HIGH RATE CLARIFICATION FOR TREATMENT OF MINE WATER

by

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Abstract

Two high-rate clarification processes are often used in mine water treatment, the high density sludge (HDS) process and the ballasted flocculation process. The purpose of this research project was to compare treatment outcomes of HDS and ballasted flocculation to the conventional active lime treatment process in terms of water and sludge quality. Additionally, the effect of replacing lime, which is typically used in mine water treatment for pH adjustment, with cement kiln dust (CKD), an alkaline by-product of cement manufacture, in these processes was investigated. Initially, a comparison between the conventional, HDS, and ballasted flocculation processes for treatment of acid mine drainage (AMD) using lime as the alkali was undertaken. It was found that the ballasted flocculation process resulted in settled water with lower concentrations of arsenic (As) and zinc (Zn) and lower turbidity compared to the other two treatment processes, confirming anecdotal evidence. This was achieved even with the considerable difference in sedimentation times for the processes, 60 minutes for conventional and HDS versus 3 minutes for ballasted flocculation. The HDS process, as its name suggests, produced the highest density sludge (i.e., lowest sludge volume and sludge volume index and highest % wet and dry solids). Further investigations into the HDS and ballasted flocculation processes, and the replacement of lime with CKD therein, revealed that solids loading had the greatest impact on floc density, settling rate, and sludge density. No difference in iron concentrations or turbidity measurements was found in ballasted flocculation-treated and clarified samples using various ballast materials (i.e., microsand, glass beads, and magnetite) as well as no ballast at all, using either lime or CKD as the alkali. Therefore it was concluded that the increased contaminant removal found with the ballasted flocculation process compared to the conventional or HDS processes was due to the higher flocculation speed used, not the addition of ballast material. Finally, a two-stage ballasted flocculation treatment process tested for remediation of high-As neutral mine drainage (NMD) was able to decrease As concentrations to below 0.10 mg/L, whereas a single-stage process could not.

List of Abbreviations and Symbols Used

μ	viscosity
ν	velocity
ρ	density
φ	shape factor
AMD	acid mine drainage
ARD	acid rock drainage, another term for AMD
As(III)	arsenite; As^{3+}
As(V)	arsenate; As^{5+}
BDAT	best demonstrated available technology
CKD	cement kiln dust
$CaCO_3$	calcite; calcium carbonate
CaO	lime; calcium oxide
$Ca(OH)_2$	hydrated lime; calcium hydroxide
C_d	drag coefficient
d	diameter
Eh	reduction potential compared to standard hydrogen electrode
g	acceleration due to gravity
G	velocity gradient, s^{-1}
HDS	high density sludge
ICP-MS	inductively coupled plasma-mass spectrometry
LOI	loss on ignition at 1000 °C
mg/L	milligrams per litre
mL/g	millilitres per gram
mL/L	millilitres per litre
mS/cm	milli-Siemens per centimeter
mV	millivolts
MMER	Metal Mining Effluent Regulations
NaOH	sodium hydroxide
NMD	neutral mine drainage

NTU	nephelometric turbidity units
OH^-	hydroxyl ion
ORP	oxidation reduction potential
rpm	rotations per minute
s^{-1}	per second
SHE	standard hydrogen electrode
SVI	sludge volume index, mL/g
TSS	total suspended solids, mg/L
USEPA	United States Environmental Protection Agency
µg/L	micrograms per litre
v/v	volume per volume

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Chapter 1 Introduction

Discharges from metal ore mines can be heavily contaminated with metals and suspended solids and are regulated in Canada by the Metal Mining Effluent Regulations (MMER; Fisheries Act 2002; Environment Canada 2012a). Even with a 99 to 100 % compliance rate with current regulations, mine water discharges in Canada have been shown to have negative effects on benthic and aquatic species downstream from discharge sites (Environment Canada 2012b). The MMER regulations are currently under review and more stringent guidelines have been proposed (Environment Canada 2012a), necessitating research into enhanced treatment processes for mine water, especially those with high concentrations of difficult-to-treat contaminants such as arsenic.

Mine water becomes contaminated through contact with ores exposed during the mining process. Sulphidic ores like pyrite (FeS_2) release soluble metals and generate acidity (i.e., H_2SO_4) when exposed to water and oxygen which further dissolves the ore releasing more contamination. Acid mine drainage (AMD) refers to contaminated mine water that has a pH below 6, while neutral mine drainage (NMD) has a pH above 6 (Kuyucak 1998; INAP 2009). In general, NMD has lower concentrations of metals and sulphate than AMD but may have high concentrations of zinc, cadmium, manganese, antimony, arsenic, and/or selenium (Kuyucak 1998, INAP 2009).

The most widely used treatment for mine water includes alkalinity addition, usually in the form of lime or hydrated lime, to raise the pH in order to neutralize acidity (if present) and precipitate dissolved metals as hydroxides (Bosman 1974; Brown et al. 2002; Younger et al. 2002; Johnson & Hallberg 2005; Zinck & Griffith 2013). Precipitated solids can then be removed by sedimentation or filtration processes. The conventional lime precipitation-sedimentation process generates high volumes of low-density sludge, typically 1 to 3 % solids, which is costly to dewater and/or dispose of (Bosman 1983; Kuyucak 1998; Aubé & Zinck, 1999; Zinck & Griffith 2013).

The two most commonly used clarification methods for mine water treatment are conventional sedimentation and high density sludge (HDS) (Zinck & Griffith 2013). The HDS process involves recycling the sludge generated by lime precipitation to the head of the treatment process. Sludge recirculation has the effect of densifying the sludge generated to between 10 and 50 % solids (Kostenbader & Haines 1970; Bosman 1974; Bosman 1983; Knocke & Kelley 1987; Kuyucak 1998; Aubé & Zinck 1999; Johnson & Hallberg 2005; Bullen 2006). Another high-rate treatment process used in mine water treatment is ballasted flocculation, which incorporates a high-density ballast material, usually microsand, into the flocculation stage of the treatment process (Tchobanoglous et al. 2003; Young & Edwards 2003). The ballast material gets incorporated into the precipitated flocs, increasing their density and therefore settling rate and also producing a denser sludge.

There are advantages and disadvantages to both high-rate treatment processes. The HDS process generates a much denser sludge than the conventional sedimentation process and therefore requires less dewatering and less space for disposal, however clarifier sizes can be quite large. Ballasted flocculation, with its rapid floc settling rate, requires much smaller clarifiers, reducing space requirements and capital costs for the treatment plant (Young & Edwards 2003). Unfortunately, sludge solids must remain low (i.e., < 2 to 3 %) in order to effectively recover the ballast material from the settled sludge using a hydrocyclone. Anecdotally, the ballasted flocculation process is said to generate higher-quality finished water in terms of TSS and metals concentrations, making it potentially better suited to meet the proposed more conservative MMER discharge guidelines. However, there is a paucity of information in published literature that supports this theory.

Typically, lime in the form of slaked or hydrated lime ($Ca(OH)_2$) is used as the alkali in mine water treatment processes (Zinck & Griffith 2013). However, the impact of lime on the environment in terms of the mining of raw materials, the fuel required for calcining, and the release of significant quantities of CO_2 during the calcining process have led to investigations into alternative alkali materials for use in mine water treatment. Cement kiln dust (CKD) is a fine-grained by-product of cement manufacture usually containing a high CaO concentration that makes it a potential alternative to lime in mine water treatment processes (Mackie et al. 2010). CKD has been shown to raise the pH of and precipitate metals from mine water equally well as lime but with a higher concentration of material required to meet the precipitation pH depending on the free lime concentration (i.e., alkalinity) of the CKD (Mackie & Walsh 2012). CKD has also been shown to reduce sludge volumes associated with precipitation of metals from AMD, even with the additional material required for effective metals precipitation (Mackie & Walsh 2012). Mechanisms of metal precipitation and sludge densification with CKD treatment have not been previously investigated.

1.1 Research Questions and Objectives

The purpose of this research project was to determine the relative effectiveness of two high-rate clarification methods for the treatment of mine water. Additionally, the mechanisms of soluble metals removal from AMD using CKD versus lime and the impacts on sludge properties were investigated. The hypothesis of this research project was that both high-rate clarification processes would increase treatment efficacy compared to conventional sedimentation, and that replacing lime with CKD as the alkali would not have a negative impact on treatment performance. This hypothesis was tested by the following specific objectives;

1. to compare the settled effluent water quality and sludge properties from HDS and ballasted flocculation treatment of mine water with the conventional precipitation-sedimentation process;

2. to investigate the contaminant removal mechanisms and sludge densification mechanisms involved in the HDS and ballasted flocculation treatment processes;

3. to investigate the impact of replacing lime with CKD in treatment of mine water in terms of effluent and sludge quality within the two high-rate clarification processes, HDS and ballasted flocculation; and

4. to investigate contaminant removal mechanisms and sludge densification mechanisms when lime is replaced with CKD.

1.2 Organization of Thesis

Background information on mine water characteristics, treatment processes, and CKD can be found in Chapter 2. Chapter 3 describes the results of a bench-scale study to examine conventional, HDS, and ballasted flocculation processes for the treatment of AMD from a lead/zinc mine using lime as the alkali. Chapter 4 outlines the results of a study that examined lime versus CKD addition in the HDS process, and Chapter 5 details the results of the same alkali comparison in the ballasted flocculation process. Chapter 6 details the results of a bench-scale study that investigated the treatment performance of a single- and two-stage ballasted flocculation processes for treatment of a high-arsenic synthetic NMD. Chapter 7 summarizes the results of this research, details the main conclusions of the thesis, and provides recommendations for future work. This thesis has been presented in publication format, with versions of Chapters 3, 4, and 6 having been published elsewhere. The author of this thesis is also the lead author of these publications and performed the research, designed and performed or directly oversaw the laboratory investigations, interpreted the resulting data, and wrote the manuscripts. The co-authors of these publications assisted with laboratory procedure development where required and edited manuscripts.

1.3 Originality of Research

The negative effects of mine water discharges on aquatic organisms downstream of mining operations, even while meeting current MMER discharge guidelines, and the proposed more stringent MMER discharge guidelines necessitate research into further reductions of final effluent contaminant concentrations using currently available treatment processes. No direct comparison of treatment efficacy between conventional sedimentation, HDS, and ballasted flocculation clarification processes could be found in the literature. Additionally, the mechanisms of sludge densification found with the HDS process are not well understood (Bosman 1974; Knocke & Kelley 1987; Aubé & Zinck 1999; Gan et al. 2005; Bullen 2006). Finally, although CKD has been shown to be able to reduce acidity and remove soluble metals from AMD, research that provides more information on the mechanisms involved or explains why CKD addition results in a denser sludge and higher suspended solids concentrations in clarified water versus lime precipitation has not been previously conducted. Further research into the impacts of replacing lime with CKD will aid in the implementation of the process at pilot- and full-scale. The research undertaken for this thesis on the impacts of sludge recycling (i.e., HDS) and ballasted flocculation on effluent water and sludge quality also has broader-reaching applicability to the water and wastewater treatment industry.

Chapter 2 Review of the Literature

Background information on mine water contamination and regulations for allowable contaminant concentrations, as well as treatment options, are reviewed in this chapter. The review focuses on treatment processes relevant to this thesis.

2.1 Mine Water

For the purposes of this study, mine water is defined as any water discharged from mining or mineral processing operations which contains some contaminant that restricts its discharge into the natural environment. This type of industrial waste water can be highly contaminated with solid and dissolved particles, metals, salts, and other elements (Kuyucak 1998; Brown et al. 2002; Lottermoser 2007). Mine water quality varies significantly with the ore type being mined and age of the mine.

Oxidation of sulphide minerals exposed to air and water during mining operations results in the generation of mine water. Mine water can be either acidic, i.e., acid mine drainage (AMD; $pH < 6$) or circumneutral, i.e., neutral mine drainage (NMD; $6 < pH < 9$) and can have low or high concentrations of contaminants (Kuyucak 1998; Lottermoser 2007; INAP 2009). Table 2.1 lists typical concentrations of contaminants found in AMD and NMD. NMD often has lower concentrations of metals and sulphate than AMD but may have high concentrations of zinc, cadmium, manganese, antimony, arsenic, and/or selenium (Kuyucak 1998; INAP 2009). Sulphide minerals can also be exposed due to natural weathering or construction activities, for instance, leading to the use of the term acid rock drainage (ARD). Iron pyrite (FeS_2) is a mineral commonly exposed during mining operations. When exposed to oxygen and water it oxidizes and releases sulphuric acid

(H_2SO_4) and soluble iron (Fe^{2+}) (Bosman 1983; Kuyucak 1998; Younger et al. 2002; Banks et al. 2002; Johnson & Hallberg 2005; Weiner 2008). The soluble iron is then slowly oxidized to Fe^{3+}. Depending on ore type and/or mineral processing method, other metals such as zinc, lead, nickel, and copper, and metalloids such as arsenic, can also be released into water during mining and processing.

Table 2.1 Typical contaminant concentrations in AMD and NMD (Plumlee et al. 1999; Younger et al. 2002; INAP 2009).

Parameter	Units	Typical AMD	Typical NMD
Aluminum	mg/L	< 10 000	< 10
Arsenic	mg/L	< 100	< 10
Copper	mg/L	< 10 000	< 1
Iron	mg/L	< 100 000	< 100
Lead	mg/L	< 10	< 1
Nickel	mg/L	< 100	< 1
Zinc	mg/L	< 10 000	< 100
TSS	mg/L	> 15	> 15
Sulphate	mg/L	< 1 000 000	< 1000
pH	N/A	2 to 6	6 to 10

2.2 Mine Water Discharge Regulations

Contaminants in mine water can be harmful to the receiving aquatic systems if not properly treated prior to discharge (Kuyucak 1998; Environment Canada 2012a). Precipitating metals can coat benthic organisms and toxic metals such as copper and arsenic can accumulate in biota and the environment, or even be acutely lethal, if not treated prior to release (CCME 1987; Brown et al. 2002; Environment Canada 2012a). Even with current regulations and a 99 to 100 % compliance rate, mine water discharges in Canada were shown to have negative effects on benthic and aquatic species downstream of mine discharges (Environment Canada 2012b).

In Canada, discharges from metal mines are regulated by the Fisheries Act's Metal Mining

Effluent Regulations (MMER; Fisheries Act 2002). These regulations are currently under review, with reductions of the current allowable discharge concentrations for some parameters and the introduction of discharge limits on iron and aluminum being proposed (Environment Canada 2012a). Table 2.2 lists the relevant current and proposed MMER monthly average discharge concentration limits. Regulations in Chile, South Africa, Spain, and the US are similar to or more stringent than those of the MMER (Environment Canada 2012a).

Table 2.2 Current and proposed MMER monthly average allowable discharge guidelines (Environment Canada 2012a).

Parameter	**Units**	**Current MMER**	**Proposed MMER**
Aluminum	mg/L	N/A	1.0[a]
Arsenic	mg/L	0.50	0.10
Copper	mg/L	0.30	0.05
Iron	mg/L	N/A	1.0[a]
Lead	mg/L	0.20	0.05
Nickel	mg/L	0.50	0.25
Zinc	mg/L	0.50	0.25
TSS	mg/L	15.00	15.00
Sulphate	mg/L	N/A	N/A
pH	N/A	6.5 to 9.5	6.5 to 9.5

[a] Al and Fe proposed guidelines suggested by the author based on other jurisdictions' regulations due to lack of official proposed MMER guideline.

2.3 Mine Water Treatment

Mine water treatment is broadly divided into two categories: active treatment and passive treatment. Passive treatment includes all processes that do not require inputs of energy to function and require minimal maintenance, such as wetlands and limestone drains (Kuyucak 1998; Brown et al. 2002; Younger et al. 2002; Johnson & Hallberg 2005). This thesis focuses on active treatment methods, which are more common for mine water treatment and are better able to handle the high volumes and contaminant loadings often found in mine water (Kuyucak 1998; Aubé & Zinck 1999; Aubé & Zinck 2003; Zinck & Griffith 2013). Active treatment processes require the input of energy, i.e., mixing, as well as continuous operation and maintenance (Kuyucak 1998; Brown et al. 2002; Younger et al. 2002; Johnson & Hallberg 2005). The main active treatment method used for mine water treatment is lime precipitation with either conventional or high density sludge (HDS) clarification process (Bosman 1974; Brown et al. 2002; Younger et al. 2002; Johnson & Hallberg 2005; Zinck & Griffith 2013).

Figure 2.1 shows schematics for the conventional, HDS, and ballasted flocculation treatment processes. All three processes use lime to precipitate metals in the mine water as hydroxides. The conventional and HDS treatment processes follow lime precipitation with polymer addition, usually anionic, and a flocculation stage at low velocity gradient to grow large flocs. Solids generated are then removed via clarification (i.e., sedimentation). Unlike in the conventional sedimentation process, in the HDS process sludge is recirculated to the head of the treatment plant. Ballasted flocculation differs from the other processes by the addition of a ballast material along with anionic polymer after the lime precipitation stage. This leads to the generation of high density flocs with very fast settling rates which allows for smaller clarifiers. The flocculation stage in the ballasted flocculation process is also run at a higher velocity gradient (i.e., 160 to 1200 s^{-1} vs. 10 to 75 s^{-1} for conventional and HDS) and with much shorter retention times in order to keep the ballast material suspended, the lower end of the range being more economical (Desjardins et al., 2002; Young & Edwards 2003). Specifics of treatment processes relevant to this thesis are outlined in the following sections.

2.3.1 Precipitation Processes

Metals in mine water are typically found in dissolved form and must be precipitated in order to be removed through solid/liquid separation processes (Kuyucak 1998; Brown et al., 2002; Aubé & Zinck 2003; INAP 2009). Precipitation of metals as hydroxides is the most commonly used mine water treatment process (Bosman 1974; Brown et al. 2002; Younger et al. 2002; Johnson & Hallberg 2005; Zinck & Griffith 2013).

In aqueous solutions, metal ions are surrounded by coordinated water molecules in an inner and outer hydration shell. For trivalent metals such as Al^{3+} and Fe^{3+}, the inner hydration shell consists of 6 octahedrally coordinated water molecules. These metal ions hydrolyze almost instantaneously, strongly attracting OH^- and releasing H^+ from the coordinated water molecules (Flynn 1984; Stumm 1992; Martell & Hancock 1996; Cornell and Schwertmann 2003; Gregory 2006; Hendricks 2006; Pham et al. 2006; Weiner 2008; Letterman & Yiacoumi 2011; Davis & Edwards 2014). Equation 2.1 shows the first step of the hydrolysis process for Fe^{3+} with the coordinated water molecules included.

$$Fe(H_2O)_6^{3+} \leftrightarrow FeOH(H_2O)_5^{2+} + H^+ \qquad \text{Equation 2.1}$$

Hydrolysis and precipitation is highly pH dependent, with increasing pH favouring the right side of the equation eventually leading to precipitation of the uncharged solid hydroxide $Fe(OH)_3$. When a solution is highly supersaturated, such as when the pH of AMD is raised close to the pH of minimum solubility of iron (i.e., 8) quickly, nucleation occurs rapidly and results in a high concentration of small precipitates (Stumm 1992; Gan et al. 2005; Pham et al. 2006). This process is termed homogeneous nucleation and results in an amorphous precipitate or polymer due to coordinated water molecules surrounding the small precipitates becoming bound in the growing precipitates (Flynn 1984; Stumm 1992; Bullen 2006; Letterman & Yiacoumi 2011). When solid particles or colloids are present, e.g., turbidity, heterogeneous precipitation dominates and precipitation occurs at the surface of these particles instead of in bulk solution. The solid particles act as catalysts and reduce the activation energy required for precipitation (Stumm 1992; Bullen 2006). The activation energy barrier is even lower if the dissolved ions and solids are a good match, i.e., have the same or similar structure (Stumm 1992). Solubility is metal-specific, highly pH dependent, and varies with oxidation state of the metal (Aubé & Zinck 2003; Weiner 2008). In ferric solutions, the precipitate is a ferric oxyhydroxide called ferrihydrite and has a variable chemical makeup. Ferric monomers are favoured at low pH, while polymers are favoured with addition of OH^- ions (i.e., at high pH). Polymer size has been shown to increase with increase in OH/Fe ratio, i.e., pH (Cornell & Schwertmann 2003), and precipitation has also been shown to occur faster at higher pH (Pham et al. 2006).

Precipitation is also used in chemical coagulation for treatment of drinking water and waste water to remove dissolved and colloidal contaminants (Tchobanoglous et al. 2003). Chemical coagulation refers to the addition of a metal salt such as aluminum or ferric sulphate to destabilize the contaminants and promote the formation of aggregates of hydrous metal oxide precipitates and primary particles called flocs which promote the removal of dissolved and colloidal organic and inorganic contaminants through direct precipitation or adsorption and/or enmeshment in the flocs. These flocs contact smaller particles and colloids during the flocculation stage, increasing contaminant removal through differential settling or sweep flocculation (Stumm 1992; Tchobanoglous et al. 2003; Gregory 2006; Hendricks 2006; Letterman & Yiacoumi 2011; Davis & Edwards

2014). There are in general four different stages or zones of coagulation that occur with increasing coagulant dose or variations in pH with regards to the pH of minimum solubility of the metal hydroxide precipitate. At low coagulant concentration and/or low pH, destabilization of colloids (i.e., charge neutralization) does not occur and high turbidity is generated in the clarified water. With an increase in chemical coagulant concentration and/or pH to destabilize the system (i.e., neutralize the negative charge of the colloids and turbidity), coagulation occurs and small precipitates are generated. Restabilization of the system occurs with further increase in coagulant dose due to the increased charge of the system which increases repulsion effects and decreases settling rates, resulting in clarified effluent with increased turbidity. A large coagulant dose above the concentration required for charge neutralization, at the appropriate pH range (i.e., pH of minimum solubility of the metal precipitate), promotes homogeneous nucleation and results in large, amorphous flocs that increase removal of turbidity through sweep flocculation (Faust & Aly 1998; Tchobanoglous et al. 2003; Gregory 2006; Hendricks 2006). At the iron concentrations typical of AMD, hydroxide formation and thus sweep flocculation is the main mechanism for removal of other particles and colloids in the mine water.

2.3.2 Arsenic Removal

Effluents containing arsenic must be treated differently because arsenic does not precipitate as a hydroxide and acts as a weak acid in solution, forming arsenious acid (H_3AsO_3) and arsenic acid (H_3AsO_4) for arsenite (As^{3+}) and arsenate (As^{5+}), respectively (Edwards 1994; Faust & Aly 1998; Raven et al. 1998; Jain et al. 1999; Goldberg & Johnston 2001; Bowell 2003; Qiao et al. 2012). Oxidation of arsenic is slow and reversible and therefore most contaminated waters contain a mixture of the two most common oxidation species (Sharma

& Sohn 2009; Sorlini & Gialdini 2010). Acidity constants (pKa) for H_3AsO_3 are 9.2, 12.1, and 13 and for H_3AsO_4 are 2.3, 6.9, and 11.5 (Raven et al. 1998; Jain et al. 1999).

Calcium arsenites/arsenates will precipitate at pH greater than 10, however these precipitates are highly unstable and result in redissolution and release of arsenic from treatment sludge (US EPA 1990; Harris 2003; Wang et al. 2003; Wang et al. 2011). The US EPA's best demonstrated available technology (BDAT) is to add ferric coagulation to the lime precipitation process for waters with low iron concentration. This allows for arsenic to be removed via coprecipitation with and/or adsorption onto ferric precipitates, which occurs at lower pH and generates more stable precipitates than calcium precipitation (US EPA 1990; Riveros et al. 2001; Harris 2003; Jia & Demopoulos 2008; Twidwell & McCloskey 2011). Also, since arsenate is generally easier to remove and generates a more stable sludge, chemical oxidation of water is usually an initial step in treatment of arsenic-contaminated water (US EPA 1990; Hering et al. 1996; Riveros et al. 2001; Bissen & Frimmel 2003; Bowell 2003; Sorlini & Gialdini 2010; Twidwell & McCloskey 2011). Oxidation of arsenic by O_2 is slow and therefore a strong chemical oxidizer such as potassium permanganate ($KMnO_4$) or sodium hypochlorite (NaClO) must be used (Edwards 1994; Bissen & Frimmel 2003; Sorlini & Gialdini 2010).

2.3.3 Alkaline Materials for Precipitation

Lime is the most commonly used alkali for precipitation of metals from AMD (Bosman 1983; Johnson & Hallberg 2005; Zinck & Griffin 2013). Quicklime (CaO) or hydrated lime ($Ca(OH)_2$) is the most cost-effective alkali for mine water treatment and can either be slaked (i.e., mixed with water) on site or be purchased in slurry form in the case of $Ca(OH)_2$.

Sodium hydroxide (NaOH), while more reactive than lime, is more expensive and usually used in remote areas or for waters with low metals loading, due to the simple, low maintenance dosing equipment required for the liquid solution (Johnson & Hallberg 2005).

Another alkali material that has been tested for treatment of mine water is cement kiln dust (CKD; Mackie & Walsh 2012). CKD is a fine, alkaline material captured in the air pollution control devices of cement kilns (Mackie et al. 2010). Its properties are similar to those of cement but with finer particles sizes. Typically, CKD is composed mainly of calcite ($CaCO_3$), anhydrite ($CaSO_4$), and soluble oxides, mainly CaO, which varies widely between cement plants (Haynes & Kramer 1982; Peethamparan et al. 2008). Mean particle sizes range from 1 to 100 μm (Peethamparan 2006; Sreekrishnavilasam et al. 2006). Its current reuse options are limited and it is usually landfilled on site (Adaska & Taubert 2008; Mackie et al. 2010). Reuse options mainly depend on free lime content or reactivity of the CKD. Previous research has shown that CKD can be used to raise pH in an active treatment process to precipitate metals such as iron, zinc, and lead from contaminated mine water, and that treatment with CKD results in lower sludge volumes compared to lime. However, CKDs with low free lime (i.e., CaO) concentrations generated higher TSS concentrations in treated effluent than those with high free lime or quicklime and treatment mechanisms remain unclear (Mackie & Walsh 2012).

2.3.4 Flocculation

The flocculation stage of a water treatment process allows for the aggregation of primary particles and/or microflocs generated during the coagulation or precipitation unit processes (Hendricks 2006). Flocculation helps grow large aggregates, or flocs, which have better settling properties and contribute to sweep flocculation. High shear rates in the flocculation stage form smaller, denser aggregates while low shear rates form large aggregates (Henricks 2006). Usually, large flocs are generated using a tapering velocity gradient in a two or three stage flocculation basin, with velocity gradients of 10 to 60 s^{-1} (Droste 1997; Gregory 2006). Too high a flocculation speed induces floc breakage, reducing size of flocs and effectiveness of sweep flocculation (Gregory 2006).

Flocculation occurs by particle-particle interactions/collisions due to Brownian motion, velocity gradients (i.e., mixing), and differential settling or sweep flocculation, where larger, faster settling particles collide with more slowly settling particles (Stumm 1992; Faust & Aly 1998; Tchobanoglous et al. 2003; Gregory 2006; Hendricks 2006). The rate of agglomeration of particles in a given volume depends on the particle size and the velocity gradient in the flocculation unit process (Stumm 1992).

