6.2% and a filter yield of 3.04 kg/m²h were achieved. Belt filter press showed a good performance in improving solids content of the sludge cake. With the ammonia-treated AMD sludge of ~0.4% solids as feed, bench-scale belt filter press achieved sludge cakes of ~10% solids.

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3. RECOVERY OF IRON AND ALUMINUM FROM ACID MINE DRAINAGE BY SELECTIVE PRECIPITATION*

ABSTRACT

The large volumes of sludge produced through the active treatment of acid mine drainage (AMD) require further processing and final disposal. AMD sludge typically contains a heterogeneous mixture of iron, aluminum, magnesium, and calcium oxides/hydroxides that are of little to no practical value. However, purified iron and aluminum hydroxides have potential commercial value. Based on the solubility of the major dissolved metals, a two-step selective precipitation process was developed to recover high purity iron and aluminum as separate hydroxide products through the manipulation of current AMD treatment operations. The recommended pH for iron precipitation was pH 3.5-4.0 with precipitate purity >93.4% and iron recovery >98.6%. AMD water after iron removal was used as source water for aluminum recovery. Aluminum precipitated best at pH 6.0-7.0 with aluminum recovery >97.2% and precipitate purity >92.1%.

Key words: Acid mine drainage; metal recovery; selective precipitation; pH adjustment; iron; aluminum

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3.1 INTRODUCTION

Acidic drainage formed through the interaction of iron pyrite (FeS_2) with water and/or air is a major source of water impairment in both coal and hard rock mining regions (Bunce *et al.*, 2001; Sasowsky *et al.*, 2000). The active treatment of acid mine drainage (AMD) involves the addition of alkaline neutralization reagents to raise pH and precipitate dissolved metals (Skousen *et al.*, 1998). Through treatment, large volumes of sludge, which require further treatment and final disposal, are generated. AMD sludge typically consists of various metal oxides/hydroxides and is of little to no practical value, making the ultimate disposal of sludge economically unfavorable. However, the recovery of precipitated metals from AMD sludge with the joint objectives of obtaining valuable products while meeting the effluent discharge limitations is one potential way to extend the use of natural resources, while maintaining an economy of sustainable development. Further, benefits such as liability mitigation and the generation of a revenue stream to offset AMD treatment costs may be realized (Rao *et al.*, 1996). Physical, chemical and biological methods have been found to be effective for metal recovery from AMD.

3.1.1 Physical treatment

Deorkar and Tavlarides (1998) developed an adsorption process comprised of inorganic chemically active adsorbents (ICAAs) to selectively recover Fe^{3+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} from AMD solutions without neutralization. Riveros (2004) found that macroporous acrylic resins were efficient and selective extractants of ferric iron from acid sulfate media. In another study, up to 94% of uranium was recovered from AMD water by ion exchange (Nascimento *et al.*, 2004).

3.1.2 Chemical treatment

Jenke and Diebold (1983) evaluated metal recovery from AMD by the addition of sulfides followed by oxidation and selective titration. Cu and Zn precipitated as sulfides and Fe, Al, Mn and Mg were recovered as hydroxides. Metal recovery >85% was obtained in distinct pH regimes. Rao *et al.* (1996) developed a three-step precipitation process: 1) iron was recovered as hydroxide in the presence of dodecylamine (DDA) at pH 3.5 through addition of lime following oxidation with H_2O_2 ; 2) zinc precipitated as sulfide through addition of Na_2S , H_2S or NaHS ; and 3) a final pH adjustment to pH 9.5 removed the residual metals. Sheremata and Kuyucak (1996) studied copper recovery at pH 3.5 by cementation with iron powder, followed by iron precipitation as $\text{FePO}_4 \cdot \text{H}_2\text{O}$ at pH 1.6 with the addition of H_3PO_4 and zinc precipitation as hydroxide using $\text{Ca}(\text{OH})_2$. Matlock *et al.* (2002) tested the addition of 1-3-benzenediamidoethanethiol dianion (BDET) to precipitate metals at low pH from AMD and determined that it was effective.

3.1.3 Biological treatment

Tabak *et al.* (2003) conducted *ex-situ* biotreatment of AMD by selective, sequential precipitation (SSP) to recover metals as hydroxides and sulfides. The following recoveries were reported using the SSP process: aluminum (as a hydroxide) 99.8%, cadmium (as a sulfide) 99.7%, cobalt (as a sulfide) 99.1%, copper (as a sulfide) 99.8%, ferrous iron (as a sulfide) 97.1%, manganese (as a sulfide) 87.4%, nickel (as sulfide) 47.8%, and zinc (as a sulfide) 100%, with purities ranging from 75.0% to 97.8%. Foucher *et al.* (2001) selectively recovered Cu and Zn at pH 2.8 and pH 3.5 respectively from AMD by using sulfate-reducing bacteria. Ni and Fe were removed as sulfides at pH 6.

3.1.4 Research objectives

Among the technological options presented above, metal recovery via chemical treatment was thought to be advantageous for the following reasons: a) widely used in existing AMD treatment plants; b) suitable to large or small flows; c) relatively inexpensive to operate; and d) easy to implement at existing AMD treatment sites by minimum manipulation of current AMD treatment operations. Chemical treatment by the addition of neutralization reagents to treat AMD and recover purified iron and aluminum as separate products was used in this study with the following objectives: 1) to evaluate the solubility of metals in AMD as function of pH; 2) to develop a selective precipitation process to recover high purity iron and aluminum hydroxides as separate products; and 3) to assess the effects of different neutralization reagents on metal recovery and precipitate purity.

3.2 EXPERIMENTAL PROTOCOLS

3.2.1 Site description

Acid mine drainage from a bond-forfeited coal mine site (Upper Freeport seam), located in north central West Virginia, was collected in an underground pool and pumped to a treatment channel on the surface. A process flow schematic of the treatment system is presented in Figure 3.1. Anhydrous ammonia was added to raise the pH from ~2.6 to above 8, and H_2O_2 was applied to oxidize Fe^{2+} to Fe^{3+} . The treated water flowed into a settling pond, where the supernatant was siphoned into a clarifying pond and discharged into a local receiving stream. The settled sludge (~30,000 m^3/yr at ~0.5-1% solids) was then pumped to a series of drying ponds for further dewatering.

Figure 3.1. Process flow schematic of AMD treatment system.

3.2.2 Water sampling and materials

Untreated AMD water samples were collected at the entrance to the treatment channel. Samples were stored in closed high-density polyethylene bottles and kept at 4°C. The AMD water was bubbled with compressed air for at least 24 hrs to ensure the complete oxidation of Fe^{2+} , prior to conducting experiments. The AMD water was then filtered to remove debris and suspended solids. The filtered water was subsequently referred to as “raw” AMD and used as feed solution for metal solubility and recovery experiments. Neutralization reagents, including caustic soda (NaOH, CAS No. 1310-73-2), soda ash (Na_2CO_3 , CAS No. 497-19-8), ammonium hydroxide (NH_4OH , CAS No. 1336-21-6), quick lime (CaO, CAS No. 1309-48-4) and hydrated lime ($\text{Ca}(\text{OH})_2$, CAS No. 1305-62-0) were acquired from *Fisher Scientific*.

3.2.3 Metal solubility

Raw AMD samples of 250 ml each were titrated to pH endpoints ranging from 4 to 12 at approximately 0.5 standard unit (SU) intervals, using 4N and 10N NaOH solutions. During titration, the AMD solution was continuously stirred and the pH was monitored. When the preset pH endpoint was reached, the titrated solution was filtered through a 0.45 μm membrane filter to remove precipitated metals. The filtrate was sampled for metal analysis to determine the concentrations of metals (Fe, Al, Mn, Ca, Mg, Ni, Cu, Zn), which were then used to characterize the metal solubility as a function of pH.