2.3.5 Clarification Processes

As noted by Aubé and Zinck (2003) the principal difference between lime treatment processes is the method of solid/liquid separation or clarification. Conventional sedimentation involves simple quiescent settling in a large tank called a clarifier. Sedimentation rates and sludge density are low for solids generated using the conventional sedimentation process (Bosman 1974; Bosman 1983; Aubé & Zinck 1999). The HDS process is a high-rate clarification process that was developed in order to generate a denser sludge, i.e., one with a higher solids concentration (Kostenbader & Haines 1970; Bosman 1974; Bosman 1983; Knocke & Kelley 1987; Kuyucak 1998; Aubé & Zinck 1999; Johnson & Hallberg 2005; Bullen 2006). The ballasted flocculation process is another high-rate clarification process that produces denser, faster settling flocs through the addition of a ballast material such as microsand during the flocculation stage (Smith & Edwards 2002; Young & Edwards 2003; Ghanem et al. 2007). The two most commonly used clarification methods for mine water treatment are conventional sedimentation and HDS (Zinck & Griffith 2013).

2.3.5.1 Conventional Sedimentation

Conventional sedimentation is the process that occurs when flocs or aggregates generated from precipitation and flocculation processes settle in a clarifier quiescently or with gentle rake action to promote sludge densification by release of water from the sludge. Settling rates of particles can depend on particle concentration, diameter of the particles, density of the particles, drag coefficient (i.e., Reynolds number), and shape of particles (Droste 1997; Faust & Aly 1998; Hendricks 2006; Gregory & Edzwald 2011). There are, in general, four types of particle settling, Types I to IV (Droste 1997; Hendricks 2006). Type I or discrete settling occurs at extremely low particle concentrations (i.e., < 1 % v/v) where no particle agglomeration occurs. Type I settling velocity (ν) depends on particle size (i.e., diameter, d), shape (φ, 1 for spherical particles, higher for more irregular shape), drag coefficient (C_d) and particle (ρ_p) and liquid (ρ) density as in Equation 2.2.

$$\nu = \sqrt{\frac{4g(\rho_p - \rho)d}{3C_d \varphi \rho}} \qquad \text{Equation 2.2}$$

The drag coefficient depends on the Reynolds number (i.e., $Re = \rho \nu d/\mu$, where μ = water viscosity) and changes depending on whether flow is laminar or turbulent (Faust & Aly 1998; Hendricks 2006). At Reynolds numbers less than 2, i.e., laminar flow conditions, substituting the value of C_d (i.e., 24/Re) into Equation 2.2 generates Stokes' Law (Equation 2.3).

$$\nu = \frac{g(\rho_p - \rho)d^2}{18\mu} \qquad \text{Equation 2.3}$$

At low particle concentrations (i.e., < 8 % v/v) with flocculation or agglomeration of particles occurring, Type II or flocculent settling dominates, where particle sizes and thus settling rates increase during sedimentation (Equation 2.2). At high particle concentrations such as those found in mine water treatment or at the bottom of a water treatment clarifier (i.e., > 8 % v/v, > 500 mg/L), Type III, hindered or zone settling, dominates and settling rate depends solely on particle concentration for a given sludge. Type IV or compression settling occurs under areas of zone settling or at solids concentrations greater than around 20 %, where compression of sludge occurs by forcing water out of pore space and is dependent only upon settling time and the weight of sludge above (Droste 1997; Hendricks 2006; Gregory & Edzwald 2011).

Conventional sedimentation of flocs generated from lime precipitation of mine water can generate high volumes of gelatinous, low solids (i.e., 1 to 5 %) sludge which requires a significant amount space for disposal and/or further treatment (i.e., dewatering) prior to disposal (Bosman 1983; Kuyucak 1998; Aubé & Zinck, 1999; Zinck & Griffith 2013). AMD sludge is most commonly disposed of in sludge ponds or co-disposed with mine tailings. Finding room for and the high cost of sludge disposal were the biggest concerns noted in a recent survey of mine water treatment plants (Zinck & Griffith 2013).

2.3.5.2 High Density Sludge

In the high density sludge (HDS) process, sludge generated during precipitation and flocculation is recycled to the head of the treatment process at a ratio of between 20: and 30:1 mass of solids recycled to solids generated (Kostenbader & Haines 1970; Bosman 1974; Bosman 1983; Kuyucak 1998; Aubé & Zinck 1999; Bullen 2006). Sludge solids can either be mixed with fresh lime slurry prior to mixing with mine water (Type I HDS) or mixed with mine water prior to addition of fresh lime (Type II HDS/Geko process; Aubé & Zinck 1999; Bullen 2006). Figure 2.1 shows a Type I HDS treatment plant and Figure 2.2 a Type II HDS plant. Both methods have been shown to result in a denser sludge (i.e., > 20 % solids) that has better dewatering characteristics than conventional lime treatment sludge (Knocke & Kelley 1987; Kuyucak 1998; Aubé & Zinck 1999; Johnson & Hallberg 2005).

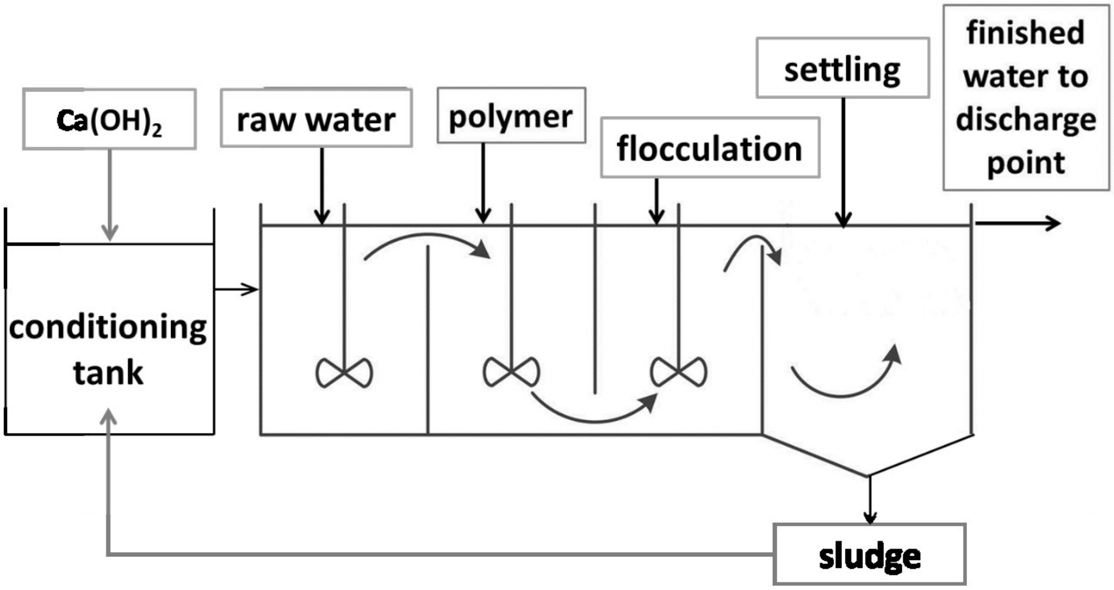

Figure 2.1 Type I HDS treatment process.

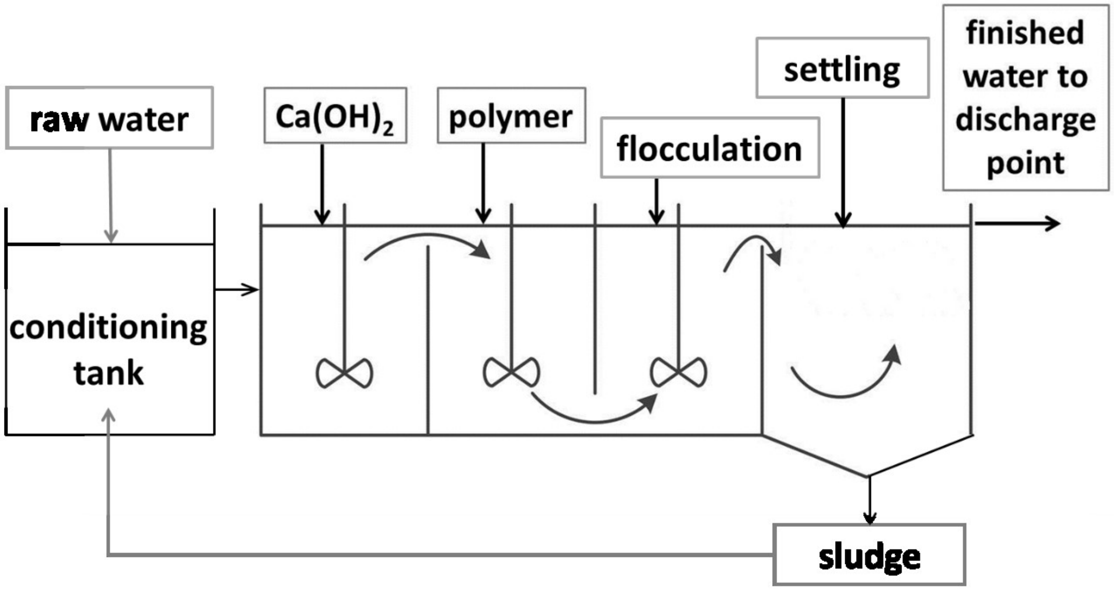

Figure 2.2 Type II HDS treatment process.

Early work with HDS treatment plants showed that sludge density depended on the ratio of sludge recycled to sludge precipitated, the total iron concentration in the mine water and the ratio of Fe^{2+} to Fe^{3+}, the amount of calcium sulphate precipitated during treatment, and the retention time and mixing speed in the sludge conditioning tank (Kostenbader & Haines 1970; Bosman 1974; 1983). Theories initially proposed for the mechanisms behind increasing density of sludge with recycle ratio for AMD treatment involved either reduction of bound water content in sludge or reduction of repelling forces between molecules, as these are the only two ways that sludge density can be increased. Slowed precipitation due to lower pH of the sludge/lime slurry than pure lime slurry (i.e., lower concentration of OH^-), increased compression effects from increase in charged ions (Ca^{2+} and Fe^{2+}), and aging and dehydration of ferric precipitates were initially proposed as mechanisms for sludge densification in the HDS process (Bosman 1974). Knocke and Kelley (1987) noted that the higher the solids concentration in the clarifier, i.e., the higher the concentration of recycled solids, the higher the sludge floc density indicating reduced bound water in the precipitated flocs. They also found that precipitated HDS flocs were larger and denser than with no sludge recycle. Aubé and Zinck (1999) offered that the high density sludge produced by the HDS process was due to the “physical attributes of the precipitates on a microscopic scale”, with HDS sludge being more crystalline in nature, compared to the amorphous oxyhydroxides formed with the conventional process. HDS sludge from full scale AMD treatment plants was also found to have a smaller particle size distribution and narrower range of particle sizes than conventional sludge (Aubé & Zinck 1999). The theories for sludge densification developed further once advances in the understanding of the mechanisms involved in hydrolysis, nucleation, and precipitation were made (Stumm 1992). Gan et al. (2005) suggested that, again, higher density sludge was formed with HDS by slowing of the precipitation process but also that recirculated sludge acted as seed particles for heterogeneous precipitation. They found that conditioning recycled iron(III) hydroxide sludge in a Type I HDS process at a pH between 3.5 and 4.5 was best for growing large precipitates, resulting in the highest density sludge in their experiments. Bullen (2006) advanced that, for Type II HDS where recirculated sludge is contacted with AMD prior to addition of fresh lime, most dissolved metals from the AMD are removed during the sludge conditioning stage by heterogeneous precipitation onto the recirculated sludge, causing a denser precipitate. He noted that too low a pH in this reactor (i.e., below the precipitated metal hydroxide’s point of zero charge) would lead to poor sludge densification due to the net positive charge on the recirculated sludge particles electrostatically repulsing the metal cations in solution.

2.3.5.3 Ballasted Flocculation

The ballasted flocculation treatment process incorporates a dense ballast material, usually microsand, into the flocs formed during treatment to generate denser, more spherical flocs that settle more quickly (Tchobanoglous et al. 2003; Young & Edwards 2003). Figure 2.3 depicts a typical ballasted flocculation treatment process, consisting of coagulation/precipitation, ballasted flocculation, and an upflow clarifier. Microsand is recovered from the sludge using a hydrocyclone and reinjected into the process, necessitating low sludge solids concentrations for efficient operation of the hydrocyclone.

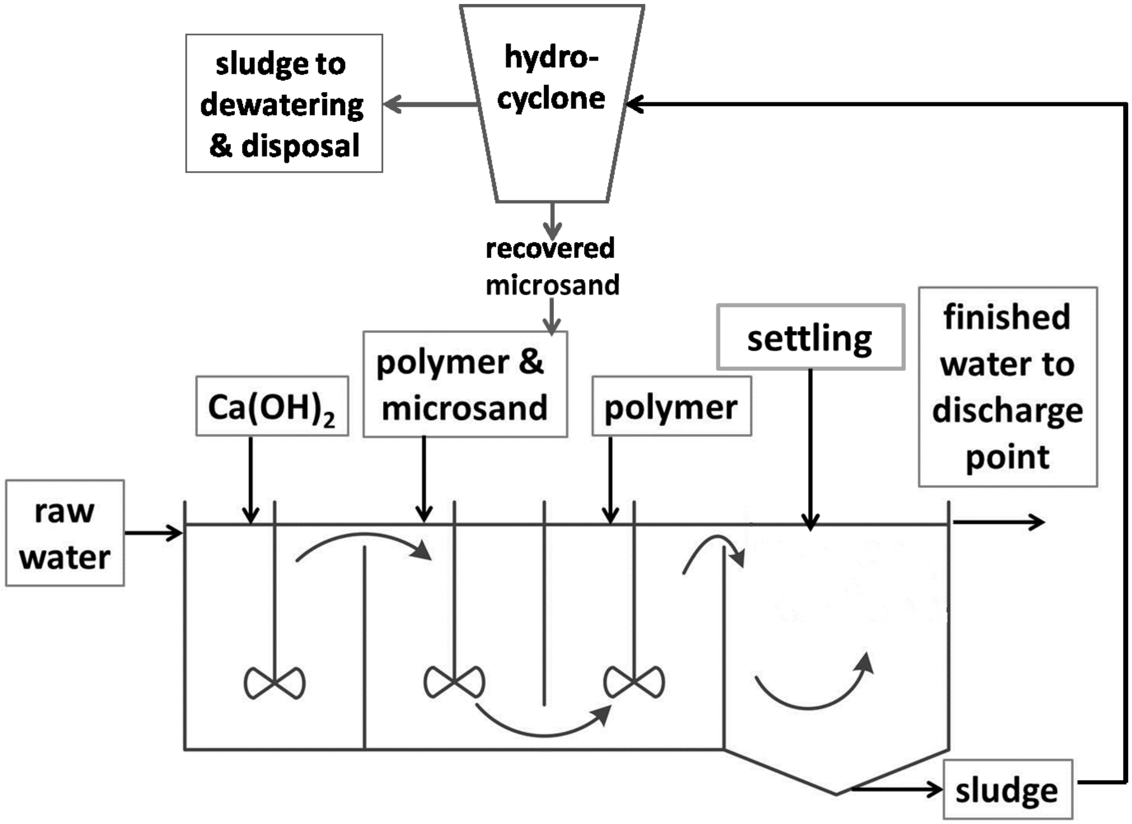

Figure 2.3 Ballasted flocculation treatment process.

While Cailleaux et al. (1992) and Chang et al. (1998) originally proposed that the ballast material acts as a seed for chemical floc formation, i.e., heterogeneous precipitation, Young and Edwards (2003) and Ghanem et al. (2007) showed that the ballast material gets introduced into the pre-formed chemical flocs by momentum, replacing bound water in the flocs and ‘sticking’ due to polymer addition. Microsand has been shown to be better incorporated, i.e., resulting in lower clarified water turbidity, when added after coagulant and polymer addition (Young & Edwards 2003) and the ballasted floc bulk density has been shown to be linearly related to the ballast dose (Ghanem et al. 2007). Ballasted flocculation can also be run at higher velocity gradients, which helps generate more spherical flocs due to shearing and reforming and contributes to higher settling rates (Desjardins et al. 2002). The settling velocity of ballasted flocs can be modeled by Equation 2.2, just like unballasted flocs, and it is the increased density and decreased shape factor of ballasted flocs that lead to faster settling rates (Young & Edwards 2003).

2.3.5.4 Comparison of Clarification Methods

In general, conventional sedimentation generates a low solids concentration sludge (i.e., 1 to 5 % solids) and the HDS process generates a denser sludge (i.e., > 20 % solids; Kuyucak 1998; Aubé & Zinck 1999; Johnson & Hallberg 2005). Ballasted flocculation generates denser, faster settling flocs than HDS and conventional and therefore decreases clarifier sizes and capital costs (Young & Edwards 2003). Ballasted flocculation sludge solids concentrations, however, must be kept low in order to recover spent microsand from the sludge in a hydrocyclone, with sludge requiring further dewatering after this unit operation and prior to disposal (Young & Edwards 2003). Comparisons between the conventional, HDS, and/or ballasted flocculation clarification methods are sparse in the literature but several are discussed presently.

Knocke and Kelley (1987) found that recycling nickel hydroxide sludge to the precipitation stage of a bench-scale continuous-flow active treatment process significantly increased thickening and dewatering rates of sludge produced during the hydroxide precipitation process. Aube and Zinck (1999) analyzed sludge from full scale treatment plants using conventional, HDS Type I, and HDS Type II processes and found that sludge properties were highly variable due to varying water quality, treatment methods, clarifier sizes, etc. In general, HDS process resulted in denser sludge than conventional sedimentation, with Type II HDS sludge having the highest degree of crystallinity and most efficient lime usage (i.e., sludge with lowest neutralization potential).

Yan et al. (2013) compared three additives, calcium hydroxide, calcite ($CaCO_3$), and preformed sludge, to the precipitation process for wastewater contaminated with heavy metals and determined that $CaCO_3$ was the best additive in terms of sludge settling and compaction properties. Smith & Edwards (2002) found that arsenic removal was equivalent or better using ballasted flocculation compared to conventional sedimentation for the treatment of drinking water and that arsenic concentrations were linked to iron concentrations, indicating an adsorption mechanism. They also noted that ballasted flocculation performed equally or better than conventional sedimentation even though much shorter flocculation (i.e., 2 min versus 20 min) and settling times (i.e., 0 versus 30 min) were used.

Chapter 3 Bench-Scale Comparison of Conventional and High Rate Clarification Treatment Processes for Acid Mine Drainage[1]

3.1 Abstract

Acid mine drainage (AMD) is characterised as having low pH and high concentrations of sulphate and dissolved metals. This study compared treated water quality and sludge properties of three process technologies for AMD: conventional sedimentation, high density sludge (HDS), and ballasted flocculation. All three processes were found to be capable of removing regulated metals to concentrations below current Canadian discharge guidelines. However, ballasted flocculation was the only technology found to be able to meet the more stringent federal guidelines proposed for future implementation under the Fisheries' Act's Metal Mining Effluent Regulations. Specifically, arsenic and zinc concentrations in AMD treated by the conventional and HDS processes were above proposed future guidelines of 0.10 and 0.25 mg/L, respectively, while lead, copper, and nickel all met respective guidelines. Concentrations of all regulated contaminants were below proposed guidelines when treated by ballasted flocculation. The HDS process was found to produce a significantly more concentrated sludge than conventional sedimentation (i.e., higher solids content [19 ± 1 % versus 7 ± 4 % wet solids] and lower sludge volume index [SVI; 8.4 ± 0.8 versus 230 ± 20 mL/g]).

Keywords: Acid mine drainage; ballasted flocculation; high density sludge; lime precipitation; sedimentation; wastewater treatment

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[1] Mackie, AL, Walsh, ME, 2015. *Water Quality Research Journal of Canada*, 50 (3), 279-286. http://dx.doi.org/10.2166/wqrjc.2015.048

3.2 Introduction

Acid mine drainage (AMD) is generated when sulphidic ores are exposed to oxygen and water during mining operations and is generally characterized as having low pH and high concentrations of sulphate and dissolved metals. This effluent must be treated prior to discharge in order to protect the receiving environment (Kuyucak 1998). In Canada, discharges from metal mines are regulated under the Fisheries' Act's Metal Mining Effluent Regulations (MMER; Fisheries' Act 2002), which are currently under review with new maximum contaminant discharge concentrations proposed (Table 3.1; Environment Canada 2012). These proposed guidelines significantly reduce the concentrations of several metals allowed in discharges from mines, as well as proposing the introduction of discharge guidelines for aluminum and iron. Most notable are proposed decreases in the allowable arsenic concentration from 0.50 to 0.10 mg/L, nickel and zinc from 0.50 to 0.25 mg/L, and copper and lead from 0.3 and 0.2 mg/L, respectively, to 0.05 mg/L, which would make Canada's discharge regulations comparable to the most stringent regulations around the globe (Environment Canada 2012).

Table 3.1 Mine water characterization and MMER discharge guidelines (Environment Canada 2012).

Parameter	**Units**	**MMER Discharge Guideline; current (proposed)**	**AMD; Total Concentration**	**AMD; Dissolved Concentration**
pH	N/A[a]	6.5 – 9.5	2.3 ± 0.2	N/A
Dissolved Oxygen	mg/L	N/A	8.0 ± 0.2	N/A
E_h	mV	N/A	870 ± 20	N/A
Conductivity	mS/cm	N/A	6.46 ± 0.05	N/A
Turbidity	NTU	N/A	100 ± 40	N/A
TSS	mg/L	15	100 ± 60	N/A
Sulphate	mg/L	N/A	N/A	3400 ± 200
Ferrous Iron	mg/L	N/A	N/A	1.6 ± 0.2
Aluminum	mg/L	N/A (TBD)	19 ± 2	19 ± 2
Arsenic	mg/L	0.50 (0.10)	9 ± 1	6 ± 1
Calcium	mg/L	N/A	186 ± 8	200 ± 20
Copper	mg/L	0.30 (0.05)	1.5 ± 0.1	1.5 ± 0.2
Iron	mg/L	N/A (TBD)	83 ± 8	79 ± 4
Lead	mg/L	0.20 (0.05)	< 0.004	< 0.004
Magnesium	mg/L	N/A	108 ± 6	110 ± 6
Manganese	mg/L	N/A	21 ± 2	21 ± 2
Nickel	mg/L	0.50 (0.25)	0.074 ± 0.002	0.074 ± 0.003
Zinc	mg/L	0.50 (0.25)	52 ± 3	52 ± 4

N/A: not applicable

TBD: to be determined

AMD is most commonly treated using the active lime treatment process. In that process, the mine water is typically aerated prior to raising the pH of the water using lime which allows dissolved metals to be precipitated as hydroxides and removed from the water phase through sedimentation in a clarifier. The most common modification to this conventional treatment process is the high density sludge (HDS) process. The HDS process is identical to active lime treatment with the exception that sludge from the clarifier is recycled at a ratio of between 10 and 30 to 1 (i.e., 10 to 30 kilograms of sludge recycled for each kilogram of sludge generated) and mixed with the lime slurry prior to addition to mine water (Kostenbader and Haines 1970; Bosman 1983; Aubé and Zinck 1999). This increases the density of the sludge in the clarifier from less than 5 % solids typically found with conventional sedimentation to greater than 20 % solids (Kuyucak 1998; Aubé and Zinck 1999). Ballasted flocculation is a high-rate clarification process that incorporates a ballasting agent (e.g., microsand) into the precipitated sludge, making it denser and thus increasing sedimentation rates to reduce the required clarifier footprint (Desjardins et al. 2002; Young and Edwards 2003; Ghanem et al. 2007). In general, ballasted flocculation is beneficial where space for the treatment plant is limited, due to its smaller footprint and lower capital costs, and HDS is beneficial where space for sludge disposal is limited or costly.

The main objective of this study was to compare at bench-scale effluent water quality and sludge properties of conventional sedimentation, HDS, and ballasted flocculation for the treatment of AMD. No direct comparison of these processes can be found in the literature. The secondary objective was to determine if these processes could reduce the final arsenic and heavy metal concentrations from AMD to below proposed future discharge guidelines in Canada (Environment Canada 2012).

3.3 Experimental

3.3.1 Mine Water

The mine water used in this study was sampled from a lead/zinc mine in Atlantic Canada that is characterized as having high concentrations of dissolved metals, mainly zinc and iron, and an acidic pH. Dissolved metals are defined as the metal concentration detected in samples after filtering through a 0.45 μm membrane. The mine water characterization from analysis performed on AMD samples collected for this study is presented in Table 3.1 along with the current applicable MMER discharge guidelines and proposed future discharge guidelines. Arsenic, copper, and zinc were all found to be above current and proposed MMER discharge guidelines in the mine water samples collected for this study. As evidenced by high dissolved oxygen and low ferrous iron concentrations, the mine water samples were highly aerated prior to testing and therefore an oxidation step was not included in bench-scale testing.

3.3.2 Bench-Scale Methods

All treatment processes were simulated at bench-scale using a standard jar test apparatus (Phipps and Bird, Fisher Scientific) with 500-mL batch tests run using glass beakers. Simulation of the HDS process was achieved following the methods of Bosman (1983) and ballasted flocculation following the procedure developed by Desjardins et al. (2002). The conventional treatment process was taken as the 'first pass' of the HDS process, where sludge was generated to be recycled into the subsequent test. All tests were run at room temperature, i.e., 21 ± 2 °C.

The conventional sedimentation and HDS jar tests followed similar procedures. At $t = 0$ min, 45 mL of the 1 % $Ca(OH)_2$ slurry (i.e., 900 mg $Ca(OH)_2$/L) was mixed with 500 mL of the mine water at a speed of 150 rpm (G-value = 140 s^{-1}). This concentration of $Ca(OH)_2$ was used to achieve a target pH of between 9 and 10, the minimum solubility range of zinc and the pH used at the full-scale treatment plant where the mine water sample was obtained (Mackie & Walsh 2012). At $t = 2$ min, 1.0 mg/L polymer was added followed two minutes later with the mixing speed being reduced to 50 rpm (G-value = 44 s^{-1}) to allow for flocculation. After 10 minutes, mixing was stopped and the mixture was transferred to a 1

L graduated cylinder and allowed to settle for 60 minutes while measuring the height of the sludge blanket. In the HDS tests, sludge from the conventional treatment process jar test was mixed with fresh $Ca(OH)_2$ for 20 minutes at 50 rpm prior to adding a fresh 500 mL portion of mine water and following the same procedure as above. This was repeated until the sludge volume remaining after 60 minutes of settling did not increase significantly in subsequent tests (Bosman 1983). For the ballasted flocculation jar tests, a constant mixing speed of 150 rpm was used and chemicals were added in the following order: 900 mg/L $Ca(OH)_2$ at $t = 0$ min, 10 g/L microsand and 0.5 mg/L polymer at $t = 2$ min, 0.5 mg/L polymer at $t = 7$ min, and finally a three minute quiescent settling period starting at $t = 10$ min. In each test, supernatant was sampled from just below the liquid surface after the specified settling period (i.e., 60 minutes for conventional and HDS processes and 3 minutes for ballasted flocculation process). The bench scale ballasted flocculation process did not include microsand recovery from settled sludge; each test used fresh microsand.

Anionic polymer (Hydrex 3551) and microsand (Actisand™, particle size = 100 μm) were provided by Veolia Water Technologies (VWT). Polymer was prepared fresh daily as a 1 g/L solution and mixed using a magnetic stir plate for 1 hour prior to use. Certified-grade hydrated lime ($Ca(OH)_2$; Fisher Chemical) was used as a 1 % w/v solution, prepared daily and continuously mixed using a magnetic stir plate.

3.4 Analytical Methods

Turbidity of the clarified water samples was measured with a HACH 2100N turbidimeter. pH and oxidation/reduction potential (ORP) were measured using an XL-50 meter with Accumet double-junction electrodes with Ag/AgCl reference and an Accumet platinum

Ag/AgCl combination electrode, respectively (Fisher Scientific). Absolute ORP readings were translated to Eh readings by adding 200 mV to the ORP reading, to normalize the values to a standard hydrogen electrode (SHE). Dissolved oxygen was measured using an Accumet BOD probe with an XL-60 meter (Fisher Scientific). The total suspended solids (TSS) concentration of the clarified samples was measured following the procedure in Standard Methods for the Examination of Water and Wastewater (APHA et al. 2005). Sulphate and ferrous iron were measured using EPA-approved colorimetric methods on a HACH DR 5000 spectrophotometer. Inductively-coupled plasma mass spectrometry (ICP-MS; Thermo Scientific X-Series 2) was used to measure all element concentrations. All samples were acidified to $pH < 2$ using trace metal-grade nitric acid prior to ICP-MS analysis. Dissolved metals samples were filtered through a 0.45 µm polysulfone membrane and acidified prior to analysis (GE Water & Process Technologies). Sludge volumes were measured using a one litre graduated cylinder (Bosman 1983; APHA et al. 2005). The specific gravity and sludge volume index (SVI) of sludge samples were measured following Standard Methods (APHA et al. 2005). The percent wet solids of the sludge was measured by weighing samples before and after vacuum filtration through a 1.5 µm filter and the percent dry solids was measured by weighing the sludge samples after drying at 105 °C overnight (APHA et al. 2005).

The results of jar testing were analyzed statistically using analysis of variance (ANOVA). The p-value noted in text indicates a significant difference in the mean value of results from the compared treatments if it is less than 0.05 (i.e., 95 % confidence level; MacBerthouex & Brown 2002). Uncertainties in data and error bars on graphs represent one standard deviation from the mean of repeated tests.

3.5 Results and Discussion

3.5.1 pH and Eh

pH during the jar test experiments was kept constant ($p > 0.05$) between the conventional sedimentation, HDS, and ballasted flocculation trials. Final pH after treatment and sedimentation was 9.8 ± 0.2 for conventional sedimentation, 9.4 ± 0.1 for HDS, and 9.5 ± 0.1 for ballasted flocculation. The pH of the fresh $Ca(OH)_2$ slurry was 12.5 ± 0.1 and that of the HDS slurry after mixing sludge with fresh $Ca(OH)_2$ for 20 minutes was 12.2 ± 0.1.

The E_h of the samples during treatment was inversely proportional to pH. E_h decreased from 870 ± 20 mV in the untreated mine water to 320 ± 20 mV within the first minute of treatment in all three treatment processes. Final E_h values were 350 ± 8 mV for HDS, 345 ± 9 mV for ballasted flocculation, and 336 ± 13 mV for conventional. E_h values of the fresh $Ca(OH)_2$ slurry (280 ± 40 mV) and the HDS slurry after 20 minutes of mixing with fresh $Ca(OH)_2$ (290 ± 20 mV) did not differ significantly ($p > 0.05$).

3.5.2 Conductivity and Turbidity

Conductivity is a measure of the ability of ions in a solution to transmit current, and is therefore related to the ionic strength of a solution or its total dissolved solids concentration (Crittenden et al. 2012). Conductivity values were not found to be significantly different ($p > 0.05$) between the three treatment processes in this study, and ranged between 5.2 and 5.7 mS/cm. This indicates that all three processes resulted in treated effluent with similar concentrations of dissolved ionic species.

Figure 3.1 shows that the turbidity measured in treated mine water samples was marginally equivalent to the TSS concentration. Due to the difficulty in measuring low TSS concentrations (i.e., < 2 mg/L) without large volumes of sample, turbidity alone was measured in subsequent tests due to the ease and speed of the test versus the TSS procedure. All of the treated mine water samples discussed in this study had turbidity measurements less than 2.0 NTU, and therefore TSS concentrations would be expected to be below the MMER discharge standard (i.e., < 15 mg/L) with any of the treatment processes evaluated in this study. Turbidity was found to be the lowest in samples treated using ballasted flocculation (0.26 ± 0.02 NTU) and highest in those treated using conventional sedimentation (1.5 ± 0.2 NTU). The HDS-treated samples resulted in average settled water turbidity measurements of 0.8 ± 0.2 NTU, with turbidity decreasing with increasing recycle ratio.

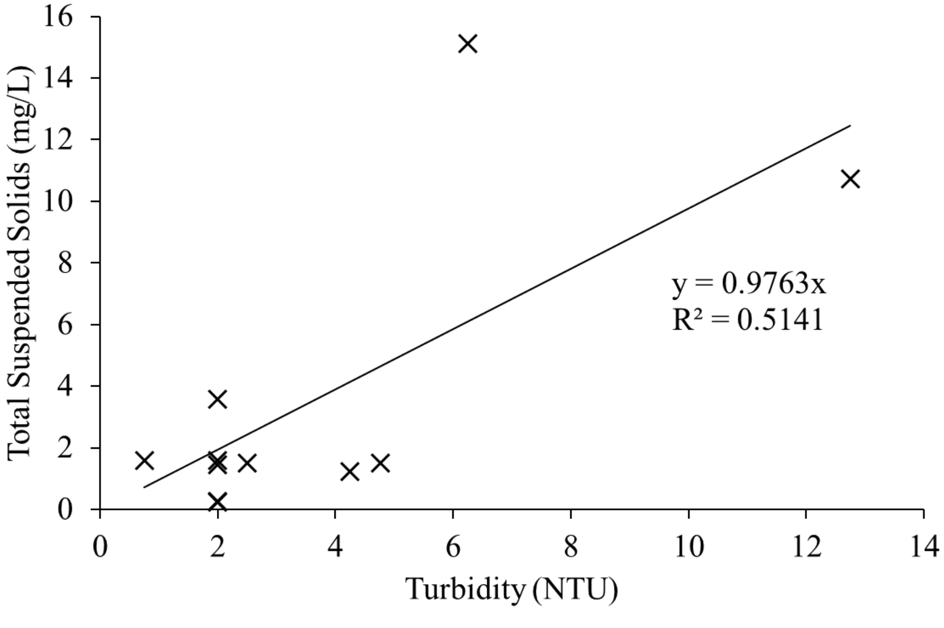

Figure 3.1 Total suspended solids (TSS) versus turbidity for treated and untreated mine water samples.

3.5.3 Metals

Figure 3.2 compares the final total concentrations of key elements in effluent from the three treatment processes to the applicable proposed MMER guidelines. All three treatment processes were able to reduce regulated metals concentrations to below current MMER discharge standards. However, only ballasted flocculation was able to reduce all regulated metal concentrations to below proposed future MMER guidelines. Lead, copper, and nickel concentrations were reduced to below proposed future MMER discharge guidelines in all three treatment processes, although lead concentrations were already under discharge guidelines and copper and nickel concentrations were low in the untreated mine water (1.5 ± 0.1 and 0.074 ± 0.002 mg/L, respectively).

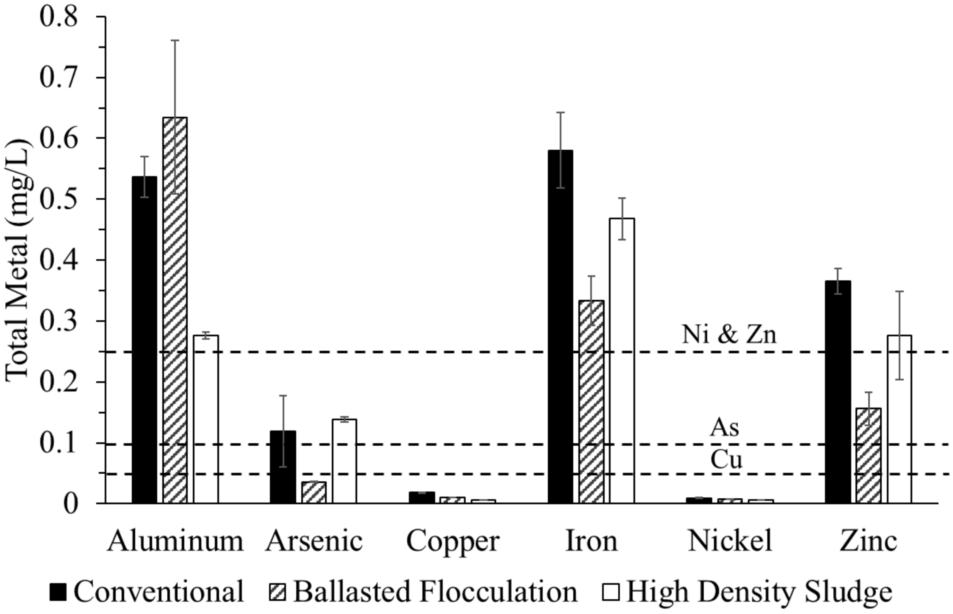

Figure 3.2 Total metals remaining in treated and clarified mine effluent with proposed new MMER guidelines.

Arsenic and zinc concentrations were only reduced to below proposed future MMER guidelines of 0.10 and 0.25 mg/L, respectively, with ballasted flocculation treatment. Final total (dissolved) arsenic concentrations were found to be 0.12 ± 0.06 (0.03 ± 0.02) mg/L for conventional, 0.14 ± 0.01 (0.11 ± 0.01) mg/L for HDS, and 0.034 ± 0.001 (0.03 ± 0.01) mg/L for ballasted flocculation and total (dissolved) zinc concentrations were 0.36 ± 0.03 (0.10 ± 0.03) mg/L for conventional, 0.28 ± 0.08 (0.13 ± 0.05) mg/L for HDS, and 0.16 ± 0.03 (0.11 ± 0.03) mg/L for ballasted. Comparing total and dissolved metals concentrations indicates that ballasted flocculation treatment results in better removal of particles greater in size than 0.45 μm than the other two processes. Aluminum and iron are not currently regulated by the MMER, but their regulation has been proposed (Environment Canada 2012). Aluminum was removed to its lowest total concentration (i.e., 0.28 ± 0.01 mg/L) with HDS treatment, while iron was removed to its lowest total concentration (i.e., 0.33 ± 0.05 mg/L) with ballasted flocculation treatment. Ferrous iron was negligible in all treated and clarified samples (i.e., < 0.02 mg/L).

Smith and Edwards (2002) found lower arsenic and iron concentrations in ballasted flocculation-treated surface and ground water compared to conventional sedimentation, although initial arsenic concentrations were extremely low in that study (i.e., 50 μg/L). That study also showed that arsenic and iron concentrations were correlated in that an increase in iron removal resulted in a proportional increase in arsenic removal, indicating that precipitated iron with adsorbed arsenic was removed in higher concentrations with ballasted than conventional sedimentation. The increased size, density, and roundness of the particles formed with ballasted flocculation allow for faster settling rates which settle more contaminants more quickly, with differential settling incorporating smaller, lighter particles as well (Young & Edwards 2003). As discussed in the previous section, ballasted flocculation also had the lowest turbidity concentrations with the three treatment processes, confirming the better settling properties of flocs and particulate matter with ballasted flocculation treatment. These results support the theory that improved settling properties of ballasted flocs are the main contributor to the decreased metals concentrations seen with ballasted flocculation.

3.5.4 Sludge Properties

Figure 3.3 shows that high density sludge (i.e., the point where further sludge volume increase is insignificant) was achieved during the bench-scale tests after approximately 20 recycles, giving a recycle ratio of 20:1 (i.e., 20 kg solids recycled for each kg of solids generated). This is in line with previous studies and full-scale plant data which suggest a typical recycle ratio of between 10 and 30 to 1 (Bosman 1983; Aubé and Zinck 1999).

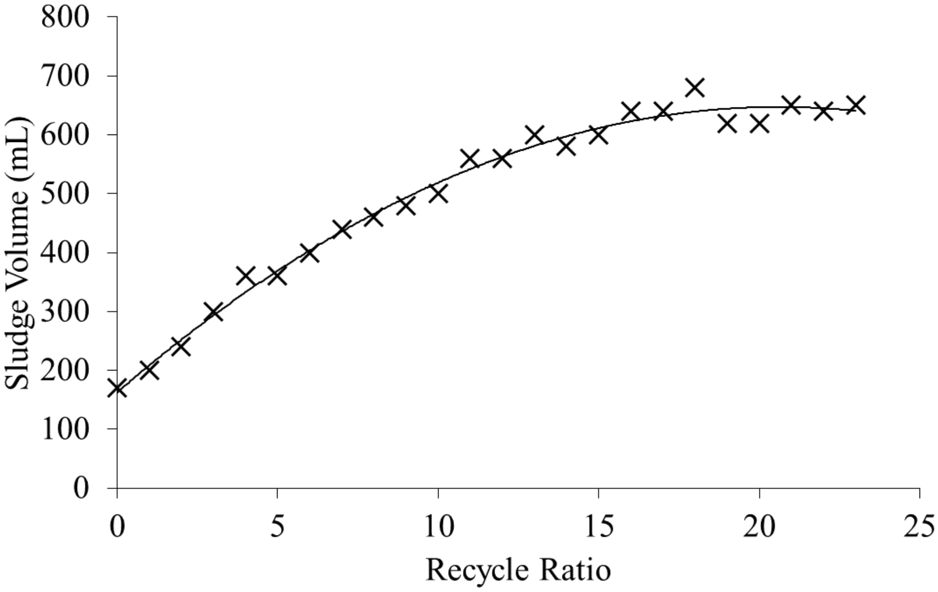

Figure 3.3 Sludge volume recycle ratio in HDS process.

Table 3.2 presents a comparison of several properties measured on the conventional sedimentation and HDS treatment process sludge samples collected in this study. Ballasted flocculation resulted in sludge volumes approximately half of those observed with conventional sedimentation after only 3 minutes of settling versus 60 minutes of settling in the conventional sedimentation process. It was observed visually that sludge began settling during the flocculation period in the ballasted flocculation tests and the remainder settled within seconds of the termination of mixing. The other sludge properties were not measured on samples collected from the ballasted flocculation tests due to the nature of the ballasted flocculation process. A low solids content (2 to 5 %) is required for efficient operation of the hydrocyclone used to recover microsand from the process, which was not modeled in the bench-scale tests. Further sludge dewatering would be required after this step in the full-scale ballasted flocculation process.

Table 3.2 Sludge properties for conventional versus HDS processes.

Parameter	**Conventional**	**HDS**
Volume (mL/L AMD treated)	180 ± 20	33 ± 5
Specific Gravity	0.98 ± 0.01	0.99 ± 0.02
% Wet Solids	7 ± 4	19 ± 1
% Dry Solids	0.44 ± 0.04	2.39 ± 0.04
Sludge Volume Index (SVI; mL/g)	230 ± 20	8.4 ± 0.8

The specific gravity of the sludge produced by both the conventional sedimentation and HDS processes was approximately that of water (i.e., 1.0), indicating a high water content in both sludges. It can be seen from the % solids and sludge volume index (SVI) values in Table 3.2 that the HDS process significantly increased the compaction of the sludge (i.e., reduced free water content). The leading theories for sludge densification in the HDS process are: 1) slowed precipitation due to lower pH of the $Ca(OH)_2$/sludge slurry versus that of $Ca(OH)_2$ alone, 2) precipitated gypsum ($Ca_2(SO_4)_3$) and/or ferric hydroxides ($Fe_x(OH)_y$) in the recycled sludge acting as seed particles for heterogeneous precipitation, 3) aging and/or dewatering effects and 4) increased compression effects due to increased concentration of Ca^{2+} and/or Fe^{2+} (Kostenbader & Haines 1970; Bosman 1974; Bosman 1983; Kuyucak 1998; Gan et al. 2005; Bullen 2006).

The pH of the fresh $Ca(OH)_2$ slurry was not found to be considerably higher than that of HDS slurry after mixing sludge with fresh $Ca(OH)_2$ for 20 minutes (12.5 ± 0.1 versus 12.2 ± 0.1, respectively). As shown in Figure 3.4, the pH of the test water increased rapidly upon addition of the lime ($Ca(OH)_2$) slurry in the conventional sedimentation and ballasted flocculation tests and upon addition of the sludge/$Ca(OH)_2$ mixture in HDS tests. The pH reached values above 6 within 15 seconds of alkali addition in both HDS and conventional tests and met the treatment target (i.e., $9 < pH < 10$) within one minute for all three processes. Therefore it is unlikely that slowed precipitation due to slower pH increase with HDS treatment is a significant contributor to the increased sludge density found with these tests.

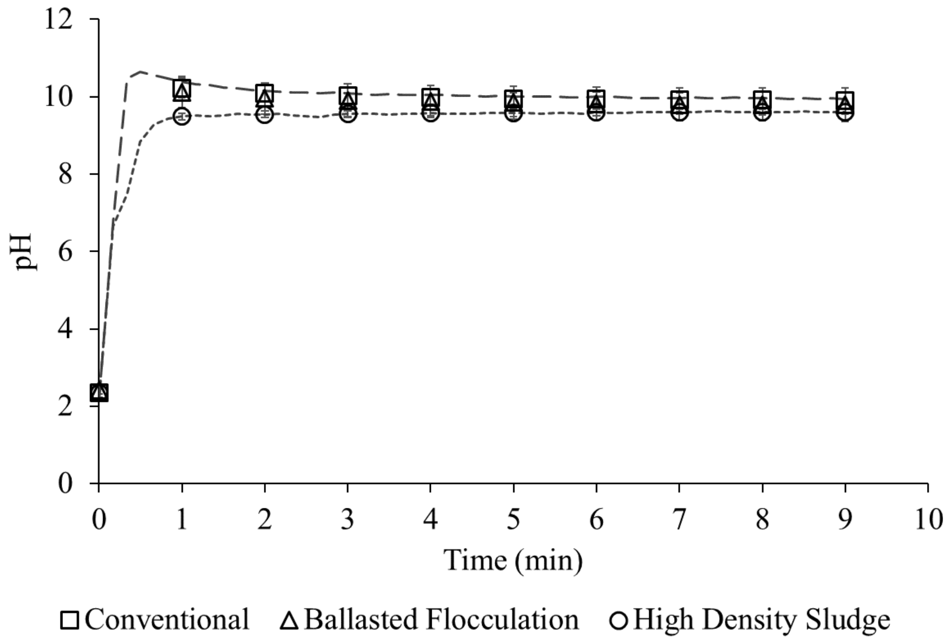

Figure 3.4 pH change during treatment tests.

Theory 2, that gypsum and/or ferrihydrites in the recycled sludge act as seed particles for further gypsum and ferric precipitation rather than homogeneous nucleation has been partially verified by the reduced gypsum scale formation on piping in HDS plants versus conventional sedimentation plants, indicating that gypsum forms on the recycled sludge particles during treatment instead of in plant piping and receiving waters after treatment (Bosman 1983). Sulphate concentrations did not increase significantly with number of recycles in the HDS process, and were equivalent between treatment processes, adding credence to this hypothesis. Sulphate concentrations in treated effluent were 3200 ± 100, 3100 ± 0, and 3000 ± 300 for conventional, HDS, and ballasted flocculation, respectively, compared to 3400 ± 200 for untreated mine water. Calcium concentrations also did not increase in treated effluent with increasing recycle ratio in the HDS treatment tests (600 ± 60 for conventional, i.e., recycle ratio = 0, versus 580 ± 20 mg/L for HDS), indicating that precipitation of gypsum is occurring during treatment. Pre-formed precipitates in the sludge would become coordinated with OH- ions during recycled sludge conditioning at high pH (i.e., > 12) so that, when contacted with metal cations in the mine water, precipitation would preferentially occur at the surface of these pre-formed particles (i.e., heterogeneous precipitation) rather than in the bulk solution (i.e., homogeneous precipitation) due to electrostatic attraction (Bosman 1974; Bullen 2006).

Theory 3 suggests that HDS sludge may have a lower chemically bound water content (i.e., hydroxide concentration) than conventional sludge, due to the dewatering of the sludge upon aging and mechanical mixing in the clarifier (i.e., polymerization/dehydration). However, this could also occur due to heterogeneous nucleation, i.e., theory 2: surface precipitation of iron on seed particles in the recycled sludge resulting in counter ions of Fe on the hydroxides instead of OH- (Bosman 1974; Bullen 2006). Theory 4 posits that increased ionic concentration, specifically Ca^{2+} and Fe^{2+}, decreases the absolute value of the zeta potential and therefore decreases the extent of the diffuse layer and allows for precipitates to pack closer together in sludge. Calcium concentrations and dissolved ion concentrations (i.e., conductivity) were not found to be significantly ($p > 0.05$) different in treated effluent between the treatment processes, and ferrous iron concentrations were negligible in all samples. However, there are higher concentrations of solids in the sludge and therefore during treatment with the HDS process due to the recycling of sludge, and it is possible that increased compression effects were a factor in sludge densification in the present study. The mechanisms behind sludge densification in the HDS process will be further studied in future work.

3.6 Conclusions

- Final pH, Eh, and conductivity values did not differ significantly between conventional, ballasted flocculation, and HDS treatment processes.
- Turbidity was less than 2.0 NTU in the clarified water samples from all processes evaluated in this study and therefore TSS was estimated to likely be below discharge guidelines (i.e., < 15 mg TSS/L) based on the relation from Figure 3.1. Turbidity was lowest in samples treated using ballasted flocculation (0.26 ± 0.02 NTU) and highest in those treated with conventional sedimentation (1.5 ± 0.2 NTU), with HDS-treated samples in between (0.8 ± 0.2 NTU).
- All treatment processes were able to reduce regulated metals to below current MMER discharge guidelines. Lead, copper, and nickel were also removed to below proposed future discharge guidelines in all processes. Ballasted flocculation was the only treatment process able to reduce total arsenic and zinc to below proposed future MMER guidelines (0.10 and 0.25 mg/L respectively).
- The HDS process resulted in significantly lower sludge volume than the conventional sedimentation process (33 ± 5 versus 180 ± 20 mL per L of mine water treated). Ballasted flocculation sludge volume was 90 mL/L. The sludge from the HDS process also had a higher solids concentration (19 ± 1 % versus 7 ± 4 % wet solids), and a lower sludge volume index (8.4 ± 0.8 versus 230 ± 20 mL/g) than that from the conventional sedimentation process, indicating that a higher density sludge was achieved.

3.7 Acknowledgements

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Chapter 4 Investigation into the Use of Cement Kiln Dust in High Density Sludge (HDS) Treatment of Acid Mine Water[2]

4.1 Abstract

The purpose of this study was to investigate the potential to replace lime with cement kiln dust (CKD) in high density sludge (HDS) treatment of acid mine drainage (AMD). The bench-scale study used two water samples: AMD sampled from a lead-zinc mine with high concentrations of iron (Fe), zinc (Zn), and arsenic (As) (Fe/Zn-AMD) and a synthetic AMD solution (Syn-AMD) spiked with ferric sulphate ($Fe_2(SO_4)_3$). Arsenic was found to be significantly reduced with CKD-HDS treatment of Fe/Zn-AMD compared to lime-HDS treatment, to concentrations below the stringent mine effluent discharge regulation of 0.10 mg As/L (i.e., 0.04 ± 0.02 mg/L). Both CKD- and lime-HDS treatment of the two AMD samples resulted in settled water Fe concentrations above the stringent discharge guideline of 0.3 mg Fe/L. CKD addition in the HDS process also resulted in high settled water turbidity compared to lime addition. CKD-HDS treatment was found to result in significantly improved settled solids (i.e., sludge) quality compared to that generated in the lime-HDS process. HDS treatment with CKD resulted in 25 to 88 % lower sludge volume indices (SVI), 2 to 9 times higher % wet solids, and 10 to 20 times higher % dry solids compared to lime addition. XRD and XPS testing indicated that CKD-HDS sludge consisted of mainly $CaCO_3$ and SiO_2 with Fe(III) precipitates attached at particle surfaces. XRD and XPS testing of the lime-HDS generated sludge showed that it consisted of non-crystalline Fe oxides typical of sludge formed from precipitates with a high water

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[2] Mackie, AL, Walsh, ME, 2015. *Water Research*, 85, 443-450. http://dx.doi.org/10.1016/j.watres.2015.08.056

concentration. Increased sedimentation rates were also found for CKD (1.3 cm/s) compared to lime (0.3 cm/s). The increased solids loading with CKD addition compared to lime addition in the HDS process was suggested to both promote surface complexation of metal precipitates with insoluble CKD particles and increase compression effects during Type IV sedimentation. These mechanisms collectively contributed to the reduced water content of CKD-HDS sludge. The results of this study suggest that solids loading is a significant factor in increased sludge density found with the HDS process compared to conventional lime precipitation-sedimentation.

Keywords: Acid mine drainage, active lime treatment, high density sludge treatment, cement kiln dust, lime sludge

4.2 Introduction

Acid mine drainage (AMD) is characterized as having a low pH and high concentrations of dissolved metals and sulphate (SO_4^{2-}) (Kuyucak 1998; Lottermoser 2007; INAP 2009). Metals and other contaminants found in AMD can be highly toxic to the receiving environment and must be treated prior to discharge in most jurisdictions. In Canada, metal mine discharges are regulated under the Fisheries Act by the Metal Mining Effluent Regulations (MMER; Fisheries Act 2002). These regulations are currently under review, with more stringent discharge guidelines proposed (Environment Canada 2012). The proposed MMER discharge guidelines most notable for this study are the reduction in allowable concentrations of arsenic (As) (0.50 to 0.10 mg/L) and zinc (Zn) (0.50 to 0.25 mg/L) and the potential introduction of a limit on concentrations of iron (Fe) (0.3 to 1.0 mg/ L) in metal mine effluent (Table 4.1). The proposed guidelines would bring Canadian mine discharge regulations in line with the more stringent regulations from around the globe (Environment Canada 2012).

Table 4.1 Relevant water quality parameters in untreated AMD with current and proposed MMER discharge guidelines (Environment Canada 2012).

Parameter	**Units**	**Fe/Zn-AMD**	**Syn-AMD**	**Current MMER**	**Proposed MMER**
pH	--	2.3 ± 0.2	2.4 ± 0.1	6.5 to 95	6.5 to 9.5
Conductivity	mS/cm	6.46 ± 0.05	1.72 ± 0.05	N/A	N/A
Turbidity	NTU	100 ± 40	25 ± 12	N/A	N/A
TSS	mg/L	100 ± 60	--	15.00	15.00
SO_4^{2-}	mg/L	3400 ± 200	720 ± 150	N/A	N/A
Fe^{2+}	mg/L	1.6 ± 0.2	3.7 ± 0.6	N/A	N/A
As	mg/L	9 ± 1	--	0.50	0.10
Fe	mg/L	83 ± 8	210 ± 50	N/A	0.3 to 1.0
Zn	mg/L	52 ± 3	--	0.50	0.25
Zeta potential	mV	--	+3.7 ± 0.4	N/A	N/A

--: not measured
N/A: not applicable

Typically, AMD is treated using the active lime treatment process in which the pH is raised through the addition of lime (CaO), allowing dissolved metals to precipitate as hydroxides and be removed through sedimentation in clarifiers (Kuyucak 1998; Aubé & Zinck 1999; Younger et al. 2002). The high density sludge (HDS) process is a modification of the active lime treatment process in which a portion of the settled solids from the clarifier (i.e., sludge) is recycled and mixed with fresh lime (i.e., conditioned) prior to contact with AMD. The HDS process, at a recycle ratio of 20 to 30 kg solids recycled to each kilogram of solids produced during treatment, has been shown to increase the density or percent solids of the sludge generated from less than 5 % solids formed in the conventional precipitation-sedimentation process to over 20 % solids with the HDS process (Bosman 1974; Kuyucak 1998; Aubé & Zinck 1999). However, the mechanisms behind the densification of sludge in the HDS process are still not fully understood (Bosman 1974; Gan et al. 2005; Bullen 2006).