3.2.4 Metal recovery through pH adjustment

A two-step process was used for metal recovery tests: iron precipitation followed by aluminum precipitation. For iron precipitation, raw AMD water samples of 500 ml were neutralized with 10N NaOH solution to pH endpoints between 3.0 and 4.5, at 0.5 SU intervals to

assess iron recovery at different pHs. After iron recovery (at pH 3.5), the filtered AMD water was used as feed solution for aluminum precipitation. Samples of 500 ml each were then neutralized with 10N NaOH to pH endpoints from 4.5 to 8.0 to determine the aluminum recovery performance over a range of pHs. In addition to NaOH, similar pH adjustment tests were conducted using Na₂CO₃, NH₄OH, CaO and Ca(OH)₂ for iron recovery at pH 3.5 and aluminum recovery at pH 6.5, to assess the performances of different neutralization reagents. NH₄OH solution of 25-30%, as acquired, and 1M Na₂CO₃ solution were added for pH adjustment. CaO and Ca(OH)₂ were applied as fine powders.

3.2.5 Metal analyses

All water samples and digested precipitate samples were analyzed for Fe, Al, Ca, Mg, Mn, Zn, Ni and Cu according to Standard Method 3111 (APHA, 1998) using an atomic absorption spectrometer (*Perkin Elmer* Model 3100). Prior to measurement, water samples were acidified with nitric acid to avoid any possible precipitation of metals due to pH changes caused by dilution during metal analysis. Samples of iron or aluminum precipitates were digested in a concentrated nitric acid solution and brought to 200 ml for analyses.

3.2.6 Quality control/quality assurance (QA/QC)

A QA/QC program was established and implemented to ensure the production of defensible data. The QA/QC protocol consisted of triplicate experiment and triplicate sampling for metal analysis. Data were considered acceptable when percent difference within triplicate samples and percent error of analytic recoveries were below 10%. The analytic values below detection limits (BDL) were managed in accordance with EPA guidelines for analyzing data (USEPA, 1998).

3.2.7 Metal recovery and precipitate purity

Metal recovery (γ), a measure of how well a particular metal was removed from solution as a metal hydroxide, was determined according to Eqn (1):

$$\gamma = \frac{C_{in} - C_{out}}{C_o} \times 100\% \quad (1)$$

where, C_o = concentration of the specific metal in the raw AMD, C_{in} = concentration of the metal in aqueous phase before pH adjustment, and C_{out} = concentration of the metal in aqueous phase after pH adjustment. Precipitate purity was defined as the amount of desired metal precipitated from each pH adjustment divided by the sum of all metals precipitated (Tabak *et al.*, 2003). Since all of the precipitated hydroxides produced from each 500 ml sample were digested, the purity (p) was calculated using Eqn (2):

$$p = \frac{C_i}{\sum_{j=1}^n C_j} \times 100\% \quad (2)$$

where, C_i = concentration of the individual desired metal in the digested solution, n = number of metals measured, C_j = concentration of metal species (j).

3.3 RESULTS AND DISCUSSION

3.3.1 Characteristics of raw AMD water

The general AMD characteristics included the low pH and high concentrations of dissolved ions, as presented in Table 3.1. The major metal ions in the raw AMD water were Fe, Al, Ca, and Mg, among which Fe and Al were potentially valuable, while others such as Mn, Zn, Ni, and Cu were present as minor metals at significantly low concentrations. The pH and

iron content of the raw water did not meet the effluent limitations of US National Pollutant Discharge Elimination System (NPDES) permit, while the Mn concentration was near the permit limitation (40 CFR, Part 434). Consequently, AMD water was treated at the site using ammonia neutralization, prior to discharge.

3.3.2 Effect of pH on metal solubility in AMD

The solubility of Fe, Al, Ca, and Mg (major metals) in raw AMD as a function of pH is presented in Figure 3.2. Almost all the iron precipitated at $\text{pH} > \sim 4$ and most of the aluminum precipitated when pH was raised above 5. However, aluminum resolubilized at pH above 10. For instance, at pH 11, aluminum concentration was 30.8 mg/L, which indicated that approximately half the original aluminum had resolubilized. Magnesium and calcium concentrations remained relatively constant when pH was below 8. Magnesium began to precipitate at $\text{pH} > 8$ and calcium became insoluble at $\text{pH} > 11$. All the solubility relationships were consistent with the behaviors anticipated from Snoeyink and Jenkins (1980) and Stumm and Morgan (1996).

Also presented in Figure 3.2 is the effect of pH on the solubility of the minor metals (Mn, Zn, Ni and Cu) in raw AMD. When pH was < 6 , the minor metals remained in solution. When pH was raised > 8.5 , most of the minor metals were coprecipitated as solids. Precipitation of minor metals could affect the purity of aluminum precipitates recovered at $\text{pH} > 6$. However, the influence of the minor metals on the precipitate purity was not expected to be significant due to their low concentrations.

Table 3.1. Characteristics of raw AMD water.

	Concentration $\pm$ Std. Dev., mg/L									
	pH	Fe	Al	Ca	Mg	Mn	Zn	Ni	Cu	SO₄
Raw AMD	2.6 $\pm$ 0.1	162 $\pm$ 23	80.8 $\pm$ 7.4	191 $\pm$ 10	50.5 $\pm$ 3.9	2.03 $\pm$ 0.21	2.72 $\pm$ 0.34	1.01 $\pm$ 0.15	0.08 $\pm$ 0.02	1,527 $\pm$ 12
NPDES permit	6.0-9.0 [*]	3.5/7.0 ^{**}	N/A	N/A	N/A	2.0/4.0	N/A	N/A	N/A	N/A

^{*}Instantaneous maximum; ^{**}Monthly average/Maximum daily; N/A not applicable.

Figure 3.2. Solubility of major metals (top) and minor metals (bottom) in AMD at different pHs.

Different solubility behaviors of the major and minor metals suggested that stepwise selective precipitation of iron and aluminum was possible, where iron is first precipitated from the AMD water at $\text{pH} \leq 4$. After solid/liquid separation of iron precipitate, effluent pH can be raised to precipitate aluminum. In order to obtain relatively pure aluminum hydroxide, precipitation of Ca, Mg and some minor metals at high pH (>8) should be avoided. Thus, a selective precipitation process, represented schematically in Figure 3.3, was proposed to recover iron and aluminum as metal hydroxides.

3.3.3 Iron precipitation

Metal concentrations in AMD water before and after iron precipitation at pH 3.0-4.5 are listed in Table 3.2. As pH increased, iron concentration decreased. When the pH was raised to ≥ 3.5 , the iron concentration was ≤ 2.36 mg/L. Consequently, most of the iron was removed from the AMD water. At $\text{pH} \leq 3.5$, the aluminum concentration remained relatively constant, indicating no simultaneous precipitation of aluminum occurred. The decrease in the aluminum concentration at $\text{pH} > 3.5$ demonstrated the simultaneous precipitation of aluminum hydroxide with iron hydroxide, which should be minimized in iron recovery operations due to its detrimental impact on product purity and subsequent opportunities for future application.

At $\text{pH} \leq 4.5$, calcium, magnesium and the minor metals remained in solution, which favored the production of a pure iron hydroxide precipitate. Iron recovery and purity of iron precipitates obtained during iron precipitation operation under different pH are shown in Figure 3.4. Iron recovery increased with increasing pH while the purity of the iron precipitate declined. Thus, the performance of the iron precipitation step must be a compromise between iron recovery and precipitate purity. Since the AMD water after iron recovery was used as source

Figure 3.3. Flowsheet of stepwise recovery of iron and aluminum hydroxides from AMD.

* pH range determined by Fe and Al precipitation processes presented in subsequent section.