Though lime is typically used in the form of slaked quicklime or hydrated lime ($Ca(OH)_2$) to treat AMD (Zinck & Griffith 2013), alternative alkali materials have been investigated due to the high environmental impact of the production of lime (CaO) from limestone ($CaCO_3$), which releases approximately one tonne of carbon dioxide (CO_2) for each tonne of CaO produced (Boynton 1980; Oates 2008). Cement kiln dust (CKD) is a fine-grained alkaline by-product of cement manufacture with a high CaO concentration and few alternatives to landfilling available for disposal (Adaska & Taubert 2008; Sreekrishnavilasam et al. 2005; Peethamparan et al. 2008; Mackie et al. 2010). CKD production has been estimated to be 15 to 20 % of cement clinker production (USEPA 2008), putting worldwide CKD production at approximately 612 to 816 million tonnes using cement production estimates from 2013 (van Oss 2015). Previous work has shown CKD to be effective as a replacement for lime in the conventional precipitation-sedimentation process for the removal of soluble metals from AMD (Mackie & Walsh 2012). CKD doses required to reach target pH in that study were found to be linearly related to free lime (i.e., alkalinity) and total lime (i.e., Ca as CaO) percentage of the CKD sample (Mackie & Walsh 2012). CKD addition was also noted to generate less sludge by volume than lime addition in that study, however no theories for mechanisms behind this were put forward. There are no published studies on the use of CKD in the HDS process, which is as commonly used as the conventional precipitation-sedimentation process for treatment of AMD.

The objective of this study was to evaluate at bench-scale the potential to replace hydrated lime with CKD in the HDS process for treatment of AMD in terms of clarified effluent and sludge quality. Two AMD samples were tested, an AMD from a lead/zinc mine in Eastern

Canada with high Fe concentration (Fe/Zn-AMD) and a synthetic AMD solution prepared using ferric sulphate ($Fe_2(SO_4)_3$) (Syn-AMD). The Syn-AMD was prepared in order to test a less complex wastewater matrix than the Fe/Zn-AMD and to determine if metals such as Zn present in CKD leach during treatment. Results from bench-scale experiments conducted using lime in the HDS process for treatment of Fe/Zn-AMD have been presented previously (Mackie & Walsh 2015) and are referenced in this study for comparison with the performance of CKD. Effluent water quality from CKD-HDS treatment was measured for turbidity, conductivity, SO_4^{2-}, As, Fe, and Zn concentrations. Settled solids characteristics were evaluated and possible explanations for observed reduced sludge volumes with CKD addition in the HDS process compared to lime addition were investigated.

4.3 Materials and Methods

4.3.1 Materials

Two test waters were used in this study. Samples were collected from a lead/zinc mine in northern New Brunswick, Canada and were characterized as having low pH (i.e., 2.3 ± 0.2) and high concentrations of dissolved Fe and Zn (Fe/Zn-AMD). A synthetic mine water (Syn-AMD) was generated by spiking 2.5 g of ferric sulphate ($Fe_2(SO_4)_3$) into 2.5 L of de-ionized water (Milli-Q) and mixing for at least 30 minutes on a magnetic stir plate. The pH of the Syn-AMD was adjusted to 2.4 ± 0.1 using 5 drops of concentrated H_2SO_4 (Fisher Chemicals). Table 4.1 outlines the relevant water quality parameters of the two test water samples used in this study, Fe/Zn-AMD and Syn-AMD, as well as current and proposed MMER discharge guidelines. Both test waters had low pH (i.e., < 2.5), total suspended solids (TSS) concentrations above current MMER discharge guidelines of 15 mg/L, and Fe concentrations above proposed MMER discharge guidelines of 0.3 to 1.0 mg/L. The Fe/Zn-AMD also had elevated concentrations of As and Zn. Metals measured in both AMD samples were 90 to 100 % in colloidal or dissolved form (i.e., < 0.45 μm).

The Syn-AMD was used in this study for several reasons. $Fe_2(SO_4)_3$ was used to generate the Syn-AMD since Fe^{3+} and SO_4^{2-} are typically found in high concentrations in AMD and, where this isn't the case, $Fe_2(SO_4)_3$ is added to the treatment process as a coagulant (Zinck & Griffith 2013). The Syn-AMD also had much lower ionic strength (i.e., conductivity = 1.7 ± 0.1 vs. 6.4 ± 0.1 mS/cm) and turbidity (i.e., 25 ± 12 vs. 100 ± 40 NTU) than the Fe/Zn-AMD, allowing for investigation into potential differences between treatments with the two alkalis, CKD and lime, in terms of solids added. The Syn-AMD was also tested to determine if MMER-regulated metals present in CKD (e.g., Pb, Zn) contribute significantly to metals concentrations in treated effluent.

CKD used in this study was sampled from a cement plant in Québec, Canada (Holcim Canada Inc.). It was comprised mainly of calcite ($CaCO_3$), determined based on the high CaO (43.1 ± 0.9 % w/w) and loss on ignition (LOI = 25 ± 0 %) percentages, quartz (SiO_2; 10.5 ± 0.1 %), and SO_3 (8.3 ± 0.3 %). The CKD sample had a free lime concentration of 6.9 ± 0.1 %, which is at the low end of the range for free lime in CKD samples found in other studies (i.e., 0 to 37 %; Sreekrishnavilasam et al. 2005; Peethamparan et al. 2008; Mackie et al. 2010; Mackie & Walsh 2012). The CKD sample also contained metals that are regulated in mine effluent in most jurisdictions such as Zn (1,150 ± 15 mg/kg), Pb (274 ± 4 mg/kg), Ni (43 ± 1 mg/kg), and Cd (7.2 ± 0.3 mg/kg). The particle size distribution of the CKD sample in terms of the D_{90}, D_{50}, and D_{10} was 20.0, 5.5, and 0.7 μm, respectively, as measured by laser diffraction in air (Malvern Mastersizer 3000).

The CKD slurry used in experiments was generated by continuously mixing the CKD at 10 % w/v with deionized water (DI; Milli-Q) using a mechanical mixer for at least 20 minutes prior to use. Certified grade $Ca(OH)_2$ (Fisher Chemicals) was continuously mixed as a 1 % w/v solution using a magnetic stir plate. Anionic polymer (Hydrex 6105, Veolia Water Technologies Canada) was mixed at 0.1 % w/v using a magnetic stir plate for one hour prior to use. Fresh reagents (i.e., synthetic AMD, CKD, $Ca(OH)_2$, and polymer) were prepared daily.

4.3.2 Methodology

The methods of Duchesne and Reardon (1998) were modified in order to determine what elements in CKD dissolved upon mixing with water and what remained as insoluble solid particles. In their study, various water:CKD ratios were contacted for four weeks to allow for secondary mineral precipitation, while in our study a 100 g sample of fresh CKD was repeatedly washed and filtered by mixing with 1 L of DI water for 20 minutes, followed by vacuum filtration through a 0.2 μm pore size filter (Whatman #5), in order to remove soluble ions from the system before secondary precipitation could occur. This was repeated until no SO_4^{2-} was detected in filtrate from three subsequent filtrate samples, indicating that the soluble $CaSO_4$ was completely dissolved (i.e., 15 rinses). This was done to more closely simulate the conditions during treatment processes. Filtrate samples were analyzed for SO_4^{2-}, Ca, and zeta potential. CKD solids remaining after repeated washing and filtering were tested for elemental composition using x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS).

A standard jar tester was used to simulate the HDS process at bench-scale following the methods of Bosman (1983), as previously described in Mackie and Walsh (2015). Treatment was initiated with the addition of $Ca(OH)_2$ or CKD to mine water samples being mixed at a velocity gradient (G-value) of 140 s^{-1} (150 rpm). Fe/Zn-AMD treatment required a CKD dose of 9,000 mg/L and lime dose of 900 mg/L as $Ca(OH)_2$ to reach a target pH of 9.5 ± 0.2. Doses of 6,000 mg/L of CKD and 600 mg/L of lime were required to achieve the target pH of 8 to 9 for $Fe(OH)_3$ precipitation in the Syn-AMD samples. The 10-fold difference between the required CKD and lime doses was due to the approximately 10 times higher concentration of CaO in hydrated lime compared to CKD. Polymer (1 mg/L) was added at t = 2 min followed by a reduction in G-value to 44 s^{-1} (50 rpm) at t = 4 min to allow for flocculation. Mixing was stopped at t = 10 min for a 60 minute sedimentation period. In each test, supernatant was sampled from just below the liquid surface and analyzed for conductivity, turbidity, SO_4^{2-}, and total and dissolved metals. Settled sludge remaining after siphoning off the majority of the supernatant was recycled into the next jar test by mixing with a fresh portion of $Ca(OH)_2$ or CKD slurry for 20 minutes at a G-value of 44 s^{-1} prior to the addition of another sample of mine water. Sludge was recycled in this fashion until settled sludge volume was no longer significantly reduced as shown in Figure 3.3 (Bosman 1983). The final, densified sludge was measured for SVI and % wet and dry solids and analyzed by XRD and XPS. All tests were run at room temperature (i.e., 21 ± 2 °C) and, at minimum, duplicates of all tests were performed. Results from bench-scale experiments conducted using lime in the HDS process for treatment of Fe/Zn-AMD have also been presented previously and are referenced herein (Mackie and Walsh 2015).

4.3.3 Analytical

A Bruker D8 Advance x-ray diffraction system (XRD) was used with a copper tube at 40 KV and 40 mA with a 0.3 sec/step analysis time and a 2θ step size. Samples were scanned from 10 to 140°. XPS was used to determine the surface composition of the sludges generated in this study using a VG Microtech Multilab ESCA 2000 at 600 μm and 50 eV. XPS spectra were normalized to adventitious carbon, C(1s), of 284.8 eV. Zeta potential was measured on a minimum of 20 individual 0.3 nm to 10 μm particles and in triplicate for each sample using a Malvern Zetasizer ZS. Turbidity of clarified water samples was measured with a HACH 2100N turbidimeter. pH was measured using an XL-50 meter with Accumet double-junction electrodes with Ag/AgCl reference calibrated daily (Fisher Scientific). SO_4^{2-} concentrations were measured using EPA-approved colorimetric methods on a HACH DR 5000 spectrophotometer using method blanks and standard checks. Inductively-coupled plasma mass spectrometry (ICP-MS; Thermo Scientific X-Series 2) was used to measure all element concentrations. All samples were acidified to pH < 2 using trace metal-grade concentrated nitric acid prior to ICP-MS analysis (APHA, AWWA and WEF 2005). Quality assurance/quality control (QA/QC) included MDL determinations, triplicate analysis of each sample, method blanks, laboratory duplicates, and standard checks for every 5 to 10 samples analyzed, with more frequent checks performed at higher element concentrations, as suggested by Standard Methods (APHA, AWWA and WEF 2005).

Sludge volumes and sludge settling rates were measured using a one litre graduated cylinder (Thermo Scientific™ Nalgene™, Fisher Scientific; Bosman 1983; APHA, AWWA and WEF 2005; Gregory & Edzwald 2011). The sludge volume index (SVI) of sludge samples was measured following APHA, AWWA and WEF (2005). The % wet solids of the sludge was measured by weighing samples before and after vacuum filtration through a 1.5 μm filter and the percent dry solids was measured by weighing the sludge samples after drying at 105 °C for ≥ 18 hours (APHA, AWWA and WEF 2005). Statistical comparisons were done using analysis of variance (ANOVA). A p-value less than 0.05 indicates that there was no significant difference in the averages of results from two or more different treatments (Mac Berthouex & Brown 2002). Error terms in text and error bars on graphs represent one standard deviation from the mean of duplicate tests at minimum.

4.4 Results and Discussion

4.4.1 CKD Characterization

The XRD patterns presented in Figure 4.1 of fresh, dry CKD versus dried CKD after repeated rinsing and filtering clearly show that the main insoluble mineral in the CKD sample used in this study was $CaCO_3$, with some SiO_2 also present (i.e., $CaCO_3$ and SiO_2 peaks are present in both fresh and rinsed CKD samples). The high concentration of $CaCO_3$ in the samples may have obscured the identifying peaks of other minerals, such as those of calcium silicates (e.g., $2\theta = 29$ to 30°), which are present in cement clinker and therefore most likely in CKD (Stutzman 1996; Madsen & Scarlett 2008). Anhydrite ($CaSO_4$), lime (CaO), calcite ($CaCO_3$), sylvite (KCl), and aphthitalite ($K_3Na(SO_4)_2$) were the main minerals that dissolved partially or completely when CKD was rinsed with water (Figure 4.1). While XRD measures the bulk composition of a sample (Suryanarayana & Norton 1998), XPS measures only the very surface of a sample (i.e., < 10 nm; Verma 2007; van der Heide 2011). XPS analysis (Figure 4.2) detected Ca (2p binding energy = 355.0, 358.5 eV), C (1s = 284.8 [adventitious], 293.0 [CO3] eV), Si (2p = 103.0 eV), Mg (1s = 1300 eV, not pictured [n.p.]), and O (1s = 531 eV, n.p.) at the surface of both fresh and rinsed CKD samples. Mg concentrations were determined by major oxide (ICP-OES) analysis to likely be present in concentrations too low to be detected by XRD (i.e., < 1 % MgO). XPS spectra from Figure 4.2 also show that fresh CKD contained Cl (2p = 199 eV), K (2p = 293, 296 eV), S (2p = 170 eV), and Na (1s = 1069 eV, n.p.) which were not present in rinsed CKD. The XPS analysis matches well with the XRD analysis in terms of soluble versus insoluble material present in CKD.

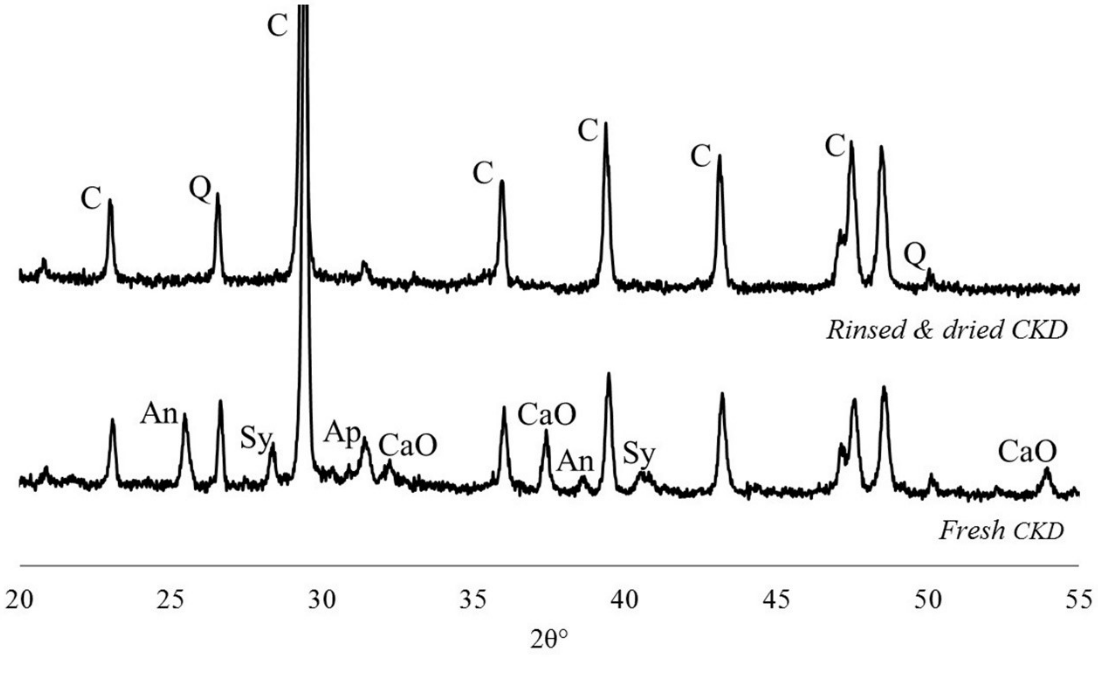

Figure 4.1 XRD relative intensity patterns for fresh CKD and dried CKD after rinsing 15 times with DI water. C = $CaCO_3$, Q = SiO_2, An = $CaSO_4$, Ap = $K_3Na(SO_4)_2$, Sy = KCl.

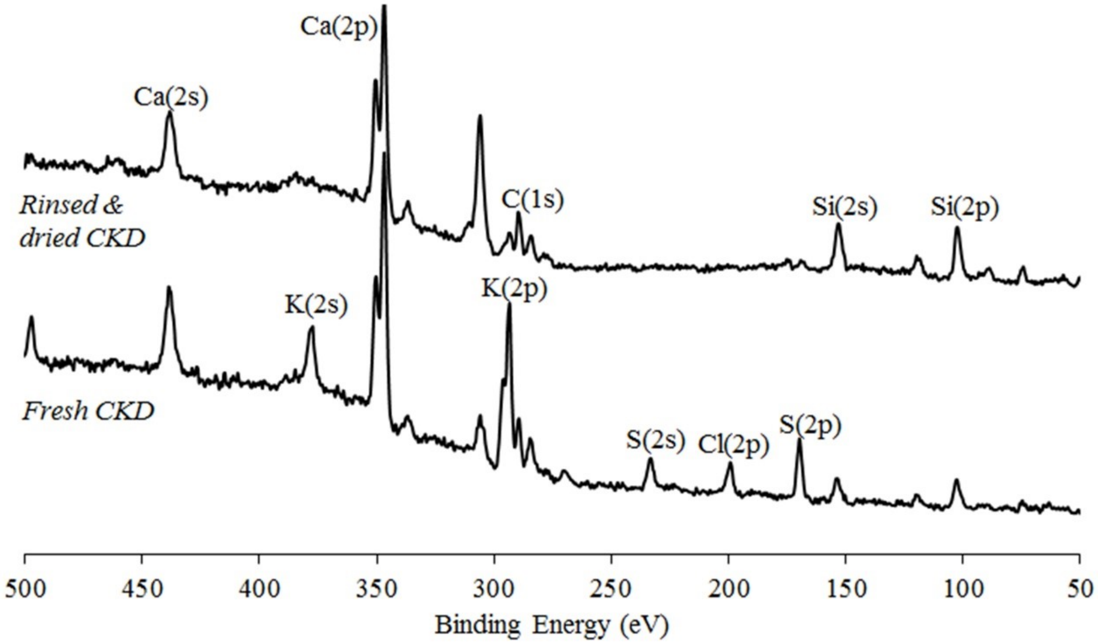

Figure 4.2 XPS spectra of fresh CKD compared to rinsed and dried CKD (C(1s) = 284.8 eV).

The zeta potential of the CKD filtrate became more positive with increasing rinses from -11 ± 1 mV from the initial filtrate to -2.9 ± 0.5 after 15 rinses. A previous study also found that CKD particles in solution at a pH below 10 had a negative surface charge (El Zayat et al. 2014). The zeta potential of filtrate from this study validates that the fine colloidal particles (i.e., < 0.2 μm) in CKD had a negative surface charge, making them stable in solution.

4.4.2 Settled Water Quality

Conductivity of the treated effluents was found to be similar between treatment with CKD and lime in the Fe/Zn-AMD experiments (5.1 ± 0.6 and 5.6 ± 0.3 mS/cm; $p > 0.05$) but significantly higher with CKD compared to lime in the Syn-AMD experiments (3.2 ± 0.2 and 1.3 ± 0.3 mS/cm; $p < 0.001$). Conductivity can be used as a proxy for the ionic strength of a solution (Droste 1997; Tchobanoglous et al. 2003). Higher conductivity was expected with CKD addition to the test waters due to the dissolution of soluble minerals in CKD upon mixing with water, as was found from XRD and XPS analysis. The high ionic strength of Fe/Zn-AMD (conductivity = 6.4 ± 0.1 mS/cm) compared to Syn-AMD (conductivity = 1.7 ± 0.1 mS/cm) may have masked the increased ionic strength that was seen with CKD addition compared to lime in Syn-AMD tests.

The average SO_4^{2-} concentration in the settled water of the CKD-HDS tests (3,300 ± 200 mg/L) was also not found to be significantly different ($p > 0.05$) from that measured in the lime-HDS tests (3,100 ± 100 mg/L) with the Fe/Zn-AMD test water. However, in the synthetic AMD experiments, SO_4^{2-} was found to be significantly higher ($p < 1x10^{-5}$) when CKD was used as the alkali (870 ± 70 mg/L) compared to lime (300 ± 0 mg/L). The concentration of SO_4^{2-} in the CKD slurry contributed to elevated SO_4^{2-} concentrations measured in the Syn-AMD compared to lime addition. SO_4^{2-} concentrations in mine effluents are not currently regulated in most jurisdictions, although increased SO_4^{2-} concentration may increase the potential for gypsum precipitation within the treatment plant and/or downstream of the discharge point. However, the lime-HDS process has been shown to reduce in-plant gypsum scaling even with higher SO_4^{2-} concentrations compared to conventional precipitation-sedimentation processes with no sludge recycling (Bosman 1983; Zinck & Griffith 2013). The reduced gypsum scaling noted with the HDS process is most likely due to the increased concentration of solids in the HDS process acting as seeds for gypsum precipitation (Bosman 1983). The same reasoning can be applied to CKD addition in the HDS process, which also introduces insoluble particles into the system onto which gypsum may precipitate.

Turbidity is proportional to the suspended solids concentration of a sample (Droste 1997; Tchobanoglous et al. 2003). Turbidity was found to be significantly higher ($p < 0.01$) in settled water samples collected from both Fe/Zn-AMD and Syn-AMD tests with CKD addition (25 ± 1 and 26 ± 4 NTU, respectively) compared to lime (0.8 ± 0.2 and 1.3 ± 0.4 NTU). Previous work that evaluated bench-scale lime treatment processes on similar test water demonstrated a conversion of 1 NTU turbidity to 1 mg/L TSS (Mackie & Walsh 2015). Therefore, the results of this study suggest that the use of CKD in the HDS process would likely result in TSS concentrations above the most stringent global discharge guideline of 15 mg/L. Experimental results also showed that the settled water turbidity increased with increasing recycle ratio in the HDS process when CKD was used as the alkali. In those tests, turbidity increased from 9 ± 2 NTU at a recycle ratio of 0:1 to 25 ± 1 NTU at a recycle ratio of 20:1 in Fe/Zn-AMD tests, and from 6 ± 3 NTU at a recycle ratio of 0:1 to 26 ± 4 NTU at a recycle ratio of 20:1 in Syn-AMD tests.

Zeta potential measurements of the clarified water samples were found to be significantly more negative ($p < 0.01$) with CKD addition (-14 ± 2 mV) compared to that measured with lime addition (-5 ± 1 mV). Given the highly negative surface charge of the added insoluble CKD particles (-11 mV ± 1 mV), these results indicate that CKD addition contributed to higher concentrations of discrete and stabilized particles that were not removed effectively in the coagulation-flocculation-clarification process. Insoluble CKD particles that may remain discrete and stable during coagulation and flocculation stages and are not incorporated into the flocs would likely not settle out during the sedimentation stage due to their extremely fine particle size. Stokes' Law, which assumes spherical particles and laminar flow conditions, was used to estimate the settling velocity of the smallest 10 % of

CKD particles (d_{10} = 0.7 μm; specific gravity = 2.7) at a water temperature of 20 °C as presented in Equation 4.1 (Droste 1997);

$$\nu = \frac{g(\rho_p - \rho)d_{10}^2}{18\mu} \qquad \text{Equation 4.1}$$

where ν is settling velocity (m/s), g is the acceleration due to gravity (9.81 m/s_2), ρ_p is the particle density (kg/m^3), ρ is the water density (kg/m^3), and μ is the water viscosity (kg/m s). These particles would settle at a velocity (ν) lower than 0.0016 m/hr, compared to an overflow rate of 0.03 m/hr minimum used for these tests.

The high turbidity of CKD-treated effluent found in this study also confirms previous observations from a bench-scale evaluation of CKD use in the conventional active lime treatment process (Mackie & Walsh 2012). In that study, settled water TSS concentrations were also found to be significantly higher with CKD compared to lime addition. Increased TSS concentrations were shown to be tied closely with the amount of CKD added to the process and its fine particle size. The poor particle removal performance and elevated turbidity and TSS concentrations observed in both studies with CKD addition could potentially be overcome by the addition of coagulant and/or by adjusting polymer type and dose used in the process. Increasing polymer dose or using a cationic instead of anionic polymer could potentially destabilize the colloids contributing to turbidity and promote optimum conditions for coagulation, although this would require further research.

The increased turbidity found with CKD-HDS treatment compared to lime-HDS is likely due to increased solids loading with CKD addition. The effects of increased solids loading with CKD addition in the HDS process are twofold. First, the addition of large quantities of fine, insoluble material in itself raises the concentration of solids in the system. This results in increased turbidity of the system prior to sedimentation. The extremely fine particle size and negative surface charge of the insoluble CKD particles results in poor coagulation, flocculation, and settling ability of these fine particles. Second, in systems where solids loading is high, turbidity of the clarified effluent is increased due to a reduction of the differential settling or sweep flocculation mechanism. This is due to the lack of formation of large, hydrous metal oxide precipitates (Parker et al. 2001). In systems where solids loading is low, such as in the typical lime treatment process, large metal hydroxide flocs precipitate rapidly and increased turbidity removal is achieved through enmeshment in the settling flocs (i.e., sweep flocculation or differential settling) (Parker et al. 2001; Hendricks 2006). Differential settling works best when the size difference of the colliding flocs and colloids is large (Gregory 2006; Gregory & Edzwald 2011; Letterman & Yiacoumi 2011). There was also a visible difference between flocs generated from CKD and lime addition (Figure 4.3). CKD flocs were noticeably denser, smaller, and rounder and settled faster than flocs from lime addition which were less spherical, lighter, and fluffier and settled more slowly. This also indicates that lime flocs have much higher water content prior to sedimentation than CKD flocs.

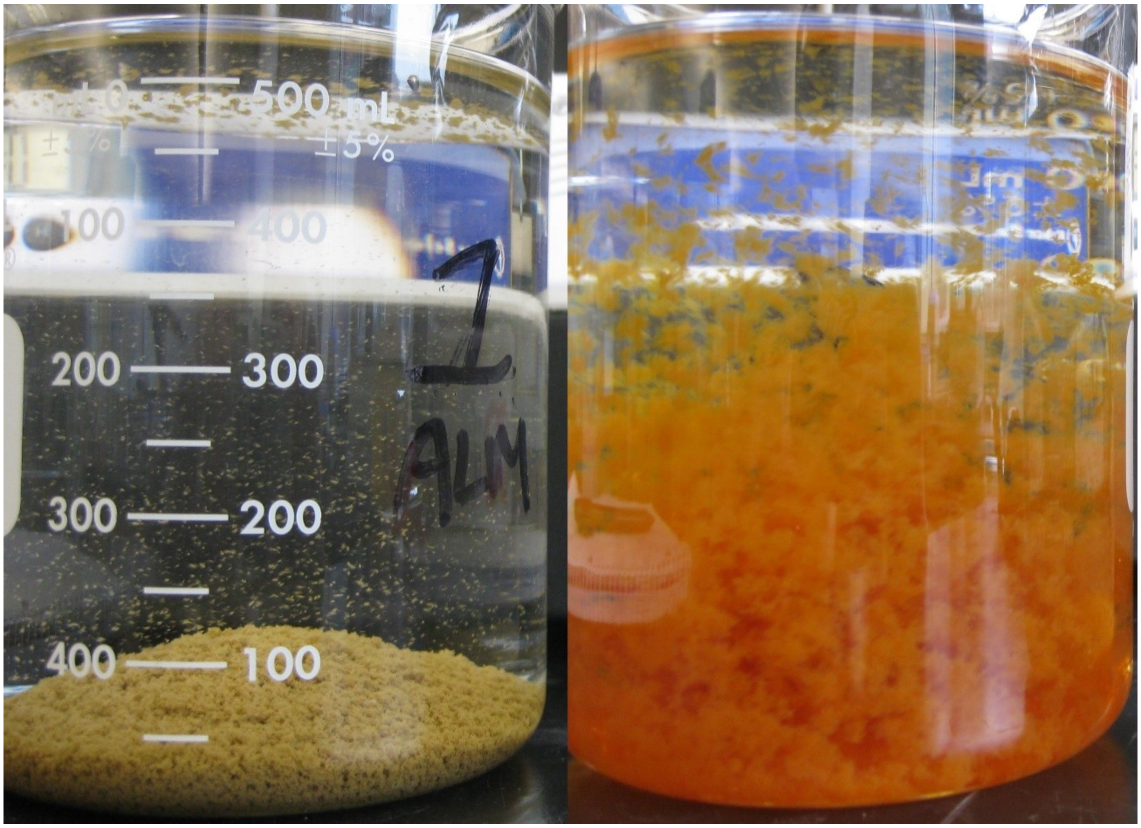

Figure 4.3 Photographs of jar testing with Syn-AMD and CKD (left) versus lime (right) at a recycle ratio of 0:1 and sedimentation time of 30 seconds.

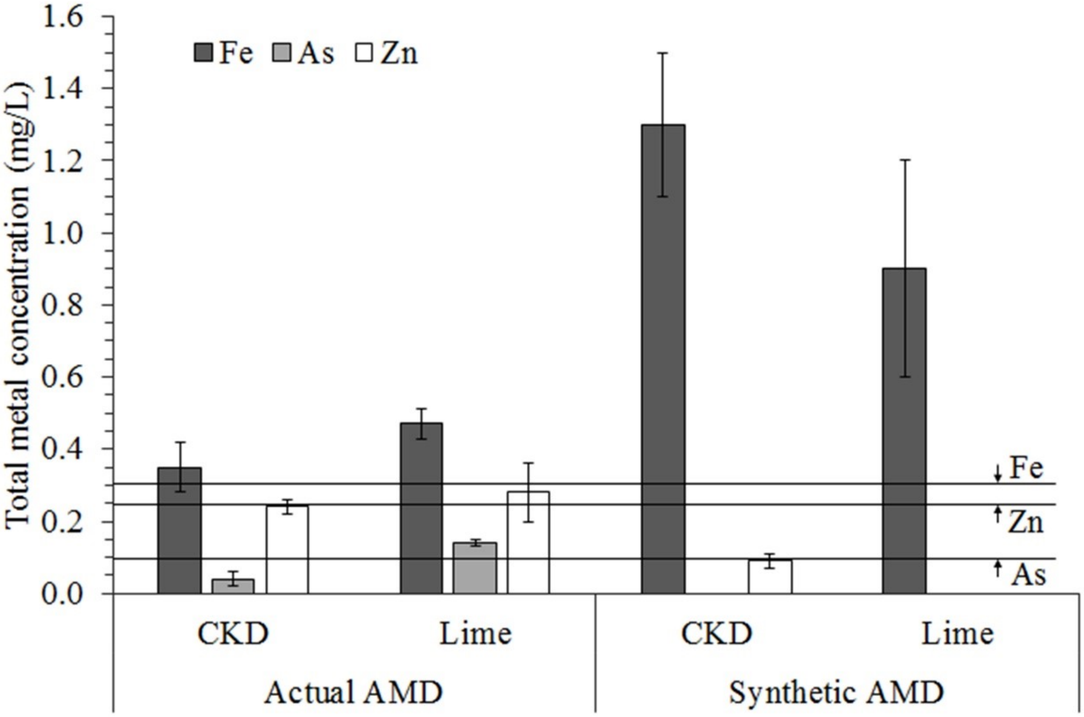

Figure 4.4 Final total Fe, As, and Zn concentrations for actual and synthetic AMD treated with CKD-HDS or lime-HDS process. Horizontal lines represent minimum discharge guidelines for the given metals.

Figure 4.4 presents the average concentrations of total Fe, As, and Zn in settled water samples from CKD-HDS and lime-HDS treatment of the two test waters. In the Fe/Zn-AMD experiments, CKD addition resulted in significantly lower ($p < 0.01$) final total As concentrations (0.04 ± 0.02 mg/L) compared to lime (0.14 ± 0.01 mg/L; Mackie & Walsh 2015). The average As concentration in the CKD-HDS experiments were below the stringent As discharge guideline of 0.10 mg/L. This is an interesting finding as previous research did not show that this guideline could be met with lime-HDS treatment (Mackie & Walsh 2015). Previous research conducted with the Fe/Zn-AMD used in this study showed that at the dissolved oxygen and Eh values of this test water, As is present as arsenate (As(V); Mackie & Walsh 2015). As(V) removal by adsorption onto and coprecipitation with $Fe(OH)_{3(s)}$ is highly pH dependent, with lower pH resulting in increased As(V) removal (Raven et al. 1998; Jain et al. 1999). The average pH of the CKD and lime tests in this study did not differ significantly ($p > 0.4$). The improved removal of As from Fe/Zn-AMD test water with CKD addition compared to lime could have been due to the addition of insoluble CKD particles. Lime is highly soluble and does not add particulate matter to the treatment process like CKD does. Similarly improved As removal was found in a study conducted by Song et al. (2006) that used $CaCO_3$ particle addition in the ferric coagulation process for enhanced removal of As from mine water. In that study, As removal was increased from 85 % using ferric coagulation alone to over 99 % with the addition of 38 to 74 μm-diameter $CaCO_3$ particles. The Fe-As precipitates were found to coat the larger $CaCO_3$ particles and therefore the settling and filtration properties of the Fe-As precipitates were improved (Song et al. 2006). Fe-As co-precipitates in that study had negative zeta potential at pH above 4.9 while $CaCO_3$ used was positively charged below pH 9.3, increasing particle interactions. Another study similarly showed that CKD removed Pb, Cu, and Cd cations from wastewater by electrostatic interactions with negatively-charged CKD particles below pH 10 (El Zayat et al. 2014). SO_4^{2-} has also been previously shown to increase removal of As using ferric co-precipitation or adsorption via ligand exchange of surface-adsorbed SO_4^{2-} with arsenate anions (Jia & Demopoulos 2005). CKD addition in the HDS process resulted in increased SO_4^{2-} addition to the treatment process compared to lime, indicating that SO_4^{2-} could have increased adsorption of As via ligand exchange with SO_4^{2-}. High SO_4^{2-} concentrations also likely contributed to high ionic strength of settled CKD-treated AMD samples. High ionic strength is known to increase compression of the electrical double layer surrounding colloids as per DVLO theory (Gregory 2006;

Letterman & Yiacoumi 2011). Increased compression of the double layer would reduce repulsive electrostatic forces between colloids, allowing for a greater proportion of collisions in the system to result in aggregation (Gregory 2006; Letterman & Yiacoumi 2011).

Figure 4.4 also shows that average Fe and Zn concentrations were not significantly different ($p > 0.05$) between experiments conducted with CKD and lime addition. Average Fe concentrations in clarified samples from both CKD-HDS (0.35 ± 0.07 mg/L) and lime-HDS (0.47 ± 0.04 mg/L) treatment of Fe/Zn-AMD were above the most stringent mine water discharge guideline found globally of 0.3 mg/L. Fe concentrations from Syn-AMD tests were even higher, averaging 1.3 ± 0.2 mg/L for CKD and 0.9 ± 0.3 mg/L for lime. Zn in clarified effluent from CKD-HDS testing of Syn-AMD averaged 0.09 ± 0.02 mg/L, well below the most stringent discharge guideline of 0.2 mg Zn/L. Zn was detected in the highest concentrations of all typically regulated metals in these tests (i.e., Pb, Ni, Zn). These results indicate that heavy metals present in CKD and therefore added into the treatment process were effectively removed during the treatment process and do not significantly contribute to metals concentrations in treated effluent.

4.4.3 Sludge Properties

The change in sludge blanket height with sedimentation time for the CKD-HDS and lime-HDS experiments with the synthetic AMD is shown in Figure 4.5. Initial sedimentation rates were calculated from the slope of the initial section of the curves (Tchobanoglous et al. 2003; Gregory & Edzwald 2011; Yan et al. 2013). The sedimentation rate of the sludge blanket interface with CKD addition (1.3 cm/s) was much faster than that found with lime addition (0.3 cm/s). Suspensions with particle concentrations higher than approximately 500 mg/L or 1 to 8 % v/v settle according to Type III (hindered or zone) settling mechanism (Hendricks 2006; Gregory & Edzwald 2011). Suspensions greater in concentration than approximately 20 g/L, generally at the bottom of zone settling suspensions, settling according to the Type IV or compression settling regime (Hendricks 2006; Gregory & Edzwald 2011). CKD-HDS suspensions had higher particle concentrations prior to sedimentation (i.e., 20 to 40 g TSS/L) than lime-HDS (i.e., 2 to 5 g TSS/L). These particle concentrations put CKD-HDS suspension settling in the Type IV region over the entire sedimentation period and lime-HDS suspension settling in the Type III region for the initial sedimentation period (i.e., $0 < t < 10$ min) followed by Type IV for the remainder (Droste 1997; Tchobanoglous et al. 2003; Hendricks 2006; Gregory & Edzwald 2011; Yan et al. 2013). The suspension particle concentration is the main controlling variable for Type III (zone) and Type IV (compression) settling rates (Droste 1997; Tchobanoglous et al. 2003; Hendricks 2006; Gregory & Edzwald 2011). Therefore, the faster sedimentation rate found with CKD addition was mainly due to the higher solids concentrations in CKD-HDS tests. The increased sphericity and density of the CKD-HDS flocs compared to the highly fractal and amorphous lime-HDS flocs likely also contributed to increased sedimentation rates in these tests.

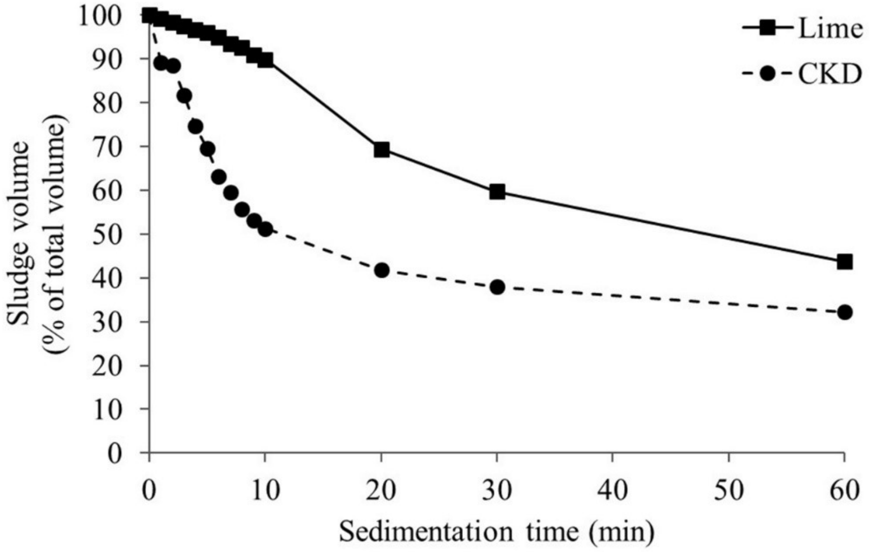

Figure 4.5 Sludge blanket height as a percentage of total height for HDS process sedimentation tests at a recycle ratio of 20:1.

Sludge volume, sludge volume index (SVI), and % wet and dry solids in sludge from both test waters with CKD addition compared to lime are presented in Table 4.2. Average sludge volumes for both test waters were found to be significantly lower ($p < 0.01$) with CKD addition compared to when lime was used as the alkali. These are interesting results in that ten times more alkali material was required to be added in the CKD experiments to achieve the target treatment pH compared to the experiments with lime addition. Similar results were found in previous research that evaluated CKD as a possible replacement for lime in the conventional precipitation-sedimentation process (Mackie & Walsh 2012). In that study, average sludge volumes in testing conducted with CKD addition ranged from 148 to 166 mL/L while quicklime addition resulted in an average sludge volume of 276 ± 54 mL/L. The lower average sludge volume found with CKD addition when compared to lime is important in that it would require less aggressive dewatering operations, which would be beneficial in terms of capital and maintenance costs.

Table 4.2 Sludge properties from HDS tests with CKD or lime addition.

	Fe/Zn-AMD		**Syn-AMD**	
Parameter	**CKD**	**Lime**	**CKD**	**Lime**
Volume (mL/L)	16 ± 1	33 ± 5	26 ± 3	43 ± 8
SVI (mL/g)	6.2 ± 0.7	42 ± 1	12 ± 9	100 ± 40
Dry Mass (Vol/SVI; g/L)	2.6	0.79	2.2	0.43
% Wet Solids	38 ± 1	19 ± 1	33 ± 3	3.6 ± 0.2
% Dry Solids	23 ± 1	2.4 ± 0.1	15 ± 1	0.8 ± 0.7

It has been found previously that up to 50 % of CKD solids dissolve upon mixing with water (i.e., slaking), dependent on the CKD's free lime concentration (Mackie et al. 2010). Assuming 50 % dissolution of CKD added in this study, the addition of 6 g/L of CKD in the jar tests performed in this study would result in approximately 3 g/L of solid CKD material ending up in the sludge, which is comparable to the measured values (Table 4.2). If a CKD sample with higher free lime is used, less material would be required to reach the target pH (Mackie & Walsh 2012) and more of that added material would dissolve, resulting in a significantly lower mass of insoluble CKD ending up in the sludge.

The results of the current study also show that when CKD was used in place of lime in the HDS process SVI was reduced by 25 to 88 %, % wet solids was increased by 2 to 9 times, and % dry solids was increased by 10 to 20 times (Table 4.2). These results verify that the lower sludge volumes measured in the bench-scale jar tests were due to lower water content in the CKD-sludge compared to the lime-sludge. It is possible that the additional solids loading with CKD applied in the HDS process either impacted sludge quality through differences in coagulation and flocculation mechanisms, increased compression effects during Type IV sedimentation (i.e., compression settling), or both. Increased shearing and aging of the sludge with HDS process due to sludge recycling has been hypothesized to reduce water content and/or promote crystallization (Bosman 1974; Aubé & Zinck 1999;

Gan et al. 2005). However, in this study, all sludges were aged and mixed at the same rate and for the same length of time therefore these variables were not included in this discussion.

The higher solids loading with CKD addition compared to treatment with lime resulted in increased particle concentration in the suspension, increasing the collision rate between particles, flocs, and colloids. As per Smoluchowski Theory, increased collision rate increases the aggregation rate of particles into flocs (Gregory 2006). Other researchers have demonstrated that the recycling of sludge or addition of solid particles into coagulation and flocculation processes results in reduced water content in flocs compared to homogeneously precipitated $Fe(OH)_3$ floc with no solid surfaces to attach to (Stumm 1992; Parker et al. 2001; Song et al. 2006; Bullen 2006; Ghanem et al. 2007).

Sludge properties were further investigated by analyzing sludge from CKD-HDS and lime-HDS tests using XRD and XPS. XRD patterns from CKD-HDS sludge resembled those from rinsed CKD samples as presented in Figure 4.1, (i.e., $CaCO_3$ and SiO_2 only), and therefore are not presented here. This indicates that the bulk of CKD-HDS sludge was insoluble CKD particles. Precipitated Fe concentrations in the sludge were likely too low for detection by XRD (i.e., < 5 %). XRD patterns of the lime-HDS sludge showed that it was composed of ferric oxide (Fe_2O_3) (Figure 4.6). Noise and less distinct peaks in the XRD pattern of the lime-HDS sludge compared to the reference pattern for Fe_2O_3 indicate a sludge with a highly disordered arrangement of Fe and O atoms, i.e., an amorphous sludge (Suryanarayana & Norton 1998; Bullen 2006; Sharma 2008; Yan et al. 2013). Fe, Ca, C, and Si were detected by XPS at the surface of CKD-HDS sludge (Figure 4.7). Fe was determined to be present as Fe^{3+}, based on the distinct satellite peak located between the

Fe 2p 1/2 and 3/2 peaks (Figure 4.7 [inset]), rather than a shoulder peak connected to Fe 2p 3/2 (Yamashita & Hayes 2008). XPS testing of lime-HDS sludge showed that its surface contained Ca and Fe (Figure 4.7). The chemical shift of the peaks of the Fe 2p and Fe 3p binding energies of lime-HDS compared to CKD-HDS sludge shown in the inset in Figure 4.7 indicates that the Fe detected comes from different compounds (Verma 2007; Yamashita & Hayes 2008; Biesinger et al. 2011). Differences between XRD and XPS measurements indicate surface deposition of precipitates (XPS) onto solids (XRD). XRD and XPS results taken together demonstrate that Fe precipitates attached to the surface of the insoluble CKD particles. XRD and XPS results also indicate that sludge from lime-HDS process was made up of non-crystalline Fe precipitates such as those typical of ferric hydroxide flocs with high water content (Bullen 2006; Yan et al. 2013).

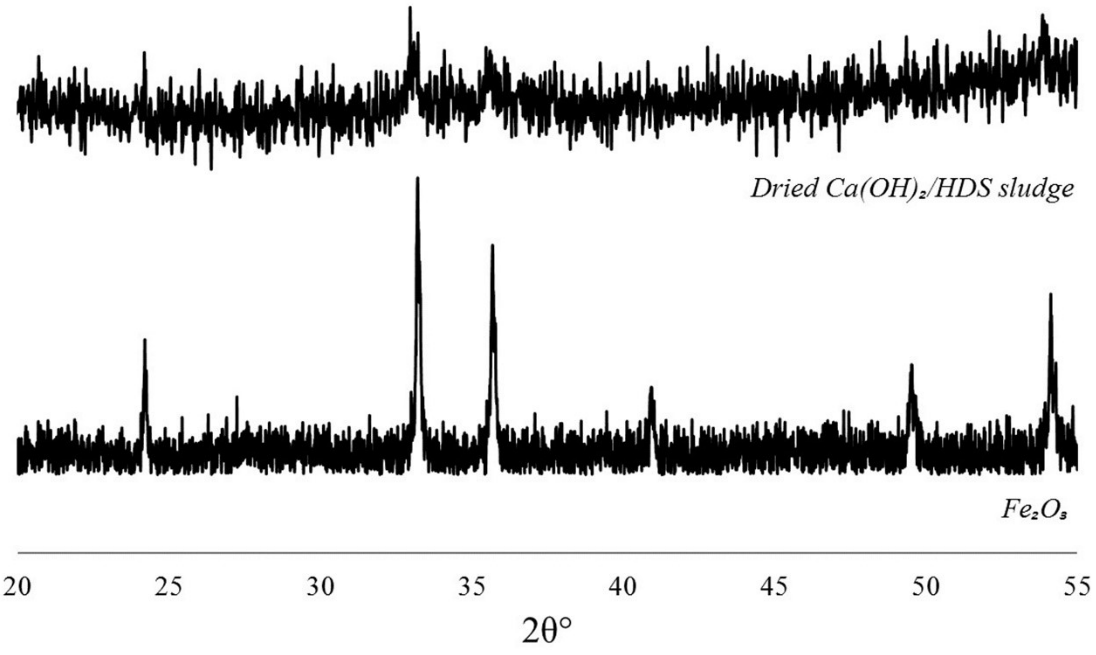

Figure 4.6 XRD relative intensity patterns for sludge from lime addition in the HDS process compared to the standard pattern for Fe_2O_3.

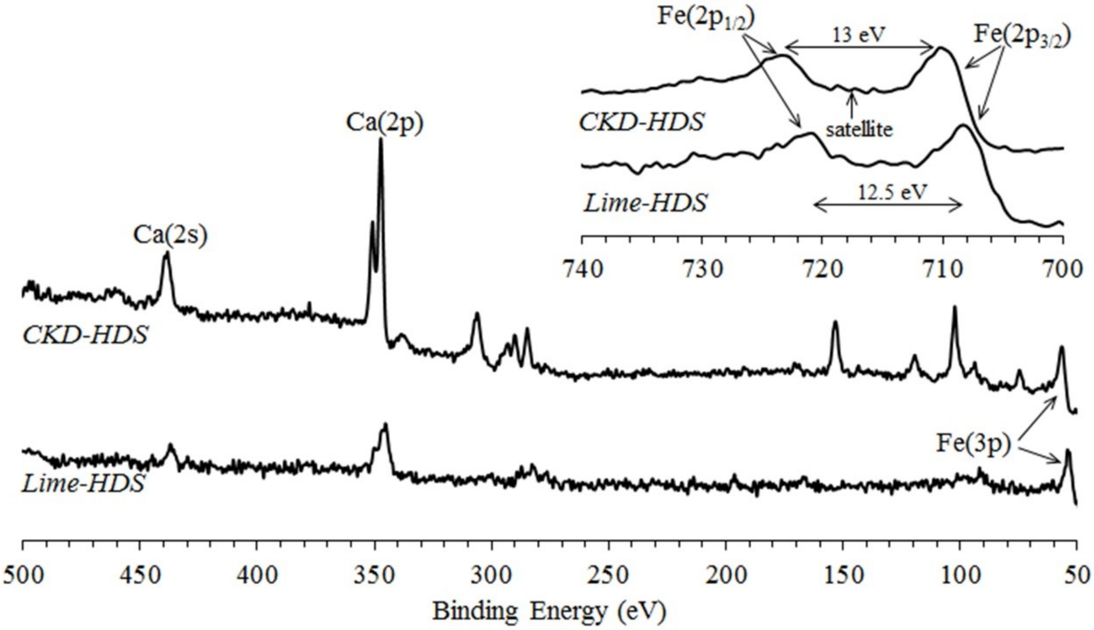

Figure 4.7 XPS spectra of CKD-HDS and lime-HDS sludge with enlarged inset of Fe(2p) region. C(1s) = 284.8 eV.

4.5 Conclusions

- Significantly lower total As concentrations ($p < 0.01$) were found in settled water from CKD-HDS treatment compared to lime-HDS treatment of Fe/Zn-AMD.
- Turbidity of clarified samples was significantly higher with CKD-HDS treatment compared to lime. Zeta potential of CKD-HDS-treated samples was also significantly more negative compared to lime-HDS, suggesting that the poor coagulation ability of insoluble CKD particles, along with their poor settling ability due to fine particle size, contributed to increased turbidity measurements in these tests. The increased turbidity could potentially be overcome by increased polymer doses but this requires more research.
- Fe concentrations in treated and settled AMD samples were similar between CKD- and

lime-HDS tests. Average Fe concentrations were greater than the most stringent global mine water discharge guidelines of 0.3 mg/L in settled samples from all tests.

- CKD addition in the HDS process was not found to impact settled water quality in terms of elevating Zn concentrations to levels above current or proposed Canadian regulations.
- Significantly lower average sludge volumes were found with CKD treatment of Fe/Zn-AMD and Syn-AMD compared to lime. This indicates that CKD sludge would require less aggressive dewatering, which would be beneficial in terms of capital and maintenance costs.
- The increased solids loading with CKD addition was shown to promote the surface complexation mechanism of metal precipitates with insoluble CKD particles and increased compression effects during sedimentation, both of which reduced water content of the sludge. This also suggests that solids loading is a significant factor in increased sludge density found with the HDS process compared to conventional lime precipitation-sedimentation.

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Chapter 5 Investigation into the Use of Cement Kiln Dust (CKD) in Ballasted Flocculation Treatment of Acid Mine Water

5.1 Abstract

The purpose of this study was to investigate the potential to replace lime with cement kiln dust (CKD) in the ballasted flocculation process for removal of soluble metals from acid mine drainage (AMD). The bench-scale study used AMD sampled from a lead/zinc mine with high concentrations of iron (Fe), arsenic (As), and zinc (Zn) (Fe/Zn-AMD) and a synthetic AMD solution (Syn-AMD) spiked with ferric sulphate ($Fe_2(SO_4)_3$). Average turbidity of settled water samples from CKD-ballasted flocculation treatment of Syn-AMD was higher (1.1 ± 0.1 NTU) than from lime-ballasted flocculation (0.4 ± 0.3 NTU). Average turbidity and total iron of settled water samples were found not to depend on ballast material type (i.e., microsand, glass beads, or magnetite) or whether or not ballast material was added at all for both CKD- and lime-ballasted flocculation tests. This unexpected result suggests that it is the increased flocculation speed used in the ballasted flocculation process that increases turbidity and Fe precipitate removal compared to other treatment processes, and not the addition of ballast material. Increases in velocity gradients during treatment may increase flocculation effectiveness due to an increase in the probability of collisions in the system. The average sludge volumes generated in CKD-ballasted flocculation tests were equivalent with or without ballast addition (66 ± 7 mL/L of AMD treated). However, sludge volume was significantly higher in lime-ballasted flocculation tests run with no ballast addition (140 ± 50 mL/L) compared to lime-ballasted flocculation tests run with ballast addition of any type (60 ± 20 mL/L). This result suggests that the insoluble particles added with CKD act as a ballasting agent to increase compression settling of sludge, as was previously hypothesized as a mechanism for increased sludge solids % in the CKD-high density sludge (HDS) treatment process compared to lime-HDS (Mackie & Walsh 2015a). The ballasted flocculation process could benefit from the use of CKD as both alkali and ballast material, negating the requirement for both lime and added ballast such as microsand and eliminating the need for microsand recovery from the sludge.

Keywords: Acid mine drainage; cement kiln dust; Wastewater Treatment; Lime Precipitation; Ballasted Flocculation

5.2 Introduction

Drainage from mining and mineral processing operations is often contaminated with high concentrations of dissolved metals and turbidity that must be removed prior to discharge in most jurisdictions. Mine effluent that is acidic (i.e., pH < 6) is termed acid mine drainage (AMD) (Kuyucak 1998; Lottermoser 2007; INAP 2009). In Canada, discharges from metal mines are regulated by the Metal Mining Effluent Regulations (MMER) which are currently under review (Fisheries Act 2002; Environment Canada 2012). Proposed new MMER guidelines include lower allowable discharge concentrations for arsenic (0.10 from 0.50 mg/L) and zinc (0.25 from 0.50 mg/L) and the potential introduction of regulations on the allowable discharge concentration of iron of between 0.3 and 1.0 mg/L (Environment Canada 2012). The regulations for allowable total suspended solids (TSS; 15 mg/L) and pH (6.5 to 9.5) are to remain unchanged. The proposed guidelines are based on the most stringent mine water discharge guidelines from across Canada and around the globe (Environment Canada 2012).