Table 3.2. Metal concentrations in AMD water before and after iron precipitation (neutralized by NaOH).

	pH	Metal Concentration, mg/L (Percent remaining in Aqueous Phase, %)							
		Fe	Al	Ca	Mg	Mn	Zn	Ni	Cu
Raw AMD	2.6	172.5 (100.0)	88.6 (100.0)	205 (100.0)	54.1 (100.0)	2.30 (100.0)	3.10 (100.0)	1.16 (100.0)	0.07 (100.0)
After Iron Precipitation	3.0	49.9 (28.9)	86.6 (97.7)	197 (96.1)	51.7 (95.6)	2.21 (96.1)	3.00 (96.8)	1.10 (94.8)	0.07 (100.0)
	3.5	2.36 (1.4)	86.1 (97.2)	199 (97.1)	51.9 (95.9)	2.21 (96.1)	3.00 (96.8)	1.11 (95.7)	0.07 (100.0)
	4.0	0.70 (0.4)	78.7 (88.8)	202 (98.5)	53.2 (98.3)	2.25 (97.8)	3.05 (98.4)	1.14 (98.3)	0.07 (100.0)
	4.5	0.15 (0.1)	28.6 (32.3)	199 (97.1)	52.9 (97.8)	2.20 (95.7)	3.05 (98.4)	1.13 (97.4)	0.06 (85.7)

water for aluminum precipitation, high iron recovery was desired to minimize residual iron that would adversely impact the purity of subsequent aluminum precipitates. Since iron recovery exceeded 98.6% at pH range from 3.5 to 4.0, the operational pH for iron precipitation was recommended to be 3.5-4.0, under which conditions a precipitate purity of > 93.4% was obtained (Figure 4). Therefore, recovery of iron hydroxide with relatively high purity was successfully achieved.

3.3.4 Aluminum precipitation

AMD water quality data before and after aluminum precipitation at pH 4.5-8.0 are presented in Table 3.3. Greater than 75% of aluminum precipitated when the pH was raised from 3.5 to 4.5. At $5.0 < \text{pH} < 8.0$, almost all aluminum was removed from solution. Aluminum began to resolubilize at $\text{pH} > 8.0$, which was consistent with the solubility data presented earlier in Figure 3.2. The residual iron (2.36 mg/L) from the iron precipitation step coprecipitated with aluminum at $\text{pH} \geq 4.5$. The concentrations of Ca and Mg remained relatively constant at $\text{pH} \leq 7.0$, which ensured the production of a high purity aluminum precipitate. At $\text{pH} > 7.0$, small amounts of Ca, Mg and some minor metals were removed with the aluminum precipitate, resulting in improved effluent water quality. However, the simultaneous precipitation was detrimental to the purity of the aluminum precipitate. The effect of pH on aluminum recovery and precipitate purity is illustrated in Figure 3.5. At $5.0 \leq \text{pH} \leq 8.0$, aluminum recovery in excess of 94.7% was maintained, though aluminum recovery in the precipitate decreased somewhat as pH was raised > 7.0 , due to the resolubilization of aluminum. As pH increased, the purity of aluminum precipitate decreased. However, relatively high purity and recovery were maintained at pHs ranging from 5.0 to 7.0, where precipitate purity was $> 92.1\%$ and Al recovery $> 97.2\%$.

Figure 3.4. Effect of neutralization pH on recovery and purity of iron hydroxide precipitate.

Since the pH limitation of NPDES permits for AMD water discharge (40 CFR, Part 434) is 6.0–9.0, the recommended pH for aluminum recovery was 6.0–7.0, over which NPDES-based metal limitations (Table 3.1) were met. Thus, relatively high purity aluminum precipitate was successfully recovered from AMD while the effluent water quality was acceptable for discharge.

3.3.5 Effect of neutralization reagents on metal recovery and purity

Chemicals used in active AMD treatment include caustic soda (NaOH), soda ash (Na₂CO₃), ammonia (NH₃), quick lime (CaO) and hydrated lime (Ca(OH)₂) (Skousen *et al.*, 1998). Reagent selection is determined by the acidity level, flow rate, metal concentration, sludge characteristics and economic factors. Results of iron recovery at pH 3.5 and aluminum recovery at pH 6.5 with the aforementioned neutralization reagents are listed in Table 3.4. All five chemicals achieved iron recoveries greater than 98.6% with precipitate purities in excess of 94.2%. Consequently, each of the five chemicals could be applied in the iron recovery step. All of the five chemicals achieved the aluminum recovery >97.2% while all but hydrated lime maintained the precipitate purity >94.1%. The low purity (72.2%) of the precipitate from hydrated lime treatment was attributed to the formation of gypsum and the presence of unreacted residuals, which were observed during neutralization tests. Since all the chemicals used in this study were of high grade and the experiments provided sufficient mixing and reaction time, the presence of hydrated lime residuals was minimized. However, unreacted residuals might pose a purity control problem for the full-scale metal recovery processes if lime or hydrated lime were added.

Table 3.3. Metal concentrations in AMD water before and after aluminum precipitation (neutralized by NaOH).

	pH	Metal Concentration, mg/L (Percent remaining in Aqueous Phase, %)							
		Fe	Al	Ca	Mg	Mn	Zn	Ni	Cu
Before Al precipitation*	3.5	2.36 (1.4)	86.1 (97.2)	199 (97.1)	51.9 (95.9)	2.21 (96.1)	3.00 (96.8)	1.11 (95.7)	0.07 (100.0)
After Al Precipitation	4.5	0.02 (~0.0)	18.7 (21.1)	193 (94.2)	53.3 (98.5)	2.20 (95.7)	3.05 (98.4)	1.13 (97.4)	0.08 (100.0)
	5.0	BDL** (~0.0)	2.3 (2.6)	193 (94.2)	52.5 (97.0)	2.10 (91.3)	3.00 (96.8)	1.12 (96.6)	0.06 (85.7)
	5.5	BDL (~0.0)	0.2 (0.2)	196 (95.6)	52.2 (96.5)	2.13 (92.6)	2.35 (75.8)	1.06 (91.4)	0.03 (42.9)
	6.0	BDL (~0.0)	BDL (~0.0)	192 (93.7)	52.3 (96.7)	2.13 (92.6)	2.55 (82.3)	1.11 (95.7)	0.03 (42.9)
	6.5	BDL (~0.0)	BDL (~0.0)	189 (92.2)	52.5 (97.0)	2.05 (89.1)	1.50 (48.4)	1.05 (90.5)	0.02 (28.6)
	7.0	BDL (~0.0)	BDL (~0.0)	193 (94.2)	51.9 (95.9)	1.88 (81.7)	0.31 (10.0)	0.73 (62.9)	0.01 (14.3)
	7.5	BDL (~0.0)	0.2 (0.2)	187 (91.2)	50.8 (93.9)	1.62 (70.4)	0.11 (3.6)	0.48 (41.4)	0.02 (28.6)
	8.0	BDL (~0.0)	0.8 (0.9)	184 (89.8)	46.9 (86.7)	0.66 (28.7)	0.03 (1.0)	0.11 (9.5)	0.01 (10.3)

*The AMD for Al precipitation was from the iron precipitation step and after solids removal; **BDL Below detection limits.

Figure 3.5. Effect of neutralization pH on recovery and purity of aluminum hydroxide precipitate.

Table 3.4. Metal recovery performances with different chemicals.*

Chemical	Fe Precipitation		Al Precipitation	
	Recovery, %	Purity, %	Recovery, %	Purity, %
NaOH	98.6	97.5	97.2	94.7
Na ₂ CO ₃	98.6	97.7	97.2	95.0
NH ₄ OH	99.0	94.2	97.2	94.5
CaO	99.2	96.6	97.2	94.1
Ca(OH) ₂	99.2	96.4	97.2	72.2

*Fe precipitation at pH 3.5 was followed by Al precipitation at pH 6.5.

The estimated reagent costs of metal recovery from the AMD site of this study are presented in Table 3.5, according to the unit prices of reagents provided by Skousen and Ziemkiewicz (1996). The average AMD flow was estimated at 379 L/min (100 gal/min). Although hydrated lime had advantage in reagent cost (Table 3.5), it was not recommended for metal recovery due to its negative impact on precipitate purity. The reagent cost of soda ash was significantly higher than that of caustic soda or ammonia. The reagent cost of ammonia was comparable to caustic soda. Consequently, both ammonia and caustic soda were economically reasonable reagents for metal recovery from AMD.