Typically, AMD is treated using the conventional active lime precipitation process, which removes dissolved metals through precipitation and sedimentation (Younger et al. 2002; Johnson & Hallberg 2005; Zinck & Griffith 2013). The ballasted flocculation process is an alternative water treatment process which incorporates a dense ballast material, usually microsand, into the flocculation stage of a coagulation-flocculation-sedimentation treatment train (Desjardins et al. 2002; Tchobanoglous et al., 2003; Young & Edwards 2003; Ghanem et al. 2007). The added ballast material generates denser, more spherical metal hydroxide flocs by replacing bound water in the flocs (Ghanem et al. 2007). These ballasted flocs then settle more quickly than typical metal precipitate flocs, reducing clarifier footprints and increasing overflow rates compared to conventional treatment processes (Desjardins et al. 2002; Tchobanoglous et al., 2003; Young & Edwards 2003; Ghanem et al. 2007). Microsand is recovered from the sludge for reinjection into the process using a hydrocyclone (Desjardins et al. 2002; Tchobanoglous et al., 2003; Young & Edwards 2003). Ballasted flocculation has also been shown to reduce concentrations of several contaminants (e.g., arsenic, turbidity) in AMD to lower concentrations than with conventional or high density sludge (HDS) treatment processes (Mackie & Walsh 2015b) and to be less sensitive to fluctuating influent water quality than conventional treatment processes (Desjardins et al. 2002; Sinha et al. 2002).

Lime in the form of slaked quicklime or hydrated lime ($Ca(OH)_2$) is usually used for metals precipitation from AMD, however, the production of lime (CaO) from limestone ($CaCO_3$) emits a significant amount of CO_2 to the atmosphere, approximately one tonne for each tonne of quicklime produced (Boynton 1980; Oates 2007). This has led to the investigation of alternative alkali materials for use in metal precipitation processes. Cement kiln dust (CKD) has been shown to be as effective as lime in the precipitation of soluble metals during treatment of AMD (Mackie & Walsh 2012; 2015a). CKD is a fine-grained alkaline by-product of cement manufacture with few alternatives to landfilling for disposal (Sreekrishnavilasam et al. 2005; Adaska & Taubert 2008; Peethamparan et al. 2008; Mackie et al. 2010). CKD has been shown to result in increases in turbidity and sludge solids percentage when compared to lime for precipitation of metals from AMD with conventional or HDS treatment processes (Mackie & Walsh 2012; 2015a).

The objective of this study was to evaluate the potential of CKD to replace lime as the alkali in the ballasted flocculation process. Two mine water samples were tested, one sampled from a lead/zinc mine in eastern Canada (Fe/Zn-AMD) and a synthetic AMD (Syn-AMD) spiked with ferric sulphate ($Fe_2(SO_4)_3$). The Fe/Zn-AMD used in this study has been evaluated previously using lime-ballasted flocculation treatment and results are referenced herein for comparison (Mackie & Walsh 2015b). Settled water samples were analyzed for turbidity, As, Fe, and Zn. Settled solids volume, sludge volume index (SVI), and % wet and dry solids were measured on samples from Syn-AMD tests and dried sludge bulk and surface compositions were analyzed using XRD and XPS, respectively.

5.3 Materials and Methods

5.3.1 Materials

Two mine waters were tested in this study, an actual AMD (Fe/An-AMD) from a lead/zinc mine in Eastern Canada with high concentrations of iron (Fe), arsenic (As), and zinc (Zn) and a synthetic AMD (Syn-AMD) made from Milli-Q water spiked with ferric sulphate ($Fe_2(SO_4)_3$) and sulphuric acid (H_2SO_4). Water quality analysis of the two test waters can be found in Table 4.1. Results from bench-scale evaluation of the lime-ballasted flocculation treatment process for Fe/Zn-AMD have been presented previously (Mackie & Walsh 2015b) and are referenced herein for comparison to CKD addition in ballasted flocculation process. The synthetic AMD was prepared daily and stored at room temperature (i.e., 21 ± 2 °C).

The CKD sample used in this study had a fine particle size (D_{10} = 0.7 µm) and contained mostly calcite along with quartz, anhydrite, and lime (free lime = 6.9 ± 0.1 %; Mackie & Walsh 2015a). CKD slurries were continuously mixed at 10 % w/v using a mechanical mixer and mixed for at least 20 minutes prior to use. $Ca(OH)_2$ slurries were continuously mixed at 1 % w/v using a magnetic stir plate. Anionic polymer (Hydrex 6105, Veolia Water Technologies Canada [VWT]) was mixed at 0.1 % w/v using a magnetic stir plate for 1 hour prior to use. Microsand (Actisand™, nominal diameter 100 µm; VWT, Québec, CA), glass beads (nominal diameter of 40 µm, specific gravity = 2.6; 3M Purification, Inc., Minnesota, US), and magnetite (D_{50} = 25 µm, D_{10} = 7.5, specific gravity = 4.8; Black Sand, Alberta, CA) were also used in this study. Fresh reagents (i.e., CKD, $Ca(OH)_2$, and polymer) were prepared daily.

5.3.2 Methodology

Simulation of the ballasted flocculation process at bench-scale was previously described in Section 3.3.2. For Fe/Zn-AMD, 30 mL of the 10 % CKD slurry (i.e., 9000 mg CKD/L) was added to reach a pH of 9.6 ± 0.3. For Syn-AMD, 6000 mg/L of CKD or 600 mg/L of $Ca(OH)_2$ was required to reach treatment pH of 9.0 ± 0.4. Supernatant was sampled from just below the liquid surface after a 3 minute settling period. All tests were run at room temperature (i.e., 21 ± 2 °C).

In order to determine the effect of various ballast material properties on clarified effluent quality, additional ballasted flocculation tests were run using glass beads or magnetite. Bench-scale tests were also run with no ballast material to determine the relative effects of ballast addition and of the higher mixing intensity used during the flocculation period with ballasted flocculation (i.e., 140 s^{-1}) versus the conventional and high density sludge (HDS) treatment processes (i.e., 44 s^{-1}). Additionally, some jar tests were run with ballast addition at $t = 0$, i.e., at the same time as lime addition and therefore iron precipitation, instead of at $t = 2$ minutes, i.e., after the precipitation and coagulation stage.

5.3.3 Analytical

Turbidity was measured in place of TSS due to the difficulty in measuring extremely low TSS concentrations (i.e., < 1 mg/L) and because it was found previously for the test waters used in this study that turbidity is loosely equivalent to TSS (i.e., 1 NTU turbidity ≈ 1 mg TSS/L; Mackie & Walsh 2015b). Turbidity of clarified water samples was measured with a HACH 2100N turbidimeter. pH was measured using an XL-50 meter with Accumet double-junction electrodes with Ag/AgCl reference (Fisher Scientific), standardized at least once daily. Zeta potential of settled water samples was measured on a minimum of 20 individual 0.3 nm to 10 μm particles and in triplicate for each sample using a Malvern Zetasizer ZS. Inductively-coupled plasma mass spectrometry (ICP-MS; Thermo Scientific X-Series 2) was used to measure all element concentrations. All samples were acidified to pH < 2 using trace metal-grade nitric acid prior to ICP-MS analysis. Dissolved metals samples were filtered through a 0.45 μm polysulfone membrane and acidified prior to analysis (GE Water & Process Technologies). Laboratory QA/QC included method blanks and calibration checks at minimum every 10 samples, sample duplicates, and triplicate analyses.

Sludge volumes were measured using a one litre graduated cylinder (Bosman 1983; APHA, AWWA, and WEF 2005). The sludge volume index (SVI) of sludge samples was measured following *Standard Methods* (APHA, AWWA, and WEF 2005). The percent wet solids of the sludge was measured by weighing samples before and after vacuum filtration through a 1.5 μm filter and the percent dry solids was measured by weighing the sludge samples after drying at 105 °C for ≥ 18 hours (APHA, AWWA, and WEF 2005). A Bruker D8 Advance x-ray diffraction system (XRD) was used with a copper tube at 40 KV and 40 mA with a 0.3 sec/step analysis time and a 2θ step size. Samples were scanned from 10 to 140°. XPS was used to determine the surface composition of the sludges generated in this study using a VG Microtech Multilab ESCA 2000 at 600 μm and 50 eV. XPS spectra were normalized to C(1s) of 284.8 eV. Statistical comparisons were done using analysis of variance (ANOVA). A p-value less than 0.05 indicates that there was no significant difference in the averages of results from two or more different treatments (Mac Berthouex & Brown 2002). Error terms in text and error bars on graphs represent one standard deviation from the mean of duplicate tests at minimum.

5.4 Results and Discussion

5.4.1 Settled Water Quality

The average turbidity of clarified samples from microsand-ballasted flocculation treatment of Fe/Zn-AMD was significantly higher ($p < 0.01$) with CKD addition (1.5 ± 0.1 NTU) compared to average turbidity from ballasted flocculation treatment with lime addition (0.26 ± 0.02 NTU), as found in a previous study which used the same Fe/Zn-AMD (Mackie

& Walsh 2015b). Average turbidity of clarified Syn-AMD samples was also higher with CKD-ballasted flocculation treatment (1.2 ± 0.2 NTU) compared to lime-ballasted flocculation (0.6 ± 0.4 NTU). These findings are consistent with previous studies of the conventional and HDS precipitation-sedimentation processes using various test waters which have found up to 60 times higher turbidity and/or TSS concentrations in settled samples when CKD was used compared to lime (Mackie & Walsh 2012; 2015a). However, CKD addition in the ballasted flocculation process resulted in clarified effluent turbidity that was considerably lower than that found with either the conventional or HDS treatment processes (Mackie & Walsh 2015a).

Zeta potential measurements of Syn-AMD samples after treatment with CKD-ballasted flocculation process were slightly but significantly ($p < 0.05$) more negative (i.e., -6.4 ± 0.4 mV) than zeta potential of samples from lime-ballasted flocculation (i.e., -4.8 ± 0.9 mV). This is also consistent with results of the HDS treatment process study, which suggested that higher turbidity of CKD-treated samples compared to lime was due to poor aggregation ability and slow settling rate of insoluble particles (Mackie & Walsh 2015a). However, the average turbidity of settled Fe/Zn-AMD and Syn-AMD samples was significantly lower ($p < 0.01$) after treatment by the CKD-ballasted flocculation process compared to treatment of the same test waters by the CKD-HDS process (Mackie & Walsh 2015a). The average zeta potential found with CKD-ballasted flocculation in this study (i.e., -6.4 ± 0.4 mV) was also significantly more positive ($p < 1\text{x}10^{-5}$) compared to that found previously for the same Syn-AMD treated with the CKD-HDS process (-14 ± 2 mV; Mackie & Walsh 2015a). The turbidity and zeta potential results indicate that the ballasted flocculation process resulted in greater removal of negatively-charged, slowly settling particles compared to the HDS process.

CKD-ballasted flocculation treatment of Fe/Zn-AMD resulted in average total As (0.034 ± 0.002 mg/L) and Zn (0.15 ± 0.03 mg/L) concentrations below the stringent discharge guidelines of 0.10 and 0.25 mg/L, respectively (Figure 5.1). Colloidal and dissolved (i.e., < 0.45 μm) As averaged 0.018 ± 0.001 mg/L and Zn averaged 0.082 ± 0.001 mg/L. Average total Fe (0.31 ± 0.05 mg/L) was just above the most stringent global guideline of 0.30 mg/L (Figure 5.1) while dissolved Fe averaged 0.134 ± 0.006 mg/L. Fe, As, and Zn concentrations were comparable to those found in a previous study for lime-ballasted flocculation treatment of the same Fe/Zn-AMD (Figure 5.1; Mackie & Walsh 2015b). Fe and As concentrations were also comparable to results of previous experiments using CKD in the HDS process for the same Fe/Zn-AMD ($p > 0.05$; Mackie & Walsh 2015a). The average total Fe concentration in settled samples from Syn-AMD treatment with CKD- and lime-ballasted flocculation (i.e., 0.32 ± 0.06 mg/L and 0.40 ± 0.38 mg/L; Figure 5.1) was comparable to results from Fe/Zn-AMD testing. This is contrary to the results of the HDS study which showed higher Fe concentrations in treated and settled Syn-AMD than Fe/Zn-AMD (Mackie & Walsh 2015a). Dissolved Fe concentrations in treated Syn-AMD averaged 0.13 ± 0.09 mg/L for lime and 0.12 ± 0.02 mg/L for CKD.

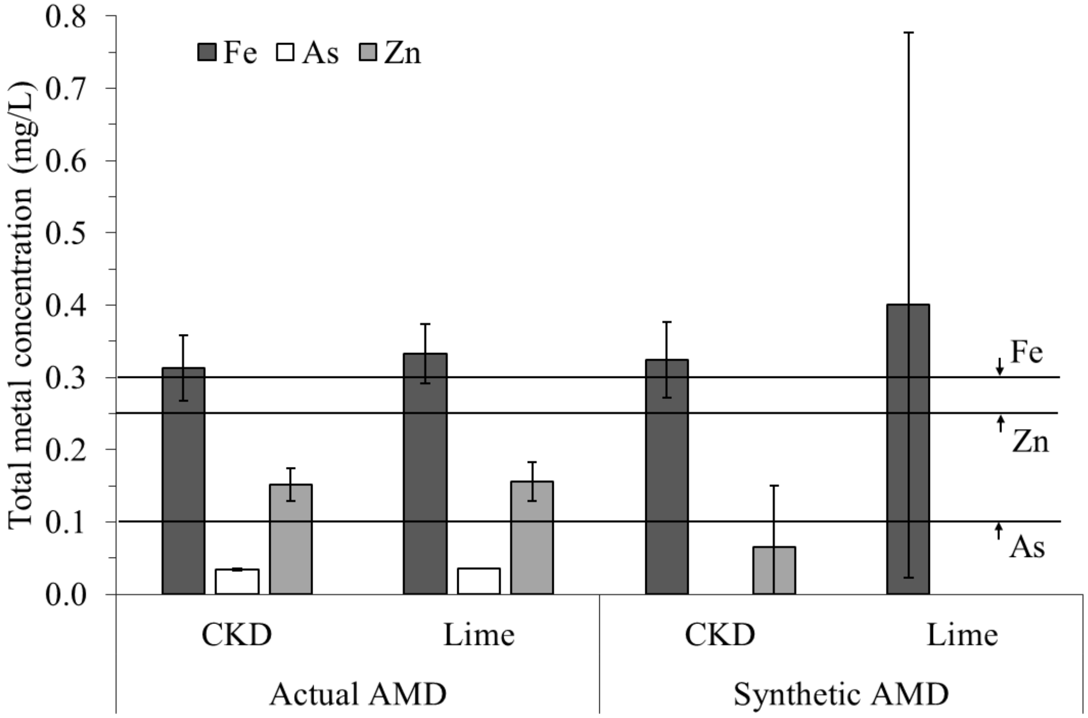

Figure 5.1 Final total Fe, As, and Zn concentrations for actual and synthetic AMD treated with CKD- or lime-ballasted flocculation process. Horizontal lines represent minimum global discharge guidelines for the given metals.

Increases in removal of contaminants (i.e., turbidity, As, Fe) from various test waters when using ballasted flocculation compared to other water treatment processes have been attributed to the improved settling ability, i.e., increased density and sphericity, of flocs formed during ballasted flocculation (Smith & Edwards 2002; Young & Edwards 2003; Mackie & Walsh 2015b). The difference in design of experimental settling times between ballasted flocculation (3 min) and other flocculation processes (60 min) makes the differences in floc settling ability between the two processes apparent. The higher density of flocs formed during ballasted flocculation has been shown to be due to collisions between the coagulated flocs and the high-density ballast material (i.e., microsand) which result in bound water being forced out of the flocs and replaced by the ballast (Ghanem et al. 2007). Ballast material is added after the coagulation stage and concentrations added range from 1 to 10 g/L in typical treatment plants. The added ballast material increases the solids loading of the system compared to conventional treatment processes. Optimum flocculation parameters have been represented by the relation in Equation 5.1 (Gregory & Edzwald 2011);

$$G t \phi = constant \qquad \text{Equation 5.1}$$

where ϕ represents the volumetric particle concentration, indicating its importance, along with shear rate, G, to flocculation processes. An increase in solids loading, i.e., the number of particles per unit volume, n, increases the collision frequency and therefore the flocculation rate, N_{ij}, of the suspension, as shown in the general relation in Equation 5.2 (Letterman & Yiacomi 2011);

$$N_{ij} = \alpha_{ij} k_{ij} n_i n_j \qquad \text{Equation 5.2}$$

where α_{ij} is the collision efficiency factor or the proportion of collisions that result in agglomeration or sticking of n particles of size i and n particles of size j. The rate constant for the process, k_{ij}, depends on the specific transport mechanism involved, particle size, and other factors (Gregory 2006; Letterman & Yiacomi 2011).

In addition to the increased solids loading, higher flocculation mixing speeds are also used with the ballasted flocculation process compared to other water treatment processes. Increasing the flocculation speed (rpm) increases the velocity gradient or shear rate (G, s^{-1}) in the system compared to traditional water treatment processes (Young & Edwards 2003; Gregory 2006; Letterman & Yiacomi 2011). Specifically, a flocculation speed of 150 rpm (G = 140 s^{-1}) was used in this study for ballasted flocculation tests, while a flocculation speed of 50 rpm (G = 44 s^{-1}) was used in the previous study of the HDS treatment process using the same CKD and test waters used in this study (Mackie & Walsh 2015a). Ballasted flocs have been suggested to have a greater shear resistance than non-ballasted flocs (Young & Edwards 2003), which is evidenced by the ability to use higher flocculation speeds without negative impacts to water quality. High flocculation speeds are necessary in order to keep the high-density ballast material and ballasted flocs suspended during flocculation (Young & Edwards 2003). This maximizes the incorporation of ballast material into the flocs by increasing the probability of collisions in the suspension. The collision rate, k, of two spherical particles of diameter d_1 and d_2 due to fluid shear, G, can be estimated by Equation 5.3 (Gregory 2006; Letterman & Yiacomi 2011).

$$k_{12} = \left(\frac{G}{6}\right)(d_1 + d_2)^3 \qquad \text{Equation 5.3}$$

Assuming collisions due to Brownian motion are negligible and collision efficiency, α, remains constant, an increase in G results in an increase in the collision rate, k, and therefore an increase in flocculation rate, N, as per Equation 5.2. The added ballast material enhances the differential settling mechanism as well (Young & Edwards 2003). The collision rate for differential settling depends on the particle density, ρ_s, the difference in particles sizes, and particle sizes overall as shown in Equation 5.4 (Gregory 2006; Letterman & Yiacomi 2011);

$$k_{ij} = \left(\frac{\pi g}{72\mu}\right)(\rho_s - \rho)\left(d_i + d_j\right)^3\left(d_i - d_j\right) \qquad \text{Equation 5.4}$$

where g is the acceleration due to gravity, and μ and ρ represent the liquid's viscosity and density, respectively. Equation 5.4 is a simplified equation used to relate these variables and assumes spherical particles and Type I (Stokes') sedimentation, as well as equivalent particle densities. Ballast material adds high-density particles of large particle size relative to Fe precipitates, increasing the differential settling rate. An increase in collision frequency due to the addition of ballast material and/or the increased flocculation speeds pushes out water from the flocs, creating higher-density aggregates (Ghanem et al. 2007). It could also be this increase in collision frequency that accounts for the increased removal of turbidity and other contaminants seen with ballasted flocculation treatment. Ballast material has also been suggested to increase interparticle bridging effects during flocculation by adding a substrate onto which polymer chains can adhere (Young & Edwards 2003). However, polymer doses were kept constant for all experiments and the effects of polymer type and dose were not investigated in this study.

In order to determine the relative impact of added ballast material compared to higher flocculation speeds on turbidity and Fe removal from Syn-AMD, additional jar test experiments were performed with either CKD or lime addition but with no ballast addition. Two additional ballast materials were also tested in addition to microsand, glass beads and magnetite. Turbidity measurements of clarified samples from tests run with and without ballast addition were not found to be significantly different ($p > 0.5$) for either lime or CKD (Figure 5.2). Average total Fe concentrations in settled samples from ballasted flocculation treatment of Syn-AMD were also consistent across ballast types, as well as for no ballast, for both lime and CKD tests, and were not significantly different between the two alkalis ($p > 0.1$; Figure 5.2). Collectively, these results indicate that it was the increased flocculation speeds, i.e., G, used with the ballasted flocculation process compared to other processes and not ballast addition that increased the removal of turbidity and Fe in this study. This was most likely achieved through increasing collisions and therefore increasing the aggregation rate of precipitates and flocs, as per equations 5.1 through 5.3. Further research is necessary to test additional mixing speeds since too a high G value can result in floc breakage and decrease flocculation effectiveness (Droste 1997; Letterman & Yiacoumi 2011).

Additional Syn-AMD jar tests with lime addition were performed with ballast material introduced at the beginning of the jar test, i.e., $t = 0$ min, at the same time as the initiation of Fe precipitation. Microsand, which is typically used in the ballasted flocculation process, was compared to highly Fe-adsorptive magnetite. Settled water Fe concentrations averaged 2.7 ± 0.6 mg/L for microsand and 0.68 ± 0.09 mg/L for magnetite addition in these tests, indicating removal of Fe was significantly affected by ballast material type in these tests. In practice and in all other tests in this study, ballast is added after the precipitation/coagulation stage. If specific adsorption of Fe were occurring during traditional ballasted flocculation process, Fe concentrations would be expected to vary between highly-adsorptive magnetite, inert glass bead, and microsand addition which, as shown in these tests, did not occur.

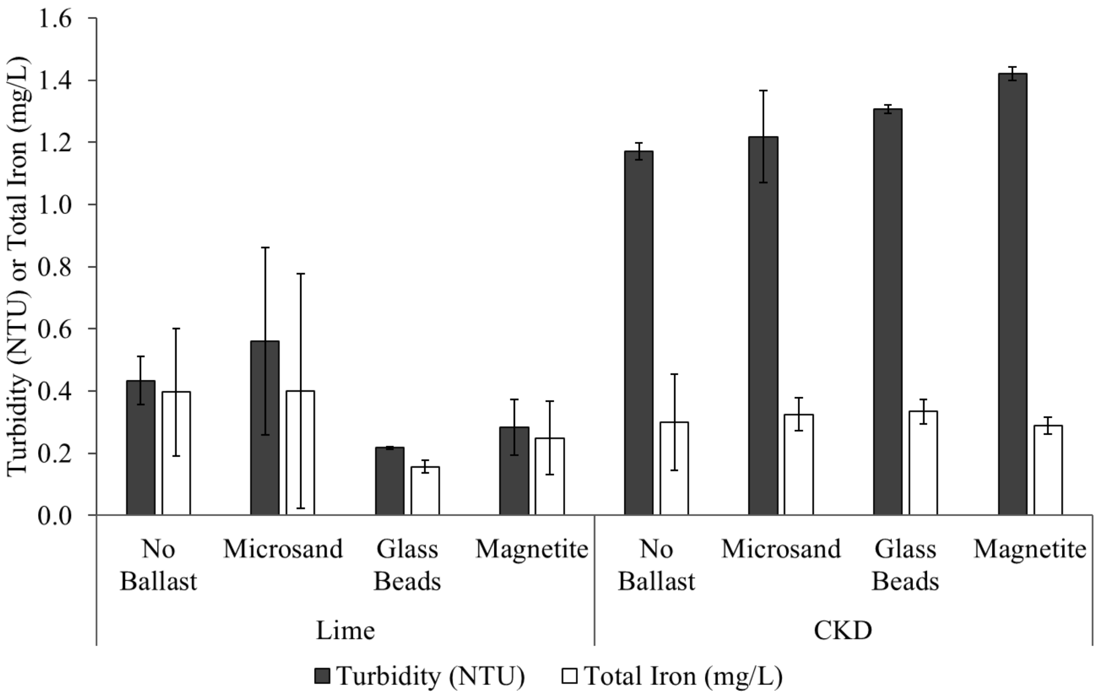

Figure 5.2 Turbidity and total iron concentrations in clarified effluent from ballasted flocculation treatment of Syn-AMD with various ballast materials and lime versus CKD addition.

5.4.2 Sludge Properties

Sludge properties were measured on samples of settled solids from Syn-AMD tests with ballast material (microsand) included. The average sludge volume generated from microsand-ballasted flocculation treatment of Syn-AMD samples did not vary significantly ($p > 0.05$) between CKD (70 ± 10 mL/L of AMD treated) and lime addition (70 ± 20 mL/L). This finding is in contrast to average sludge volumes generated from CKD addition in the conventional or HDS precipitation-sedimentation processes, which were previously shown to be only 48 to 60 % of sludge volumes generated from lime addition in those processes (Mackie & Walsh 2012; 2015a). Average sludge volumes also did not vary with ballast material type, including no ballast, for CKD-ballasted flocculation (Figure 5.3). However, lime-ballasted flocculation tests run with no ballast addition did result in a higher average sludge volume (140 ± 50 mL/L) than tests with ballast addition of any type (Figure 5.3). Both the addition of ballast material (e.g., microsand) and the insoluble particles added with CKD reduce sludge volumes, likely due to the increased solids loading of both processes. This finding is consistent with the findings of a previous study investigating the use of CKD in the HDS process (Mackie & Walsh 2015a). That study showed that the increased solids loading was an essential factor in the decreased sludge volumes found with CKD addition in the HDS process compared to lime. Increased solids loading was linked to both promotion of surface complexation mechanisms such as adsorption and surface precipitation and increased compression effects during sedimentation (Mackie & Walsh 2015a). Added ballast material is also known to reduce water content of flocs (Ghanem et al. 2007).

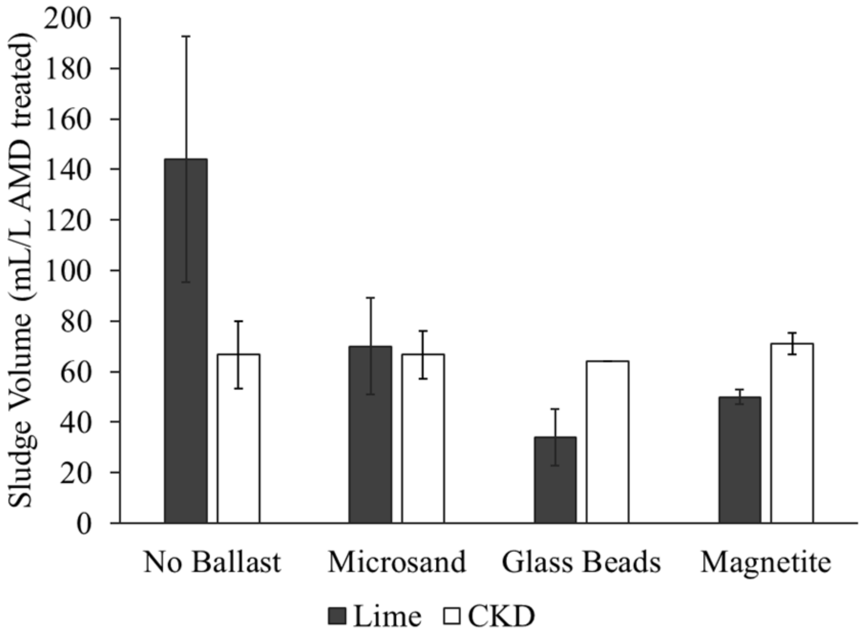

Figure 5.3 Sludge volumes for ballasted flocculation treatment using various ballast materials and lime or CKD addition.

Even though sludge volumes were not significantly different between CKD and lime addition in the ballasted flocculation process, sludge volume index (SVI) and percent wet and dry solids did vary between treatments with the two alkalis. Sludge volume index (SVI) is a measure of the volume one gram of sludge occupies after settling and was significantly lower (p-value < 0.01) in sludge from CKD-ballasted flocculation tests (6.5 ± 0.2 mL/g) compared to lime-ballasted flocculation tests (10 ± 3 mL/g). Total mass of dry material in sludge was lower when lime was used versus CKD (i.e., average = 11 vs. 7 g/L AMD), with the bulk of the solid material being from the addition of microsand or microsand and CKD and not Fe precipitates. Sludge from CKD-ballasted flocculation tests also had significantly higher ($p < 0.05$) wet (21 ± 1) and dry (17 ± 1) percent solids compared to lime-ballasted flocculation (17 ± 1 and 12 ± 2 %, respectively). A higher percent solids in settled sludge indicates less water in the sludge and therefore a sludge that requires less dewatering.

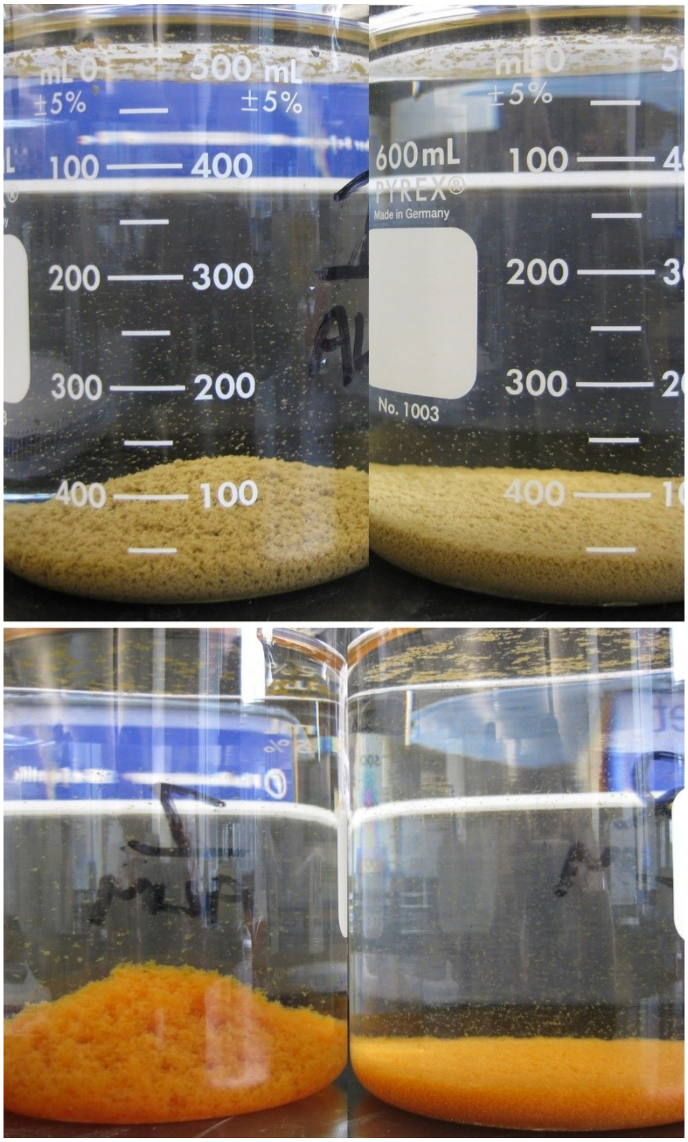

Figure 5.4 Settled solids from CKD (top) and lime (bottom) ballasted flocculation tests using no ballast (left) versus microsand (right) after 1 minute and 2 minutes settling time for CKD and lime, respectively.

The higher solids loading when CKD is used in this process compared to lime could account for the higher sludge SVI and % solids. However, the addition point of the ballast material compared to CKD could have influenced sludge water content as well. Ballast addition, which occurs after precipitation and coagulation stages, reduces water content in flocs and therefore settled sludge through increased shear rates and collisions which force out water from the preformed flocs and replacing it (Ghanem et al. 2007). When CKD is used, it's added at the beginning of the treatment process and, due to its high alkali concentration, increases the pH which initiates Fe precipitation. The insoluble, negatively charged particles in CKD act as a solid substrate for surface precipitation of Fe (Boonrattanakji et al. 2011; El Zayat et al. 2014; Mackie & Walsh 2015a). The addition of the solid particles with CKD at the initiation of precipitation and coagulation processes reduces the water content in the aggregates by promoting heterogeneous precipitation over bulk precipitation (Stumm 1992; Parker et al. 2001; Song et al. 2006; Bullen 2006; Boonrattanakij et al. 2011). CKD addition in mine water treatment processes results in smaller but denser and rounder flocs than typical metal precipitate flocs. Ballast addition also results in rounder, denser flocs than typical water treatment processes (Ghanem et al. 2007). These findings are illustrated in Figure 5.4, which show photographs of settled solids for jar tests using ballast (microsand) versus no ballast for CKD- and lime-ballasted flocculation tests. Sedimentation time = 1 min for CKD (top) and 2 min for lime (bottom).

XRD measures the bulk mineral composition of a sample (Suryanarayana & Norton 1998) while XPS measures the atomic structure of the surface (i.e. < 10 nm) of a sample (Verma 2007; van der Heide 2011). It can be seen from the XRD patterns presented in Figure 5.5 that all peaks present in patterns from the CKD-ballasted flocculation sludge sample analysis were accounted for from either CKD (mainly $CaCO_3$) or microsand (mainly SiO_2) patterns. XRD patterns of lime-ballasted flocculation sludge indicated the bulk of this sludge was composed of microsand (Figure 5.5). Fe was not detected by XRD in sludge from CKD- or lime-ballasted flocculation tests, likely due to low concentrations (i.e. < 5 %). XPS testing of the surface of sludge samples from CKD and lime-ballasted flocculation tests detected C, O, Ca, Fe, and Si, with higher concentrations of Ca in CKD-ballasted flocculation sludge and higher concentrations of Si in lime-ballasted flocculation sludge (Figure 5.6). XRD and XPS results, when taken together, indicate that sludge from ballasted flocculation of Syn-AMD with CKD is a mixture of CKD and microsand with Fe present at particle surfaces. Sludge from lime addition in ballasted flocculation tests was found by XRD and XPS to be basically iron-coated microsand with some calcium also present at the particle surfaces.

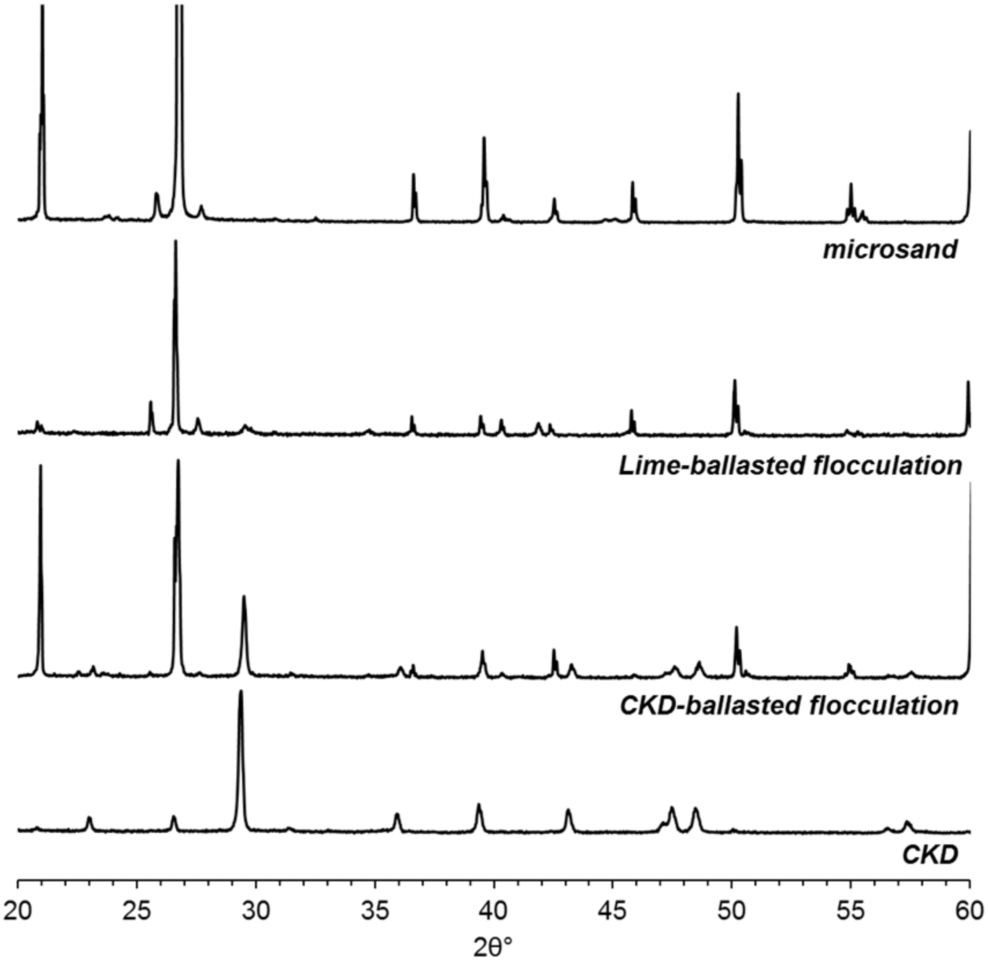

Figure 5.5 XRD relative intensity patterns for CKD-ballasted flocculation sludge, CKD, lime-ballasted flocculation sludge, and microsand.

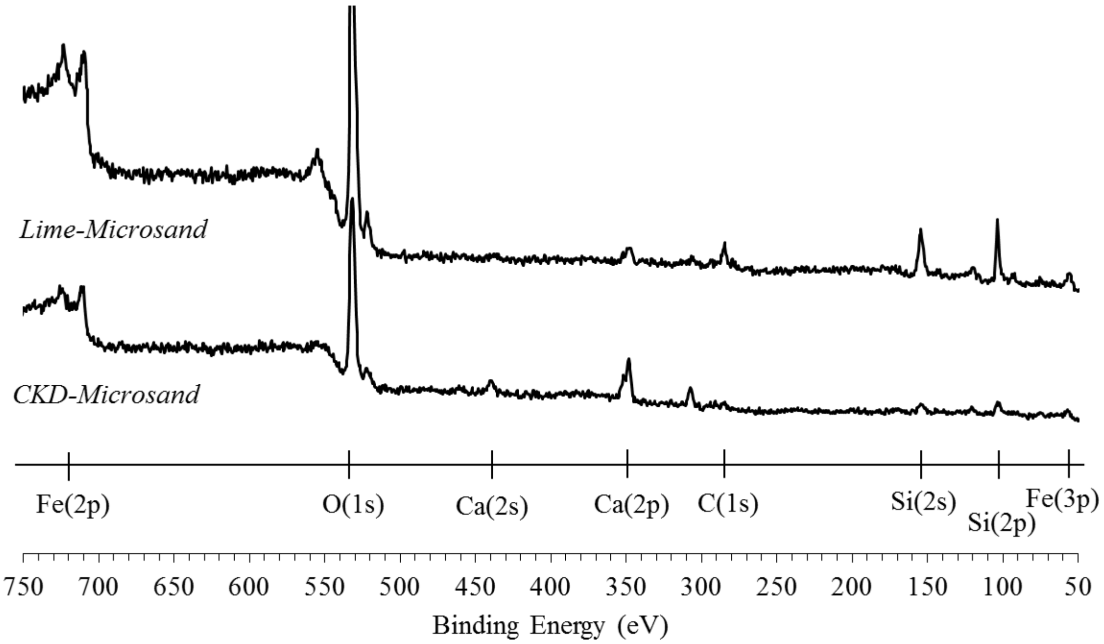

Figure 5.6 XPS spectra of lime- and CKD-ballasted flocculation sludge samples. C(1s) = 284.8 eV.

The results presented here indicate that CKD can replace both lime (alkali) and microsand (ballast) in the ballasted flocculation process without any significant impacts to water or sludge quality. Typically, microsand used in the process as ballast is recovered from the sludge with a hydrocyclone (Young & Edwards 2003). Hydrocyclones require that the sludge have a low solids concentration, 2 to 3 %, meaning a significant benefit of ballasted flocculation, reduced sludge volumes, is not being realized in practice. Replacing microsand with CKD would eliminate the need for this unit operation, allowing increased densification of sludge in clarifiers prior to disposal, reducing secondary dewatering requirements.

5.5 Conclusions

- Turbidity concentrations in all samples treated using CKD-ballasted flocculation were lower than previously found for other treatment processes (i.e., HDS and conventional). However, turbidity was still higher with CKD addition compared to lime.

- Settled water turbidity and Fe concentrations were found not to depend on ballast type or even the addition of ballast material at all for both CKD and lime tests. This was linked to the higher mixing speeds used in the ballasted flocculation process which increased the probability of collisions during treatment sufficiently to increase removal of turbidity and Fe precipitates.
- Sludge volumes were consistent between CKD (70 ± 10 mL/L of AMD treated) and lime (70 ± 20 mL/L) ballasted flocculation treatment. This is contrary to previous studies which showed significantly lower sludge volumes from various water treatment processes when CKD was used in place of lime, due to the increased solids loading of CKD processes. The equivalent sludge volumes between CKD and lime treatment in this study was determined to be due to the increased solids loading with ballast material addition, which also reduces the water content of metal hydroxide flocs. Lime-ballasted flocculation tests run with no ballast addition (i.e., low solids loading) resulted in significantly higher sludge volumes (140 ± 50 mL/L).
- Due to the potential for CKD addition in the ballasted flocculation process to replace both lime (alkali) and microsand (ballast), it is recommended that pilot- and full-scale investigations be pursued. Using CKD in place of lime and microsand in the process could reduce reagent costs in addition to eliminating the need for microsand recovery with hydrocyclones. Additionally, because hydrocyclones require sludges with low solids concentrations (i.e., < 2-3 % solids), sludge density from primary clarification can be significantly improved with the use of CKD, reducing sludge dewatering and

disposal costs as well.

5.6 Acknowledgements

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Chapter 6 Comparison of Single and Two-Stage Ballasted Flocculation Processes for Enhanced Removal of Arsenic from Mine Water[3]

6.1 Abstract

Single- and two-stage treatment processes using ferric sulphate ($Fe_2(SO_4)_3$) coagulation, lime precipitation, ballasted flocculation, and sedimentation were compared for the removal of high concentrations (i.e., 60 mg/L) of arsenic in a synthetic mine water (SMW). Single-stage treatment was found to reduce arsenic to 0.39 ± 0.04 mg/L in As(V) SMW and 0.78 ± 0.07 mg/L in As(III) SMW using either pre-oxidation with $KMnO_4$ or higher pH and coagulant dose compared to As(V) (i.e., 9.0 to 9.5 vs. 5.5 to 6.0 and 151 vs. 76 mg Fe/L), above the proposed Canadian Metal Mine Effluent Regulations (MMER) discharge guideline of 0.10 mg As/L. The two-stage treatment process was able to reduce total arsenic concentrations to 0.004 ± 0.002 mg/L for As(V) SMW using coagulation and ballasted flocculation alone in Stage 2, 0.010 ± 0.008 mg/L for As(III) with oxidation upstream of the second coagulation stage, and 0.037 ± 0.006 mg/L for As(III) with pH adjustment downstream of it. The two-stage process was shown to achieve improved performance at colder operating temperatures (i.e. 3 versus 23 °C).

Keywords: Industrial Water, Arsenic, Water Treatment, Temperature Effects, Coagulation, Oxidation, Mine water, Ferric sulphate, Ballasted flocculation

6.2 Introduction

Drainage from metal and coal mines are often contaminated with arsenic, amongst other

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[3] Mackie, AL, Laliberté, M, Walsh, ME, 2015. *Journal of Environmental Engineering*, Available online 18 September. http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0001030

heavy metals. Globally, arsenic concentrations in mining-impacted surface waters or acid mine drainage have been found to range from 0.01 to 4000 mg/L with varying ratios of arsenate (As(V)) to arsenite (As(III)) (Williams 2001; Bowell 2003; Clark & Raven 2004; Bednar et al. 2005; Wang & Mulligan 2006).

In Canada, mine water discharges to any receiving water body must meet quality targets outlined in the Metal Mining Effluent Regulations (MMER) under the Fisheries Act (Fisheries Act 2002). The MMER is currently under review, with a proposed decrease of the allowable monthly average effluent arsenic concentration from 0.50 to 0.10 mg/L (Environment Canada 2012). In addition to other criteria, the pH must be between 6.5 and 9.5 and the mine effluent must not be acutely toxic to certain aquatic species (Fisheries Act 2002). Similar regulations are in place in the United States (Ore Mining and Dressing Point Source Category 2011) and globally (Environment Canada 2012).

Arsenic in the environment is mainly found in two oxidation states: As(III) which is generally more prevalent in reducing conditions and As(V) in oxidizing conditions. The oxidation of As(III) to As(V) is reversible and depends on dissolved oxygen concentrations, oxidation/reduction potential, the presence of organic material, etc., leading to a mixture of the two states in contaminated waters (Sharma & Sohn 2009; Sorlini & Gialdini 2010). In aqueous solution, As(III) is found as H_3AsO_3 or its deprotonated anions and As(V) as H_3AsO_4 or deprotonated anions, dependent on pH (Edwards 1994; Faust & Aly 1998; Raven et al. 1998; Jain et al. 1999; Goldberg & Johnston 2001; Bowell 2003; Qiao et al. 2012).

Conventional treatment for heavy metal contaminated mine water typically consists of raising the pH using quicklime or hydrated lime ($Ca(OH)_2$) to target the pH of minimum solubility and produce metal hydroxide precipitates that can be removed by sedimentation processes. When lime precipitation is used for remediating waters contaminated with arsenic, a high pH (i.e., > 11) is required in order to form calcium arsenate ($Ca_3(AsO_4)_2$) or calcium arsenite ($CaHAsO_3$), and the resulting sludge can be highly unstable, reacting with atmospheric carbon dioxide (CO_2) to resolublize arsenic (US EPA 1990; Harris 2003; Wang et al. 2003; Wang et al. 2011). Co-precipitation of arsenic with ferric hydroxides by adding ferric-based coagulants prior to the lime precipitation process results in higher removals at lower pH (i.e., 5 to 9) and more stable sludge. The ferric coagulation with lime precipitation process has been determined by the United States Environmental Protection Agency (US EPA) to be the Best Demonstrated Available Technology (BDAT) for the treatment and disposal of arsenic-contaminated wastewater (US EPA 1990; Riveros et al. 2001; Harris 2003; Jia & Demopoulos 2008; Twidwell & McCloskey 2011).

Other studies have demonstrated that As(V) is easier to remove than As(III) in coagulation processes, and chemical oxidation pre-treatment is required for enhanced removal of As(III) (US EPA 1990; Hering et al. 1996; Riveros et al. 2001; Bissen & Frimmel 2003; Bowell 2003; Sorlini & Gialdini 2010; Twidwell & McCloskey 2011). Because natural oxidation of As(III) is extremely slow, a strong chemical oxidizer such as potassium permanganate ($KMnO_4$) or sodium hypochlorite ($NaClO$) is required for rapid oxidation (Edwards 1994; Bissen & Frimmel 2003; Sorlini & Gialdini 2010). The presence of other ions such as zinc, sulphate, or calcium and two step processes have been shown to increase arsenic removal and improve stability of precipitates (Parks et al. 2003; Jia & Demopoulos 2005; Twidwell & McCloskey 2011; Jia et al. 2012).

Most treatment studies using ferric coagulation for arsenic removal have been conducted with low initial concentrations of arsenic such as those typically found in groundwater or drinking water reservoirs (i.e. ≤ 0.5 mg/L) and required high Fe:As molar ratios for effective arsenic removal (i.e., 10 to 250; Hering et al. 1996; Hering et al. 1997; Meng et al. 2000; Mercer & Tobiason 2008). Lower Fe:As molar ratios (i.e. < 10) can be used with higher initial concentrations of arsenic, however, low final arsenic concentrations (i.e., < 1 mg/L) cannot be achieved with one stage of coagulation and conventional sedimentation treatment alone (Qiao et al. 2012; Wang et al. 2011; Harper & Kingham 1992).

The ballasted flocculation process incorporates a dense microsand or other material into flocs as they form, increasing floc density and therefore increasing settling rates according to Type II sedimentation theory (Droste 1997). Ballasted flocculation has been shown to remove more arsenate from groundwater than conventional sedimentation processes (Smith & Edwards 2002). Because the microsand-ballasted flocs settle much more quickly than traditional flocs which have a density close to that of water, a much smaller clarifier can be used for the same throughput of treated effluent, reducing capital costs and footprint requirements (Young & Edwards 2003; Ghanem et al. 2007). Spent microsand is separated from precipitated sludge in a hydrocyclone for recycling into the process.

The objective of this study was to investigate single- and two-stage treatment of mine water with elevated arsenic concentrations (i.e., 60 mg/ L) using coagulation with ferric sulphate ($Fe_2(SO_4)_3$), lime precipitation, ballasted flocculation, and sedimentation treatment trains (i.e., US EPA’s BDAT with ballasted flocculation and sedimentation for clarification step) to meet stringent arsenic discharge guidelines (i.e., 0.01 to 0.10 mg/L). Chemical oxidation with potassium permanganate ($KMnO_4$) was evaluated for enhanced arsenite (As(III)) removal in both single- and two-stage treatment processes. The effect of arsenic oxidation state (i.e., As(III) versus As(V)) and process temperature (i.e., 3 vs. 23 °C) on treatment performance was also evaluated.

6.3 Materials and Methods

6.3.1 Materials and Reagents

Synthetic mine water (SMW) used in this study was prepared to simulate average effluent characteristics from Giant Mine in Yellowknife, NT, Canada. Only major chemical species were included in the SMW because trace amounts of heavy metals present in the wastewater would only be expected to improve treatment effectiveness (Jia & Demopoulos 2005; Twidwell & McCloskey 2011; Jia et al. 2012). Two separate synthetic water samples were evaluated: one with arsenic in the trivalent form (i.e., As(III) SMW) and one with arsenic in the pentavalent form (i.e., As(V) SMW). The 500 mg/L As(III) and As(V) stock solutions were prepared following methodology outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA/AWWA/WEF 2005) using reagent A.C.S. grade arsenic trioxide (As_2O_3) and sodium arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$), respectively (Anachemia Chemicals). SMW was made in 4 or 20 L batches, stored at 3 ± 1 °C, and used in experiments within seven days for As(V) SMW and three days for As(III) SMW (to prevent oxidation). The initial arsenic concentration in each SMW was approximately 60 mg/L and the characteristics of the SMW are presented in Table 6.1.

Table 6.1 Synthetic mine water (SMW) chemical analysis.

Parameter	**Units**	**As(III) SMW**	**As(V) SMW**
pH	N/A	8.1 ± 0.1	7.9 ± 0.2
Eh	mV	440 ± 20	580 ± 30
Alkalinity	mg $CaCO_3$/L	250 ± 0	275 ± 0
Arsenic	mg/L	59 ± 3	59 ± 1
Calcium	mg/L	215	199
Magnesium	mg/L	65.7	61
Sodium	mg/L	280	177
Sulphate	mg/L	602	436
Chloride	mg/L	223	279

Liquid ferric sulphate coagulant (Hydrex 3253), anionic polymer (Hydrex 3551), and microsand (Actisand™, nominal diameter 100 µm) were used in this study (Veolia Water Technologies Canada; VWS). The initial ferric sulphate dose of 76 mg Fe/L was chosen to give a low Fe:As molar ratio (i.e. 1.7). Polymer and microsand doses, 1.0 mg/L total and 10 g/L, respectively, were chosen to mimic typical full-scale treatment plant operation. Lime used in this study for pH adjustment was prepared as a 1 % $Ca(OH)_2$ solution using reagent grade hydrated calcium hydroxide, continuously mixed on a magnetic stir plate. Reagent grade $KMnO_4$ was used as a 1 % solution in tests including chemical oxidation. Sodium hypochlorite (NaOCl) has also been shown to effectively oxidize low concentrations of arsenic (Bissen & Frimmel 2003; Bowell 2003; Sorlini & Gialdini 2010). However, $KMnO_4$ was chosen for this study as it does not produce toxic disinfection byproducts (DBPs) when it reacts with organics present in the water, which would increase the potential for failure of the acute lethality testing required for mine effluent under MMER guidelines (Faust & Aly 1998; Fisheries Act 2002).

6.3.2 Bench-Scale Experimental Protocol

In this study, the US EPA's BDAT, i.e., coprecipitation of arsenic using ferric coagulant followed by lime precipitation (with pre-oxidation if As(III) present), was compared to a two-stage process for enhanced arsenic removal from high initial concentrations. Ballasted flocculation with sedimentation was used as the clarification step in all treatment trains. The batch treatment processes were simulated at bench-scale using a standard jar tester (Phipps and Bird, Fisher Scientific) and methodology outlined by Desjardins et al. (2002), with 500 mL samples of SMW tested in 600 mL glass beakers. The bench-scale process simulated a hydraulic retention time (HRT) equivalent to an overflow rate of 40 m/h, with a constant mixing speed of 150 rpm ($G = 100\ s^{-1}$). Both As(V) and As(III) SMW with an initial concentration of 60 mg/L of arsenic were evaluated.

The single-stage treatment tests followed Stage 1 of the two-stage process outlined in Figure 6.1 and were modeled on the US EPA's BDAT for arsenic removal from wastewater (US EPA 1990). In the Stage 1 treatment train, ferric sulphate coagulant was added at a dose of 76 mg Fe/L for the As(V) SMW and 76 or 151 mg Fe/L for the As(III) SMW and mixed for two minutes at a coagulation pH between 5 and 6. The lime precipitation unit operation was run through addition of 100 to 800 mg/ L of hydrated lime ($Ca(OH)_2$) mixed for five minutes to achieve pH targets ranging from 6 to 11 to compare treatment at varying pH. The subsequent ballasted flocculation treatment step was simulated at bench-scale through the addition of 10 g/L of microsand and 0.5 mg/L of polymer mixed for five minutes, followed by an additional dose of 0.5 mg/L of polymer and three minute mixing period. The treated water was then settled quiescently for three minutes, after which samples were taken from just below the surface of the sample jars for water quality analysis.

Additional control trials were also conducted using the above single-stage treatment process for As(III) SMW with an initial oxidation stage to oxidize As(III) to As(V). In these tests, pre-oxidation with $KMnO_4$/L (HRT = 5 min) was followed by coagulation with 76 mg Fe/L and pH adjustment to 9.1 ± 0.2 with $Ca(OH)_2$ (HRT = 2 min and 5 min, respectively). The As:MnO_4 stoichiometric equivalent dose of 85 mg $KMnO_4$/L as well as a lower dose, 60 $KMnO_4$/L, were tested to determine the effect of nearly complete versus incomplete oxidation of As(III). The water was then treated with ballasted flocculation and sedimentation processes as outlined above.