3.3.6 Iron oxidation

Oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) is essential to the precipitation of iron at low pH (Sandstrom and Mattsson, 2001). According to Snoeyink and Jenkins (1980), Fe^{3+} precipitates at pH 3-4 while Fe^{2+} does not precipitate at pH<6. Therefore, conversion of Fe^{2+} to Fe^{3+} is critical in order to precipitate iron at pH 3.5-4.0 and to recover high purity aluminum hydroxide at pH 6.0-7.0. In this study, untreated AMD water was bubbled with compressed air for 24 hrs to oxidize Fe^{2+} . Iron removal of 99.6 % was achieved when the pH of raw AMD water was adjusted from ~2.6 to ~4 (Table 3.6), indicating that nearly all the iron in the raw AMD was in Fe^{3+} state. Consequently, the overnight air bubbling of AMD was sufficient to ensure the nearly complete oxidation of iron. It is reported that the abiotic oxidation of ferrous iron to ferric iron proceeds very slowly at pH<3 (Park and Dempsey, 2004). Also, the oxidation of iron is limited by the availability of dissolved oxygen. Therefore, mechanical aeration or gravity aeration may not provide sufficient oxidation in a full-scale metal recovery process. As a result, the oxidation of ferrous iron could be a rate limiting step in full-scale metal recovery. However,

Table 3.5. Reagent cost estimation of metal recovery from AMD.*

Reagent	Reagent Price (\$/ton)**	Reagent consumption (ton/yr)	Reagent cost (\$/yr)
Caustic soda	242.5	162.9	39,508
Ammonia	330.7	114.4	37,844
Soda ash	308.6	238.4	73,585
Hydrated lime	66.1	202.6	13,403

*Estimation was based on the AMD flow rate of 100 gal/min (379 L/min);

**Skousen and Ziemkiewicz (1996).

Table 3.6. Iron concentration change in AMD water after pH adjustment (~4) with NaOH.

No.	Raw AMD		Treated AMD		Iron Removal, %
	pH	Fe, mg/L	pH	Fe, mg/L	
1	2.65	176	3.96	0.74	99.6
2	2.63	169	3.97	0.63	99.6
3	2.64	173	4.01	0.70	99.6

iron oxidation can be enhanced by addition of oxidizers such as hydrogen peroxide (H_2O_2), catalysts, and/or biological treatment (Rao *et al.*, 1996; Stumm and Lee, 1961; Dempsey *et al.*, 2001).

3.4 SUMMARY

Simultaneous metal recovery and AMD treatment were achieved using a selective precipitation process based on solubility characteristics of the major and minor metals in the AMD. Separate iron and aluminum hydroxide products with relatively high purity were successfully recovered via iron precipitation at pH 3.5-4.0 followed by aluminum precipitation at pH 6.0-7.0, while simultaneously meeting the NPDES effluent discharge standards. The proposed metal recovery process was relatively easy to implement in the field because it only required the manipulation of the current AMD neutralization operations.

In this study, iron precipitate purity >93.4% was achieved with iron recovery >98.6%, while aluminum precipitate purity reached >92.1% at a recovery >97.2%. During each metal recovery operation, other metals remained in solution, which ensured the relatively high purity of precipitate products. All of the five neutralization reagents commonly used in AMD treatment can be used for iron and aluminum recovery. However, ammonia and caustic soda were recommended for metal recovery because unreacted hydrated lime might pose a threat to the purity of precipitate products if lime or hydrated lime was added in the full-scale processes. In the full-scale systems, the oxidation might be enhanced by addition of oxidants.

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4. SYNTHESIS OF MAGNETITE NANOPARTICLES WITH FERRIC IRON RECOVERED FROM ACID MINE DRAINAGE: IMPLICATIONS FOR ENVIRONMENTAL ENGINEERING*

ABSTRACT

Synthesis of magnetite nanoparticles has been the focus of numerous recent research efforts, and application of magnetite nanoparticles in environmental engineering is promising. All the previous research of magnetite nanoparticle synthesis utilized reagent-grade chemical as the iron source, and hence the raw chemical costs could limit the application of magnetite nanoparticles in full-scale water or wastewater treatment. It is known that acid mine drainage (AMD) in the *Mid Appalachian* region is low in pH and high in dissolved metals, of which iron is most abundant. In this study, ferric iron recovered from AMD via oxidation-selective precipitation process was used as feed stock to synthesize magnetite nanoparticles by coprecipitation of ferric and ferrous iron at the pH 9.5 under the atmosphere of nitrogen. X-ray diffraction analysis confirmed that the iron oxide phase in the black precipitate was magnetite. Through scanning and transmission electron microscopic studies, it was demonstrated that most of the magnetite particles ranged from 10 to 15 nm and were spheroidical or cubic in shape. Thus, the synthesis of magnetite nanoparticles with the iron recovered from AMD was feasible. Consequently, the need for low-cost raw feed stocks in nanoparticle manufacturing was addressed, providing great opportunity for the application of magnetite nanoparticles in environmental engineering.

Key words: Magnetite nanoparticles, acid mine drainage, synthesis, coprecipitation, metal recovery.

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4.1 INTRODUCTION

Magnetite nanoparticles have been applied in a variety of fields, ranging from ferrofluid technology (Love *et al.*, 2005), information storage (Chakraborty, 1999), biomedicine (Kim *et al.*, 2003), controlled drug delivery (Gupta and Wells, 2004), to nano-absorbents for environmental engineering, due to their size effect and superparamagnetic property. Thus, synthesis of magnetite nanoparticles is a focus of many recent research attempts from different disciplines. The technological routes to synthesize magnetite nanoparticles include ball milling (Goya, 2004), chemical precipitation, thermal decomposition (Teng and Yang, 2004; Woo *et al.*, 2004), and sonochemical synthesis (Vijayakumar *et al.*, 2000). Among them, chemical precipitation is the most common approach with relatively good control over the size and morphology of nanoparticles. Synthesis of magnetite through chemical precipitation includes 1) coprecipitation of Fe^{3+} and Fe^{2+} , 2) partial reduction of Fe^{3+} and 3) partial oxidation of Fe^{2+} , followed by coprecipitation. Aqueous coprecipitation of $[\text{Fe}^{3+}]:[\text{Fe}^{2+}]$ at a ratio of 2:1 to prepare the magnetite nanoparticles is usually carried out in the presence of a base at pH 9-12 under anaerobic conditions (Schmidt, 2005; Jolivet, *et al.*, 2004; Harris, *et al.*, 2003; Dresco *et al.*, 1999; Massart, 1981). Ferrous and ferric chlorides or sulfates were usually used as the iron source, and sodium or ammonium hydroxide as the base in the synthesis. Sidhu *et al.* (1978), Andrade *et al.* (2005), and Rabelo *et al.* (2001) synthesized magnetite nanoparticles by partial oxidation of FeSO_4 with NaNO_3 or KNO_3 at elevated pH and temperature (60-100°C), where nitrates functioned as electron acceptors to form $\text{NO}_{(\text{g})}$. Magnetite nanoparticles were prepared via partial reduction of FeCl_3 with sodium sulfite (Sun *et al.*, 2004) or hydrazine (Merikhi and Feldmann, 2000) as reductants.

Specifically, in environmental engineering, Hu *et al.* (2004) examined the removal of Cr^{6+} from wastewater with the magnetite nanoparticles (c.a. 10 nm) prepared through coprecipitation. They found that adsorption of Cr^{6+} by magnetite followed the *Freundlich* isotherm and was pH and temperature dependent. Mak and Chen (2004) reported the efficient removal of color (methylene blue) with polyacrylic acid-bound magnetite nanoparticles. Maximum adsorption was 0.199 mg/mg and the adsorption process was described by the *Langmuir* isotherm. Magnetically active polymeric particles (MAPPs) and dual-zone sorbents (DZS) were prepared by dispersing magnetite nanoparticles within the polymer phase and were examined for their performance in removing contaminants such as Cu, Zn, As and dichlorophenol (Leun and SenGupta, 2000; Cumbal and SenGupta, 2005). MAPPs and DZS showed unique characteristics which were absent in the current polymeric or inorganic exchangers. Moeser *et al.* (2002) prepared magnetite nanoparticles (~7.5 nm) coated with bifunctional polymer layer (~9 nm in thickness), consisting of an outer hydrophilic polyethylene oxide region and an inner hydrophobic polypropylene oxide region. The nanoparticles showed a high affinity to various synthetic organic compounds (toluene, *o*-dichlorobenzene, and naphthalene *etc.*) from contaminated water, and the particles could be recovered with high-gradient magnetic separation with ~98% efficiency. However, all the previous research on magnetite nanoparticle synthesis utilized commercial, reagent-grade chemical as the iron source. Consequently, high raw chemical costs could limit the utilization of magnetite nanoparticles for environmental engineering in the full-scale process, since water or wastewater treatment usually entails large volumes of flow with a heterogeneous mixture of pollutants.

Acid mine drainage (AMD), formed due to the oxidation of sulfide minerals in the presence of oxygen and water, poses an environmental problem to aquatic ecosystems in coal

and hard rock mining areas and related watersheds (Williams and Smith, 2000; Johnson, 2003). AMD is characterized as low pH, high acidity effluents with high sulfate content and various dissolved metals such as Fe, Al, Mn, Zn, Cu, Ni, Ca, Mg, and Cr *etc.* (Kim *et al.*, 2002; Bird, 2003; Kuyucak, 1998). Active AMD treatment involves addition of neutralizing agents (lime, ammonia, sodium hydroxide, limestone and sodium carbonate) to raise the pH of the AMD water and precipitate the metal ions. Although the exact scale of negative AMD impact is difficult to assess on a world-wide basis, the remediation cost was estimated above \$5 billion for Pennsylvania alone, using current technologies (Hammarstrom *et al.*, 2003). Another problem associated with AMD treatment is the disposal of the voluminous sludge, typically containing 2-4% solids, which is difficult to dewater (Johnson and Hallberg, 2005).

However, AMD is a potential source of valuable metals, provided that the technically and economically efficient recovery processes are developed and applied (Wei, *et al.*, 2005; Tabak *et al.*, 2003; Matlock *et al.*, 2002; Jenke and Diebold, 1983). Metal recovery from AMD typically involves the strict pH adjustment and addition of chemicals to achieve sequential precipitation of metals as hydroxides or sulfides, while traditional AMD treatment usually renders the metals non-recoverable. Among the metallic ion species in AMD, iron is the ubiquitous, staple metal due to the omnipresence of pyrite and its tendency to be oxidized (Johnson and Hallberg, 2005; Kim *et al.*, 2002). In fact, iron oxide is the dominant constituent (ranging from 20-70%) in AMD sludges from both passive and active treatment (Kirby *et al.*, 1999). In view of the great amount of AMD generated annually, the potential to recover iron from AMD is significant. The potential can be further magnified if value-added products are made from the recovered iron. Unfortunately, relatively little research is found in the literature related to the value-added use of the metals recovered from AMD.

This study addressed the need to explore value-added use of the recovered metals from AMD and the high cost issue related to the use of magnetite nanoparticles in water or wastewater treatment by developing a low-cost approach to magnetite nanoparticle synthesis. Ferric iron was first recovered from AMD via an oxidation-selective precipitation process. Magnetite nanoparticles were then synthesized as value-added product by using the ferric iron recovered from AMD via the coprecipitation process. X-ray diffraction, scanning and transmission electron microscopic studies were carried out to characterize the magnetite nanoparticles. Comparisons were made between magnetite nanoparticles synthesized with ferric iron from AMD and those prepared with reagent-grade chemicals. Finally, the implication for environmental engineering is discussed regarding the synthesis of low-cost magnetite nanoparticles with recovered iron from AMD.

4.2 EXPERIMENTAL PROTOCOLS

4.2.1 Water collection and materials

AMD water samples were collected at the entrance to the treatment channel of an AMD treatment facility, located in north central West Virginia, where AMD, formed at abandoned underground coal mines (Upper Freeport coal seams), was pumped to the surface and treated with anhydrous ammonia and hydrogen peroxide to raise the pH, oxidize ferrous iron, and precipitate metals. The solids and debris in the water samples were removed by settling and the remaining suspended solids were removed by filtration through a 0.45 μm membrane. Samples were stored at 4 °C in closed high-density polyethylene bottles before used for metal recovery.

All chemicals, including ferric sulfate, ferrous sulfate, hydrochloric acid, sulfuric acid, sodium hydroxide, ammonium hydroxide and hydrogen peroxide, were of reagent-grade

acquired from *Fisher Scientific*, and used in this study without further purification. Hydrogen peroxide solution of 50% H_2O_2 and ammonium hydroxide solution of 6.4M NH_4OH were used in this study. *Millipore* deionized water was deoxygenated by N_2 bubbling for a half hour prior to use.

4.2.2 Metal recovery

Iron recovery from AMD was achieved by an oxidation-selective precipitation process (Wei, *et al.*, 2005). AMD water was first oxidized with hydrogen peroxide to convert ferrous iron to ferric iron. Then, the pH of AMD water was raised to pH 3.5-4.0 with the addition of 4 N sodium hydroxide solution, where iron precipitated as ferric hydroxide and was separated from AMD by centrifugation at 4,000 rpm in a *Sorvall RC-5C* centrifuge. The solids obtained, mainly ferric hydroxide, were resolubilized with sulfuric acid to achieve a clear solution, which was used as feed stock to synthesize magnetite nanoparticles. The supernatant from centrifugation was further neutralized with sodium hydroxide to pH 6.0-7.0 and aluminum-rich precipitate was obtained after settling for 4 hr. The resulting AMD water was discharged. Samples were taken from the raw AMD and supernatants after each pH adjustment to determine metal concentrations (Fe, Al, Ca, Mg, Mn, Ni, Zn and Cu) in the water according to Standard Method 3111 (APHA, 1998) using an atomic absorption spectrometer (*Perkin Elmer* 3100).

4.2.3 Magnetite nanoparticle synthesis

The method to synthesize magnetite nanoparticles was coprecipitation at room temperature, which required the presence of both ferric and ferrous iron at a ration of 2:1. The ferric iron source was the resolubilized ferric iron solution from the iron recovery process. Reagent-grade ferric sulfate was also used to prepare nanoparticles in order to compare with

those synthesized with ferric iron from AMD. The ferrous iron source for both cases was reagent-grade ferrous sulfate. A typical synthesis process was as follows: solution of $[\text{Fe}^{3+}]:[\text{Fe}^{2+}] = 0.04\text{M}:0.02\text{M}$ was prepared and mixed for 30 min with N_2 bubbling to prevent oxidation by complete removal of dissolved oxygen from the solution (Kim *et al.*, 2001). Then, 6.4 M NH_4OH solution was added to raise pH up to 9.5 and let the crystals grow for 30 min with vigorous mixing and N_2 bubbling. After that, the black precipitate (magnetite) was isolated from solution using an external magnetic field. The black precipitate was then washed 3 times with deoxygenated deionized water until the pH was near neutral (c.a. 7.5). Lastly, the black precipitate was vacuum-dried.

4.2.4 Nanoparticle characterization

The iron oxide phase in the vacuum-dried powders obtained from the synthesis tests was identified with powder X-ray Diffraction (XRD), using a *PANalytical* X'Pert PRO diffractometer with a graphite monochromator and $\text{Cu K}\alpha$ radiation (45 kV, 40 mA, $\lambda = 1.542 \text{ \AA}$). Scans were made from 25 to 75° (2 θ) with a constant step width of 0.033°. The particle size and morphology of synthesized particles were examined with both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The vacuum-dried magnetite samples were used for SEM analysis, which was carried out with a *HITACHI* S-4700 electron microscope. The sample preparation for TEM analysis was as follows: After washing three times with deoxygenated deionized water (before vacuum-drying), a small aliquot of the black precipitate was taken, and 0.01 M HCl was added to neutralize the anionic charge on the surface of magnetite particles. Then, the positively charged colloidal particles were concentrated by centrifugation at 4,000 rpm for 20 min and peptized with deoxygenated deionized water. The diluted magnetite suspension was then ultrasonicated for 15 minutes. Finally, a drop of the as-prepared magnetite suspension

was put on a 400-mesh copper grid and allowed to dry under ambient conditions. TEM examination was performed by using a *JEOL* 1000 electron microscope.

4.3 RESULTS AND DISCUSSION

4.3.1 Iron recovery

Typically, AMD water contains both ferric and ferrous iron in ratios that depends on the geological conditions and the access of oxygen. According to Snoeyink and Jenkins (1980), Fe^{3+} precipitates at pH 3-4 while Fe^{2+} does not precipitate at pH < 6. In order to precipitate all the iron at low pH (<4) and avoid the simultaneous precipitation of other metals, it is necessary to oxidize ferrous iron into ferric iron, followed by pH adjustment. The reactions of oxidation with hydrogen peroxide and precipitation of ferric hydroxide by neutralization are as follows:

The dissolved metal concentrations in AMD during the metal recovery process are presented in Table 4.1. The raw AMD water was low in pH and contained elevated dissolved metals (Fe, Al, and Mn *etc.*). When the pH was raised from 2.6 to 3.5, the dissolved iron concentration dropped from 169 mg/L to 4.17 mg/L, indicating ~97.5% of iron was recovered as iron hydroxide. At pH 3.5, the metal concentrations other than iron remained nearly unchanged or dropped slightly, which ensured the iron precipitate obtained was of high purity. When the pH was adjusted to pH 6.7, almost all the Al precipitated and the remaining Fe (4.17 mg/L) was removed as well. At pH 6.7, the water quality met the National Pollutant Discharge Elimination System (NPDES) requirements for the coal mining industry. The iron hydroxide precipitate from

Table 4.1. Dissolved metal concentration (mg/L) in AMD during metal recovery process.

	pH	Fe	Al	Ca	Mg	Mn	Zn	Ni	Cu
Raw AMD	2.6	169	71.0	166	38.7	2.22	2.95	1.10	0.48
pH Adjustment	3.5	4.17	69.6	165	37.7	2.16	2.90	1.03	0.39
	6.7	0.09	0.2	156	36.6	1.85	0.28	0.69	0.02
NPDES permit*	6.0-9.0**	3.5/7.0***	N/A	N/A	N/A	2.0/4.0***	N/A	N/A	N/A

*NPDES permit for coal mining; **Instantaneous maximum; ***Monthly average/Maximum daily; N/A not applicable.

Table 4.2. Metal concentrations in the iron precipitate resolubilized with H₂SO₄.

Metals	Fe	Al	Ca	Mg	Mn	Zn	Ni	Cu
Concentration (mg/L)	6950	51.3	1.23	1.01	0.9	0.4	0.4	0.19
Metal Mass Fraction (%)	99.21	0.73	0.018	0.014	0.013	0.006	0.006	0.003

AMD was resolubilized with sulfuric acid to obtain ferric sulfate solution. The concentrations of the metals present in the solution are listed in Table 4.2. The predominant metal was Fe (99.21%), along with some Al (0.73%). Other metals were present at very low concentrations. Consequently, ferric iron with relatively high purity was successfully recovered with oxidation-selective precipitation process while the resulting solution met NPDES permit requirement.

4.3.2 Magnetite nanoparticle synthesis

Upon the addition of NH_4OH solution to bring the pH above 9.5 during the synthesis tests, a brief brown-colored phase was observed prior to the formation of a black precipitation. XRD patterns of the black precipitate samples obtained with ferric iron from AMD and from the reagent-grade chemical are presented in Figure 4.1. The peak positions of Plane (220), (311), (400), (511), and (440) for both samples matched consistently with those of standard data for magnetite (JCPDS 19-629), demonstrating that the synthesized black powders were magnetite particles. The chemical reaction for magnetite synthesis via coprecipitation of Fe^{3+} and Fe^{2+} (Kim *et al.*, 2001) is:

In order to obtain magnetite precipitate instead of other iron oxide phases, it was critical to maintain the $[\text{Fe}^{3+}]:[\text{Fe}^{2+}]$ molar ratio at 2:1 (as in the structure of magnetite) at pH ~9.5 without the presence of oxygen. The occurrence of oxidation during the reaction would have resulted in a failure to obtain magnetite particles, and the precipitated particles would be iron hydroxide. In the meanwhile, the XRD pattern of magnetite powder synthesized with ferric iron from AMD (trace a, Figure 4.1) was almost identical with that of the sample prepared with reagent-grade chemicals (trace b, Figure 4.1), indicating that the purity of the resolubilized ferric sulfate solution recovered from AMD was sufficient for magnetite nanoparticle synthesis.

The SEM micrographs for magnetite particles synthesized with ferric iron reclaimed from AMD under different reactant concentrations are shown in Figure 4.2. The particles in both cases had a rather narrow distribution, where most of the magnetite particles were within 10-15 nm. Therefore, the magnetite nanoparticles were successfully synthesized with ferric iron from AMD. As comparison, the SEM micrographs for magnetite particles prepared with ferric iron of reagent-grade chemical are presented in Figure 4.3, and the size and morphology of the magnetite particles were almost the same as those synthesized with ferric iron recovered from AMD (Figure 4.2). The micrographs in Figure 4.2 and 4.3 also indicated that the magnetite nanoparticles agglomerated into clusters during the vacuum-drying process. Agglomeration while drying was a problem in many nanoparticle systems, which could significantly reduce the surface area and active sites for adsorption or reaction. Fortunately, in the application of magnetite nanoparticles for water or wastewater treatment, there is no need for drying of the nanoparticles, and thus the agglomeration problem is mitigated significantly to keep their unique properties of nanoparticles.

The high resolution TEM micrographs for magnetite particles synthesized with ferric iron from AMD and from reagent-grade ferric sulfate are presented in Figure 4.4 and 4.5, respectively. The TEM images of the single layer particles re-confirmed that the magnetite nanoparticles were narrowly distributed within 10-15 nm for samples synthesized with ferric iron from AMD and from reagent-grade chemical under both reactant concentrations: (a) $[\text{Fe}^{3+}]:[\text{Fe}^{2+}] = 0.02\text{M}:0.01\text{M}$; (b) $[\text{Fe}^{3+}]:[\text{Fe}^{2+}] = 0.04\text{M}:0.02\text{M}$. The morphology of the particles for both cases ranged from cubic to spheroidal in shape, which was consistent with the results by Jolivet *et al.* (2004), Harris *et al.* (2003), and Kim *et al.* (2001). The particle morphology indicated that the crystal forms of magnetite nanoparticles were of either octahedron or rhombo-dodecahedron

Figure 4.1. XRD patterns of magnetite particles synthesized with ferric iron from AMD and reagent-grade chemical. Reactant concentration: $[\text{Fe}^{3+}]: [\text{Fe}^{2+}] = 0.08\text{M}:0.04\text{M}$.

Figure 4.2. SEM micrographs for magnetite particles synthesized with ferric iron from AMD under different reactant concentrations: (a) $[\text{Fe}^{3+}]: [\text{Fe}^{2+}] = 0.02\text{M}:0.01\text{M}$; (b) $[\text{Fe}^{3+}]: [\text{Fe}^{2+}] = 0.04\text{M}:0.02\text{M}$.

(a)

(b)

Figure 4.3. SEM micrographs for magnetite particles synthesized with ferric iron from reagent-grade ferric sulfate under different reactant concentrations: (a) $[\text{Fe}^{3+}]: [\text{Fe}^{2+}] = 0.02\text{M}:0.01\text{M}$; (b) $[\text{Fe}^{3+}]: [\text{Fe}^{2+}] = 0.04\text{M}:0.02\text{M}$.

(a)

(b)

Figure 4.4. TEM micrographs for magnetite nanoparticles synthesized with Fe³⁺ from AMD at different reactant concentrations: (a) [Fe³⁺]:[Fe²⁺] = 0.02M:0.01M; (b) [Fe³⁺]:[Fe²⁺] = 0.04M:0.02M.

(a)

(b)

Figure 4.5. TEM micrographs for magnetite nanoparticles synthesized with Fe^{3+} from reagent-grade ferric sulfate at different reactant concentrations: (a) $[\text{Fe}^{3+}]:[\text{Fe}^{2+}] = 0.02\text{M}:0.01\text{M}$; (b) $[\text{Fe}^{3+}]:[\text{Fe}^{2+}] = 0.04\text{M}:0.02\text{M}$.

(Cornell and Schwertmann, 2003). The particle size and morphology were almost identical for both samples obtained from AMD and from reagent-grade chemicals (Figure 4.4 and 4.5). Consequently, ferric iron recovered from AMD could be a low-cost feedstock substitute for the reagent-grade ferric sulfate to synthesize magnetite nanoparticles.

According to Jolivet *et al.* (2004), the surface characteristics were the dominant factors for the particle stabilization and control of particle size and morphology. The surface charge of metal oxides was pH dependent, and the point of zero charge (PZC) was expressed as the pH conditions in solution where the surface charge was zero. The PZC of magnetite particles reported in the literature ranged from 6.3 to 7.2 (Cornell and Schwertmann, 2003; Jolivet *et al.*, 2004). The surface potential of metal oxides (ψ_0), as a result of surface charge, could be approximately described with the following equations (Fuerstenau and Pradip, 2005):

$$\psi_0 = 2.3 \frac{RT}{F} [pH_{pzc} - pH] = 0.059 [pH_{pzc} - pH] \text{ Volts} \quad (5)$$

where R was the universal gas constant, F the Faraday constant, and T the absolute temperature. Therefore, the surface potential for magnetite nanoparticles was from -135.7 mV to -188.8 mV (corresponding to the above PZC range) during the synthesis at pH ~9.5. The negative sign indicated that the magnetite nanoparticles formed at elevated pH possessed a negative charge at their surfaces. The repulsive force between the charged particles prevented the growth of even bigger particles, therefore ensuring the stability of the nano-suspension system.

4.3.3 Implications for environmental engineering

AMD is an environmental problem with long-term liability for the mining industry or water management units, and sludge treatment/disposal is difficult and costly to implement. The oxidation-selective precipitation process used in this study converted traditional AMD treatment

into metal recovery process, while ensuring the effluent met NPDES permit requirements. The advantage of the proposed metal recovery processes required only minimum manipulation of the traditional AMD treatment processes, which raised the pH and precipitated the metals together. Consequently, the proposed process would be easy to implement at the treatment site. It also mitigated the AMD sludge disposal problems. This process had the potential to cover its treatment costs if value-added uses of the recovered metals, such as magnetite nanoparticle synthesis, could be put into practice.

The synthesis of magnetite nanoparticles was intensively studied and the application of magnetite nanoparticles in environmental engineering was promising. Magnetite nanoparticles have a large specific surface area, making them ideal as nano-sorbents for some contaminants (Hu *et al.*, 2004; Mak and Chen, 2004; Leun and SenGupta, 2000). In the structure of magnetite nanoparticles, one third of the total iron was in the ferrous state with reducing power, which made it very useful in remediation or wastewater treatment to reduce some metal ions to less soluble forms or to detoxify some metals such as Cr^{6+} (Cornell and Schwertmann, 2003; Hu *et al.*, 2004). Another feature of magnetite nanoparticles, which made them promising in environmental treatment or remediation, was their superparamagnetic property. After sorption, the contaminant compounds along with magnetite nanoparticles could be separated from the wastewater using high gradient magnetic separation (HGMS) techniques (Ebner and Ritter, 2004; Moeser, *et al.*, 2002; Leun and SenGupta, 2000), making the regeneration and reuse of nanoparticles possible.

In environmental engineering, however, the utilization of magnetite nanoparticles prepared from reagent-grade chemicals could not be cost-effective in the full-scale process, due to the characteristics of water or wastewater, such as high flow rate, and the presence of various

pollutants, and associated high consumption and loss of nanoparticles. The results of this study demonstrated that the iron hydroxide precipitate had a relatively high purity, and after resolubilization, the magnetite nanoparticles synthesized with ferric iron from AMD showed the same quality as those prepared with reagent-grade chemicals. Thus, this study provided a great opportunity for manufacturing of low-cost magnetite nanoparticles for water and wastewater treatment, and hence the overall waste minimization was achieved.

4.4 SUMMARY

Ferric iron was recovered from AMD with relatively high purity via oxidation-selective precipitation process, while the resulting effluent was eligible for discharge. The proposed metal recovery processes required only minimum manipulation of the traditional AMD treatment processes, which would be easy to implement at the treatment site. Synthesis tests demonstrated that it was feasible to prepare magnetite nanoparticles via the coprecipitation method with the recovered ferric iron from AMD. Scanning and transmission electron microscopic studies demonstrated that most of the magnetite nanoparticles ranged from 10 to 15 nm in size and were spheroidical or cubic in shape. Consequently, the recovered ferric iron from AMD could be a low-cost substitute feedstock for reagent-grade chemical for magnetite nanoparticle preparation, which provided great opportunity for the application of magnetite nanoparticles in environmental engineering.

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5. CONCLUSIONS

Detailed experimental research was carried out for sludge characterization, dewaterability, iron and aluminum recovery, and synthesis of magnetite nanoparticles, by using AMD water and sludge samples collected from a bond-forfeited coal mine site (Upper Freeport seam) in north central West Virginia. The following conclusions were drawn:

1. The AMD sludge from ammonia neutralization was characterized by high pH and alkalinity, high total Fe and Al, elevated sulfate, and low solids ($0.72 \pm 0.24\%$). The particles in the sludge were fine, with a mean of $12 \pm 1.5\mu\text{m}$, which fitted the *Rosin-Rammler* distribution. Compared with lime-treated AMD sludge, this sludge was relatively pure in composition with the iron and aluminum hydroxides as the main solids constituents. Consequently, potential value-added uses of sludge from ammonia-treated AMD existed. Coagulation and flocculation treatment did not effectively reduce the final volume of the settled sludge. Poor performances of coagulation and flocculation might be caused by the high ionic strength of the sludge suspension.
2. The *SRF* values were $1.31 \pm 0.32 \times 10^{11}$ m/kg for ammonia-treated AMD sludge. Compared to other AMD sludges and metal hydroxide sludges, ammonia-treated AMD sludge demonstrated relatively good dewaterability in terms of *SRF* values. Further, filterability could be improved considerably through the addition of appropriate polymeric flocculants. The compressibility coefficient (1.07) demonstrated the ammonia-treated AMD sludge was compressible.

3. The total solids content in the sludge cakes obtained from vacuum filtration tests with Buchner funnel and filter leaf ranged from 4.5 to 6.3% for ammonia-treated AMD sludge, which was not improved by polymer addition. A vacuum of 50.8 kPa was the appropriate level for vacuum filtration. The appropriate immersion time was 60 seconds for a vacuum filter, and a total solids content of 6.2% and a filter yield of 3.04 kg/m²h were achieved. Belt filter press showed a good performance in improving solids content of the sludge cake. With the ammonia-treated AMD sludge of ~0.4% solids as feed, the bench-scale belt filter press achieved sludge cakes of ~10% solids.
4. Simultaneous metal recovery and AMD treatment were achieved using a selective precipitation process based on solubility characteristics of the major and minor metals in the AMD. Separate iron and aluminum hydroxide products with relatively high purity were successfully recovered via iron precipitation at pH 3.5-4.0 followed by aluminum precipitation at pH 6.0-7.0, while simultaneously meeting the NPDES effluent discharge standards. The proposed metal recovery process was relatively easy to implement in the field because it only required the manipulation of the current AMD neutralization operations.
5. Iron precipitate purity >93.4% was achieved with iron recovery >98.6%, while aluminum precipitate purity reached >92.1% at a recovery >97.2%. During each metal recovery operation, other metals remained in solution, which ensured the relatively high purity of precipitate products. All of the five neutralization reagents commonly used in AMD

treatment can be used for iron and aluminum recovery. However, ammonia and caustic soda were recommended for metal recovery because unreacted hydrated lime might pose a threat to the purity of precipitate products if lime or hydrated lime was added in the full-scale processes. In the full-scale systems, the oxidation might be enhanced by addition of oxidants.

6. An approach to synthesize low-cost magnetite nanoparticles was developed with the recovered ferric iron from AMD as iron source, and it was proven feasible. Scanning and transmission electron microscopic studies demonstrated that most of the magnetite nanoparticles ranged from 10 to 15 nm in size and were spheroidal or cubic in shape. Consequently, the recovered ferric iron from AMD could be a low-cost substitute feedstock for reagent-grade chemicals for magnetite nanoparticle preparation, which provided great opportunity for the application of magnetite nanoparticles in environmental engineering.

APPDNDIX A

Figure A.1. Vacuum filtration or *SRF* test apparatus.

Figure A.2. The apparatus for filter leaf tests.

Figure A.3. Rotary drum vacuum filtration apparatus (Eckenfelder, 2000).

Figure A.4. Relationship between V and t/V based on test data from *Omega Site* sludge.

Figure A.5. The typical size distribution of the ammonia-treated AMD sludge.*

* R stands for the retained weight fraction (%), and X is the size in microns. The data plotted are transformed by taking natural logarithms.

Figure A.6. Effect of applied vacuum on total solids content of the sludge cake.

Figure A.7. Effect of polymer addition on total solids content of the sludge cake.*

*Tests were conducted at 50.8 kPa at polymer concentration of 100ppm.

Figure A.8. Percent settled sludge at different concentrations of bentonite clay.

Figure A.9. Percent settled sludge at different concentrations of alginic acid and starch.

APPDNDIX B

Table B.1. Percent settled sludge at different concentration of coagulants/flocculants

Chemical	Floc-A						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	69.7	70.4	70.8	71.0	73.5	77.0

Chemical	Floc-B						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	68.8	70.7	71.5	73.9	75.5	78.4

Chemical	Floc-C						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	68.0	68.0	69.7	71.5	71.1	72.3

Chemical	Floc-D						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	71.2	71.9	71.1	70.3	71.5	77.5

Chemical	Floc-E						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	70.4	69.7	69.5	69.6	69.5	72.6

Chemical	Floc-F						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	69.3	68.5	68.3	67.1	66.9	65.7

Chemical	Floc-H						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	68.0	68.8	67.8	67.3	65.6	66.2

Chemical	Floc-I						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	66.3	64.5	62.3	60.6	60.3	59.0

Chemical	Floc-J						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	69.0	68.7	69.5	71.0	72.0	73.3

Chemical	Floc-K						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	67.7	65.6	65.0	67.1	69.3	70.1	71.0

Chemical	Coag-A						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	54.5	55.5	55.4	57.4	58.8	60.5	64.6

Chemical	Coag-B						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	55.0	54.9	55.4	56.9	57.9	60.5	64.6

Chemical	Aluminum sulfate						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	58.0	56.8	57.4	57.8	56.7	57.5	57.9

Chemical	Ferrous sulfate						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	55.0	57.2	58.4	58.8	59.6	58.3	58.3

Chemical	Ferric chloride						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	56.0	56.2	56.4	56.8	56.7	57.0	56.9

Chemical	Ferric sulfate						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	58.8	58.6	58.8	59.1	59.6	59.8	59.3

Chemical	Starch						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	60.8	61.0	61.8	60.0	60.4	61.2	61.7

Chemical	Bentonite clay						
Concentration (ppm)	0	100	200	400	600	1000	1500
Percent settled sludge	59.0	59.2	58.8	56.2	56.1	54.9	54.4

Chemical	Alginic acid						
Concentration (ppm)	0	10	20	40	60	100	150
Percent settled sludge	61.0	60.6	61.4	62.2	62.4	64.1	64.2

Table B.2. Effect of polymer addition on *SRF* of AMD sludges.*

Chemicals	<i>SRF</i> (m/kg)
Control	1.70×10^{11}
Floc-D	1.49×10^{11}
Floc-F	1.88×10^{11}
Floc-G	0.61×10^{11}
Floc-H	1.71×10^{11}
Floc-K	171×10^{11}
Floc-I	1.45×10^{11}

* The applied vacuum was 50.8 kPa and polymer concentration was 100 ppm.

Table B.3. Effect of applied vacuum on *SRF*

<i>P</i> (kPa)*	<i>SRF</i> (m/kg)	Log(<i>P</i>)	Log(<i>SRF</i>)
44.02	9.79×10^{10}	1.64	10.99
50.79	1.13×10^{11}	1.71	11.05
60.95	1.42×10^{11}	1.78	11.15
74.49	1.7×10^{11}	1.87	11.23

* *P*: the applied vacuum.

Table B.4. Effect of applied vacuum on total solids content of filter cake and filter yield.*

Vacuum (kPa)	Total solids contents (%)	Filter yield (kg/m ² h)
44.02	5.93	2.87
50.79	6.16	3.04
60.95	6.27	2.97
74.49	6.29	2.96

* Experimental conditions were 60 sec. for immersion, 60 sec. for drying and 30 sec. for cake removal.

Table B.5. Effect of immersion time on total solids content of filter cake and filter yield.*

Immersion time (sec)	Total solids contents (%)	Filter yield (kg/m ² h)
30	6.16	3.04
60	5.89	3.62
90	5.39	3.67
120	5.18	3.60

* The applied vacuum was 50.8 kPa with 60 sec. for drying and 30 sec. for cake removal.

Table B.6. The dissolved metal concentrations of AMD at different pHs.

pH	Metal concentrations (mg/L)							
	Al	Fe	Mn	Ca	Mg	Cu	Ni	Zn
2.65	76.40	136	1.97	188	50.4	0.1	0.98	2.6
4.03	62.60	0.73	1.95	190	50.3	0.1	0.96	2.65
4.49	26.10	0.3	1.93	186	48.9	0.09	0.98	2.65
4.95	3.70	0.14	1.9	195	48.7	0.06	0.96	2.6
5.64	0.3	0.12	1.88	188	48.6	0.03	0.95	2.35
5.96	0.1	0.1	1.85	192	49.8	0.02	0.93	2.00
6.69	0.1	0.12	1.64	184	47.6	0.01	0.63	1.6
7.04	0.1	0.09	1.53	194	47.9	0.01	0.53	0.2
7.58	0.1	0.08	1.07	192	47.6	0.02	0.22	0.11
8.08	0.1	0.1	0.33	182	43.9	0.02	0.07	0.08
8.57	1.9	0.08	0.07	185	36.1	0.02	0.06	0.07
9.09	4.8	0.04	0.04	189	24.7	0.01	0.04	0.06
9.52	7.1	0.06	0.01	186	10.33	0	0.03	0.06
9.98	11.7	0.08	0.02	180	1.86	0.02	0.05	0.05
11	30.8	0.04	0.02	174	0.02	0.01	0.07	0.05
11.55	30.8	0.07	0.02	91	<0.01	0.01	0.04	0.06
12.14	32.6	0.06	0.02	22	<0.01	0.01	0.03	0.07

Table B.7. Effect of neutralization pH on recovery and purity of iron hydroxide precipitate.

pH	Recovery (%)	Purity (%)
3.0	71.1	99.8
3.5	98.6	97.5
4.0	99.6	93.4
4.5	99.9	74.0

Table B.8. Effect of neutralization pH on recovery and purity of iron hydroxide precipitate.

pH	Recovery (%)	Purity (%)
4.5	76.4	96.9
5.0	94.7	97.2
5.5	97.1	96.1
6.0	97.2	95.8
6.5	97.2	94.7
7.0	97.2	92.1
7.5	97.1	90.6
8.0	96.4	79.5

VITA

Xinchao Wei was born in Mengcheng, Anhui Province, People's Republic of CHINA. He graduated from Bozhou No.1 High School, Bozhou, Anhui Province in 1989, and enrolled in Northeastern University (NEU), Shenyang, Liaoning Province. He received his Bachelor and Master Degrees in Mineral Processing Engineering in 1993 and 1996, respectively. After graduation, he worked in Department of Mineral Processing Engineering, NEU until 2002. He was admitted into West Virginia University in spring 2002, studying for his Master degree in Mining Engineering. He worked under the advisement of Dr. Felicia F. Peng and his thesis work focused on fine coal separation, and evaluation and assessment of carbon dioxide mitigation technologies, especially mineral sequestration of CO₂ by carbonation. After he received his Master degree in 2003, he started his Ph.D. study in Civil and Environmental Engineering at West Virginia University under the supervision of Dr. Roger C. Viadero Jr. His doctoral work focused on acid mine drainage treatment, sludge dewatering, metal recovery, and synthesis of magnetite nanoparticles.