For the two-stage treatment trials, the Stage 1 treated effluent was collected and further treated in a coagulation, ballasted flocculation, and sedimentation treatment train (Stage 2, Figure 6.1). In Stage 2, for both As(V) and As(III) SMW tests, coagulant was added at a dose of 19 mg Fe/L followed by seven minutes of mixing. For the As(III) SMW, the Stage 2 process was also modified to include additional test runs with (1) oxidation through addition of 5 mg/L $KMnO_4$ to ensure complete As(III) oxidation (HRT = 5 min) upstream of the coagulation process and (2) lime precipitation through addition of 40 mg/ L $Ca(OH)_2$ (HRT = 5 min) downstream of the coagulation process. Ballasted flocculation and sedimentation unit operations in Stage 2 were run according to specifications outlined above.

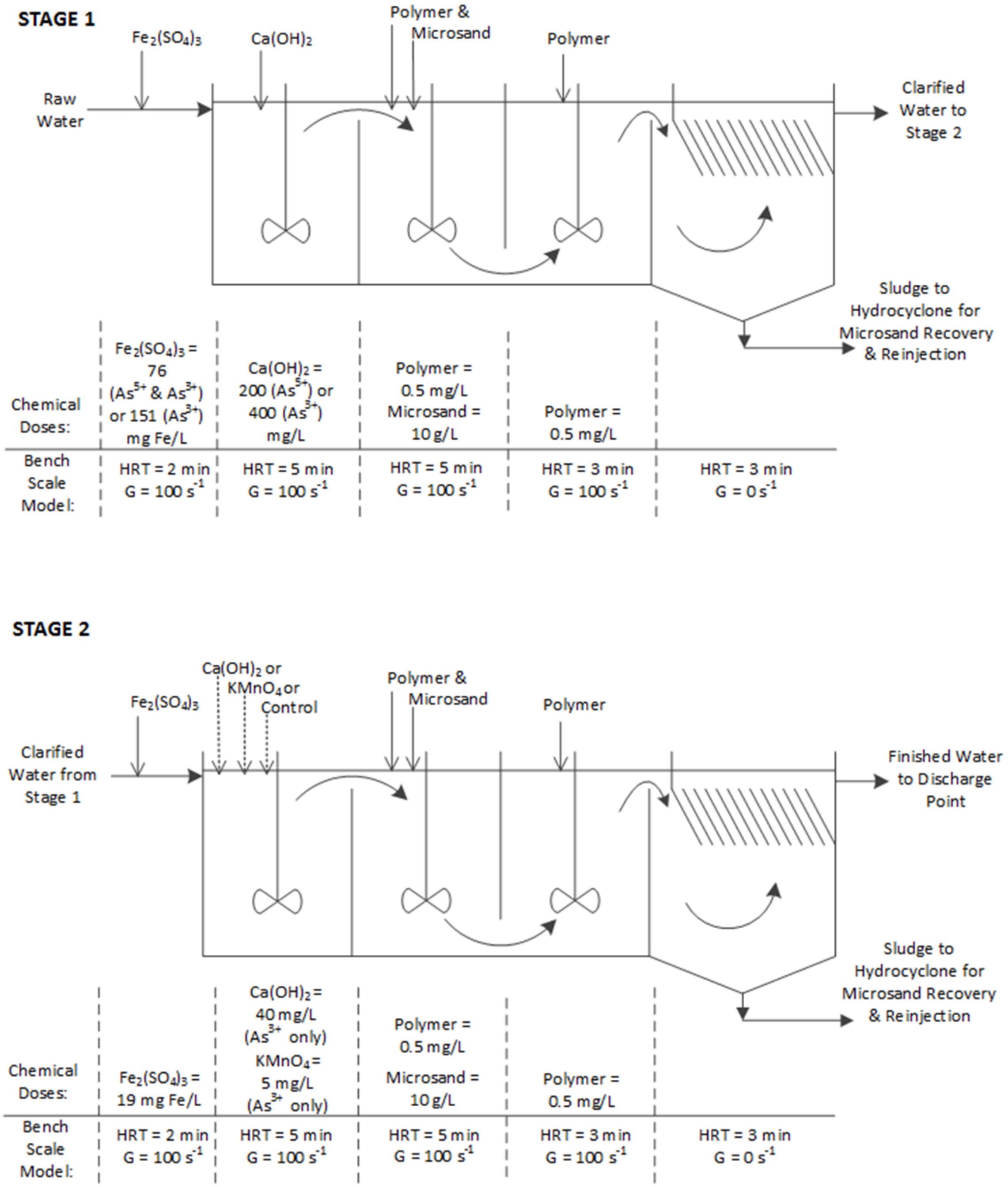

Figure 6.1 Two-stage ballasted flocculation process.

All trials were conducted at cold water conditions (i.e., 3 ± 2 °C) unless otherwise noted. The effect of temperature on the single-stage treatment process was tested by comparing the process run at 3 ± 2 and 23 ± 2 °C using 76 mg Fe/L coagulant and varying the pH from

5.5 ± 0.3 to 10.5 ± 0.4 for As(V) SMW and 151 mg Fe/L coagulant with varying pH from 8.4 ± 0.2 to 9.9 ± 0.3 for As(III) SMW. Temperature control was achieved using a chiller (Thermo Neslab RTE 111) attached to a circulating water bath to maintain water temperature targets in the test jars. Warm water tests were run without the circulating water bath (i.e., at room temperature). At minimum, duplicates of all tests were performed in this study.

6.3.3 Analytical Methods

Clarified water samples were analyzed for turbidity on a HACH 2100N turbidimeter. pH was monitored with a HACH PHC101 pH probe attached to an HQ40D multimeter, calibrated at minimum once daily. Total and dissolved metals were measured using a Thermo Scientific XSeries 2 ICP-MS unit. Dissolved metals were defined as those detected in filtrate samples after passing through a 0.45 µm membrane filter.

Analysis of variance (ANOVA) was used for statistical comparisons. The p-values reported in text indicate a significant difference in the mean value of results from the compared treatments if it is less than 0.05 (i.e., 95 % confidence level; MacBerthouex & Brown 2002). Uncertainties in data and error bars on graphs represent one standard deviation from the mean of repeated tests.

6.4 Results and Discussion

6.4.1 Single Stage Treatment

The results of the single-stage treatment tests are presented in this section. As(V) and As(III) SMW treatment results are discussed in terms of the effects of pH and temperature.

The effects of pre-oxidation are then discussed for As(III) SMW only.

All of the clarified water samples from single-stage As(V) and As(III) SMW trials were found to have turbidity measurements less than 1.0 NTU. No correlation between turbidity and pH or final total arsenic concentration was found ($R^2 = 0.36$ and 0.56, respectively), suggesting that effective clarification was achieved with the ballasted flocculation and sedimentation process. The majority of arsenic that was not removed during treatment remained in dissolved form. Final dissolved arsenic concentrations after Stage 1 treatment ranged from 65 to 100 % of final total arsenic concentrations.

6.4.1.1 Effect of pH

In the As(V) SMW tests with 76 mg Fe/ L coagulant dose, increasing the $Ca(OH)_2$ dose from 0 to 400 mg/L increased the test water pH from 5.7 ± 0.5 to 10.8 ± 0.1. The average final total arsenic concentrations for pH of 5.7 ± 0.5, 7.6 ± 0.2, 9.6 ± 0.4, and 10.8 ± 0.1 were 0.30 ± 0.06, 0.45 ± 0.07, 0.30 ± 0.10, and 0.60 ± 0.10, respectively, equivalent to greater than 99 % removal of arsenic (total dissolved and undissolved). No significant difference in final total arsenic concentration was found with varying pH from 5.7 ± 0.5 to 9.6 ± 0.4 (p-value > 0.05). However, raising the pH of the test water to 10.8 resulted in significantly higher final total arsenic concentrations (i.e., 0.60 ± 0.10 mg/L; $p < 0.05$), likely due to desorption of arsenic anions and.or dissolution of ferric precipitates causing release of adsorbed arsenic (Faust & Aly 1998; Qiao et al. 2012).

In the As(III) SMW tests with a dose of 76 mg Fe/L of coagulant, increasing $Ca(OH)_2$ dose from 100 to 500 mg/L resulted in the test water pH increasing from 7.3 ± 0.6 to 11.7 ± 0.2 (Figure 6.2). The average total arsenic concentrations in the clarified water decreased with increasing pH to 9.6 ± 0.2 (Figure 6.2), resulting in a minimum average final total arsenic concentration of 8.1 ± 0.6 mg/L at this pH. Increasing the treatment pH above 9.6 resulted in decreased removal of arsenic, though average final arsenic concentration decreased again slightly as pH was increased above 11 (Figure 6.2). This may have been due to the formation of $CaHAsO_3$ compounds or adsorption onto magnesium hydroxides as reported in other studies (McNeill & Edwards 1997, Qiao et al. 2012).

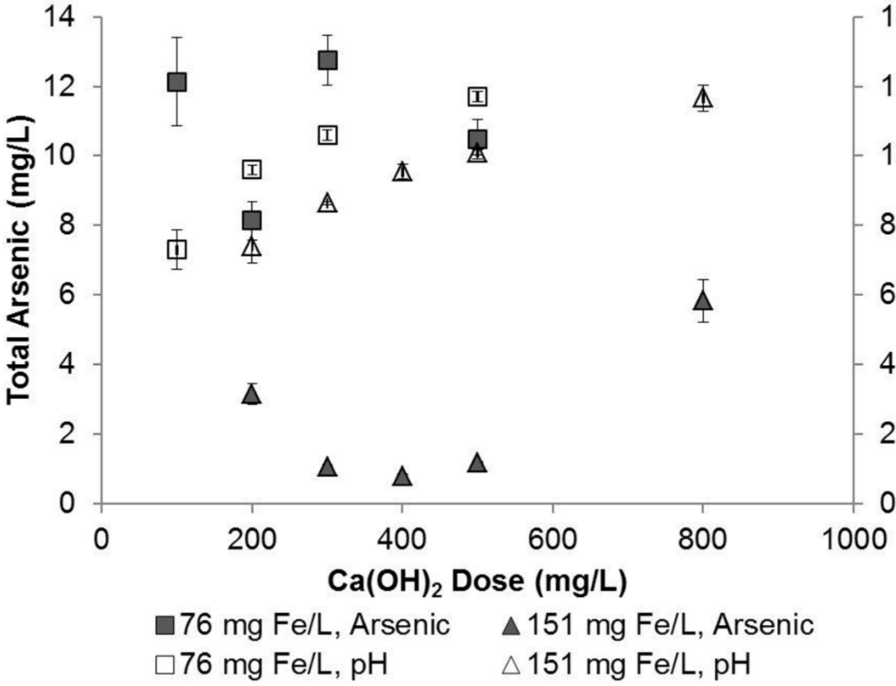

Figure 6.2 Single-stage clarified average total arsenic concentrations and final pH versus $Ca(OH)_2$ doses from As(III) SMW tests ($2 \leq n \leq 5$).

Additional tests were conducted with the coagulant dose increased to 151 mg Fe/ L (i.e., Fe:As molar ratio = 3.4) to try to reduce the final arsenic concentration in the As(III) SMW single stage treatment trials. For these experiments, the lime dose was also increased to counteract the pH depression from the increased coagulant addition. Increasing the lime dose from 200 to 800 mg/ L resulted in an increase in the test water pH from 7.4 ± 0.5 to

11.7 ± 0.4 (Figure 6.2). The best treatment results were achieved at a pH of 9.5 ± 0.3, which resulted in an average total arsenic concentration of 0.78 ± 0.06 mg/L (n = 5; Figure 6.2). Total arsenic concentrations in the settled water were found to be greater than 0.8 mg/ L at pH levels both above and below pH 9.5. A further increase in coagulant dose to 189 mg Fe/L at the optimal pH (i.e., 9.5) did not significantly ($p > 0.05$) reduce final total arsenic concentrations in the treated water.

Previous studies have shown an optimal pH range between 3.5 and 6.5 for As(V) removal with ferric coagulants at room temperature (Meng et al. 2000; Nishimura & Umetsu 2000; Wang et al. 2000; Bowell 2003; Wang et al. 2003; Pakzadeh & Batista 2011; Qiao et al. 2012). Ferric hydroxide is increasingly soluble at pH below 3.0, and therefore less surface area of the metal precipitate is available for adsorption and surface precipitation reactions. Above pH 7.0 arsenate is doubly deprotonated ($HAsO_4^{2-}$) and the surface of ferric hydroxide is increasingly negative (point of zero charge [PZC] ≈ 8), resulting in repulsion effects and therefore reduced capacity for arsenic removal (Pierce & Moore 1980; Raven et al. 1998; Wang et al. 2003; Pakzadeh & Batista 2011; Qiao et al. 2012). In this study, the SMW samples were coagulated for a period of two minutes at a coagulation pH of 5.2 ± 0.2 prior to lime addition and pH increase (Figure 6.1). This provided optimum coagulation conditions for arsenate adsorption/co-precipitation with ferric hydroxide precipitates. Increasing the pH with lime addition after coagulation did not show to have an effect on arsenic removal in the As(V) SMW treatment experiments until the pH of the test water was raised above 10. This process design allows for the optimal removal of As(III) or other metals that precipitate at alkaline pH with further pH adjustment after the initial coagulation stage run at acidic pH.

The pH corresponding to the maximum removal of As(III) (i.e., 9.5 ± 0.2) found in this study is in agreement with other published studies on ferric precipitation of As(III) at room temperature (Raven et al. 1998; Meng et al. 2000; Nishimura & Umetsu 2000; Wang et al. 2000; Bowell 2003; Wang et al. 2003; Qiao et al. 2012). This pH target of 9.5 is near the first pK_a value of arsenite (i.e., 9.2), where the non-ionic (i.e., H_3AsO_3) and singly deprotonated anionic (i.e., $H_2AsO_3^-$) forms of the acid are in equilibrium. This has been hypothesized by other researchers as an explanation for the maximum removal of As(III) at this point, that both of these species are required to be in equimolar concentrations for effective specific adsorption of weak acids above the PZC of the adsorbent (i.e., pH > 8) (Hingston et al. 1972; Sigg & Stumm 1981; Raven et al. 1998; Faust & Aly 1998; Jain et al. 1999). At a pH above the PZC of the adsorbent (i.e., more negative surface charge on ferric hydroxide), deprotonation at a pK_a of a weak acid requires the least amount of energy. This proton can then react with a hydroxyl ion on the adsorbent surface, freeing up a spot for the anion (Hingston et al. 1972; Faust & Aly 1998). Above pH 10 ferric solubility increases and the surface charges of the remaining ferric hydroxide precipitate and arsenic anions become more negative, increasing repulsion effects and decreasing arsenic removal (Faust & Aly 1998; Qiao et al. 2012).

6.4.1.2 Effect of temperature

As presented in Figure 6.3, running the single-stage treatment process at the higher operating temperature of 23 °C resulted in significantly higher ($p < 0.05$) total and dissolved arsenic concentrations in the settled water compared to arsenic concentrations achieved under cold water (3 °C) operating conditions. Final total arsenic concentrations ranged from 0.33 to 1.74 mg/L with varying pH for As(V) SMW and 1.06 to 1.83 mg/L for As(III) SMW when treated at 23 °C, compared to 0.25 to 0.83 mg/L for As(V) and 0.72 to 1.20 mg/L for As(III) SMW at 3 °C. Final total iron concentrations and turbidity measurements were not found to be significantly ($p > 0.05$) different at 3 versus 23 °C.

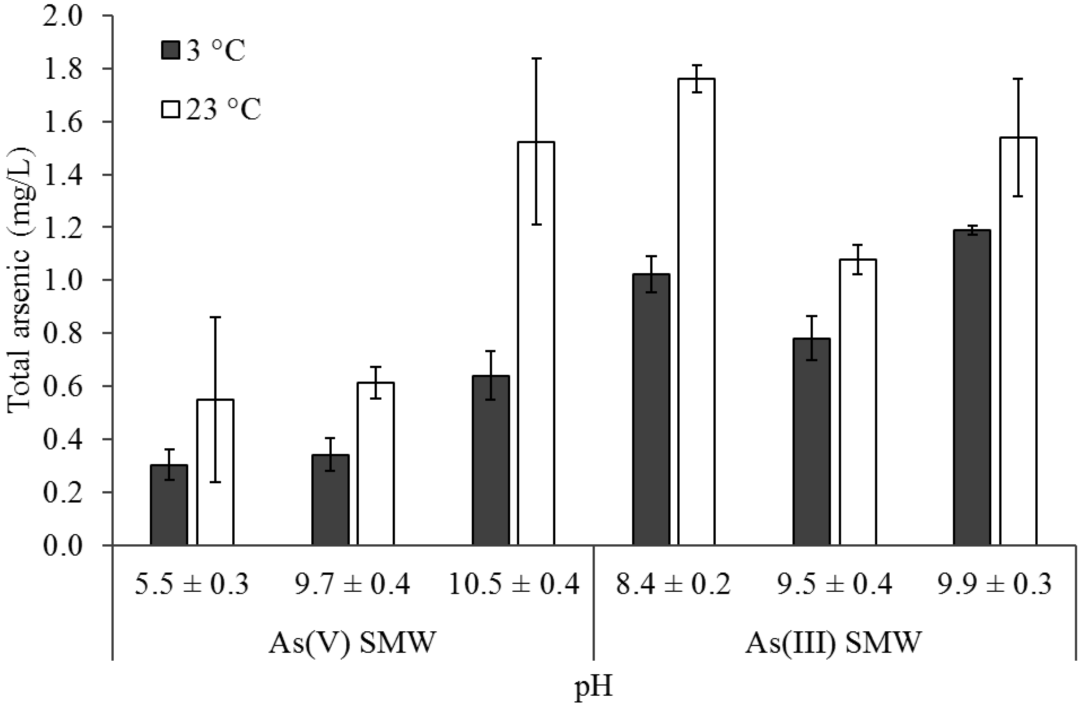

Figure 6.3 Single-stage clarified total arsenic concentrations at 3 and 23 °C versus pH ($2 \leq n \leq 5$).

The treatment process in this study involved coagulation with $Fe_2(SO_4)_3$, flocculation, and sedimentation processes, which are all more effective at warmer temperatures due to increased precipitation rates, better coagulant dispersion, and higher sedimentation rates because of decreased water viscosity (Morris & Knocke 1984; Kang & Cleasby 1995; Faust & Aly 1998; Exall & Vanloon 2000; Braul et al. 2001; Desjardins et al. 2002; Fan et al. 2003; Fitzpatrick et al. 2004). In contrast, adsorption of arsenic to ferric precipitates increases at colder temperatures due to the lower energy requirements in the exothermic adsorption reactions (Faust & Aly 1998; Fan et al. 2003). The reduced removal of arsenic observed in the Stage 1 treatment under warmer operating temperatures along with equivalent iron and turbidity concentrations between operating temperatures indicates that adsorption mechanisms are prevalent in the Stage 1 integrated treatment train. Ferric hydroxide flocs also precipitate and agglomerate more quickly at higher temperatures, resulting in larger flocs with reduced surface area for adsorption reactions, which would be more detrimental to treatment of waters with high arsenic concentrations using low Fe:As ratios (Kang & Cleasby 1995; Fitzpatrick et al. 2004). The detrimental effects of slower sedimentation rates due to smaller particles and higher viscosity water in cold water conditions have been shown to be counteracted by the increased floc density with the ballasted flocculation process (Desjardins et al. 2002; Smith & Edwards 2002; Young & Edwards 2003; Ghanem et al. 2007).

6.4.1.3 Effect of pre-oxidation (As(III) only)

In order to compare treatment of As(III) SMW to the BDAT for arsenic removal from industrial wastewater, control trials were conducted on As(III) SMW with a pre-oxidation step using $KMnO_4$. A target pH of 9.3 ± 0.3 and 76 mg Fe/L coagulant and was used for these tests, compared to 151 mg Fe/L coagulant used in As(III) tests without pre-oxidation. The 85 mg/L $KMnO_4$ dose resulted in an average final total arsenic concentration equivalent to that of Stage 1 treatment without pre-oxidation, 0.75 ± 0.10 mg/L versus 0.78 ± 0.06 mg/L. The lower dose of 60 mg $KMnO_4$/L did not perform as well as tests run without pre-oxidation (i.e., 3.3 ± 0.2 mg As/L), likely due to incomplete oxidation of arsenite. Iron concentrations remaining in treated water were significantly lower in tests involving pre-oxidation (i.e., 0.17 ± 0.09 mg/L for 60 mg $KMnO_4$/L and 0.058 ± 0.002 for

85 mg $KMnO_4$/L) versus those without pre-oxidation (i.e., 0.32 ± 0.07 mg Fe/L for As(III) SMW tests with 151 mg Fe/L coagulant and 0.19 ± 0.05 for As(V) SMW) likely due to lower coagulant doses. Secondary treatment would be necessary in all cases to reach more stringent proposed discharge guidelines (i.e., 0.10 mg As/L; Environment Canada 2012).

6.4.2 Two-Stage Treatment Process

In this study, the single-stage treatment processes evaluated were not able to reduce arsenic concentrations to below the proposed MMER discharge guideline of 0.10 mg/L. Therefore a two-stage coagulation, ballasted flocculation and sedimentation treatment process was investigated. Stage 1 of this process was performed using the optimum conditions (i.e., coagulant and lime dose/pH) that resulted in the lowest settled water total arsenic concentrations found for single-stage treatment without oxidation. The single-stage treatment process with pre-oxidation in As(III) SMW tests did not show significant reductions in total arsenic concentrations from the non-oxidized treatment tests, and therefore was not included in the two-stage treatment process evaluated in this study. All tests were run at 3 ± 2 °C.

For As(V) SMW, Stage 1 of the two-stage treatment process involved coagulation with 76 mg Fe/L coagulant, pH adjustment to 9.6 ± 0.4 with 200 mg $Ca(OH)_2$/L, and ballasted flocculation with microsand (10 g/L) and polymer (1.0 mg/L) addition. The total arsenic concentration after Stage 1 of the treatment process was 0.39 ± 0.03 mg/L (dissolved arsenic = 0.22 ± 0.04 mg/L). Stage 2 of the process consisted of coagulation with 19 mg Fe/L coagulant (Fe:As molar ratio = 65) and addition of polymer and microsand as in Stage 1 (Figure 6.1). This resulted in a final pH of 6.1 ± 0.4 and final average settled water total arsenic concentration of 0.004 ± 0.002 mg/L, an additional 99 % arsenic removal from Stage 1 effluent giving an overall treatment process arsenic removal of 99.99 % (Table 6.2). This is well below the current and future proposed MMER guideline and also below the drinking water criteria of 0.010 mg/L (WHO 2011; Health Canada 2012; US EPA 2012) and the Canadian Council of Ministers of the Environment (CCME) criteria of 0.050 mg/L for the protection of freshwater aquatic life (CCME 2007). The final pH of the clarified water, 6.1 ± 0.4, would have to be raised to meet the MMER discharge guideline of 6.5 to 9.5, or less coagulant could be used in Stage 2 of the process (since arsenic concentrations are so far below the regulatory limit) which would also result in increased pH.

Table 6.2 Final (i.e., two-stage) treatment testing results (n = 4).

SMW	**Stage 2 Treatment**	**pH after Stage 1**	**pH after Stage 2**	**Final total arsenic (mg/L)**	**Arsenic % Removal**
As(V)	coagulation/BF	9.6 ± 0.4	6.1 ± 0.4	0.004 ± 0.002	99.99
As(III)	coagulation/BF	9.4 ± 0.2	5.5 ± 0.4	0.32 ± 0.06	99.47
As(III)	coagulation/BF + oxidation	9.4 ± 0.2	5.7 ± 0.3	0.010 ± 0.008	99.98
As(III)	coagulation/BF + pH adjustment	9.4 ± 0.2	8.9 ± 0.1	0.037 ± 0.006	99.94

For As(III) SMW, Stage 1 of the two-stage treatment process involved coagulation with 151 mg Fe/L coagulant, pH adjustment to 9.4 ± 0.2 with 400 mg $Ca(OH)_2$/L, and ballasted flocculation with microsand (10 g/L) and polymer (1.0 mg/L) addition. This resulted in a total arsenic concentration going into the second stage of the process of 0.80 ± 0.20 mg/L (0.63 ± 0.01 mg dissolved As/L). Stage 2 of the process was initially tested with a coagulant dose of 19 mg Fe/L coagulant (Fe:As molar ratio = 32), ballasted flocculation, and sedimentation only. This resulted in final average total arsenic concentration after two stages of treatment of 0.32 ± 0.06 mg As/L (Table 6.2) which is above the proposed MMER guideline. The addition of either 5 mg $KMnO_4$/L upstream or 40 mg $Ca(OH)_2$/L to achieve a pH target of 9.5 downstream of the coagulation process in Stage 2, followed by ballasted flocculation and sedimentation, successfully reduced the average clarified total arsenic concentration to 0.010 ± 0.008 and 0.037 ± 0.006 mg As/L for $KMnO_4$ and $Ca(OH)_2$ addition, respectively (Table 6.2). The pH for the Stage 2 settled water when treated with oxidation in Stage 2 was below the guideline range for discharges (i.e., 5.7 ± 0.3) and would therefore have to be raised prior to discharge, while treatment with pH adjustment instead of oxidation in Stage 2 achieved a pH within the allowable discharge range (i.e., 8.9 ± 0.1).

Final turbidity measurements were less than 0.50 NTU for all settled water samples after the two-stage treatment process. No correlation between final turbidity and final total arsenic concentration was found ($R^2 = 0.48$).

Several studies have looked at coagulation with ferric salts for removal of arsenic, usually at extremely low (i.e., ≤ 0.5 mg/L) initial arsenic concentrations. Mercer and Tobiason (2008) found that high Fe:As molar ratios (i.e., 15 to 150) were required for removal of As(V) below 0.1 mg/L from a 0.5 mg As/L high ionic strength solution, using $FeCl_3$ and micro- or ultrafiltration. Studies that have looked at removal of higher concentrations of arsenic as As(V) (i.e., > 1 mg/L) using ferric coagulation showed poorer removals than the current study, using additional treatment process steps (i.e., carbon adsorption, filtration) and/or extremely long retention times (i.e., 15 hours) (Harper & Kingham 1992; Wang et al. 2011; Qiao et al. 2012).

There is a general convention that arsenate (As(V))is easier to remove in water and wastewater treatment processes than arsenite (As(III)), therefore requiring oxidation of arsenite prior to coagulation for effective removal (McNeill & Edwards 1997; Hering et al. 1996; Twidwell & McCloskey 2011). Recent research with wider pH ranges and higher initial arsenic concentrations compared to those used in other studies has shown that arsenite and arsenate removal are highly pH dependent, with arsenite being preferentially removed at higher pH and arsenate at lower, indicating differing mechanisms of attachment between the two (Raven et al. 1998; Wang et al. 2000; Goldberg & Johnston 2001; Qiao et al. 2012). Evidence of different mechanisms of arsenic attachment to ferric precipitates at low versus high Fe/As molar ratios has also been found (Jain et al. 1999). As elucidated by Qiao et. al. (2012), arsenite and arsenate removal are highly pH dependent and thus oxidation of arsenite may not be necessary prior to ferric coagulation processes. Most conventional and innovative treatments use oxidation as a pre-treatment to coagulation or adsorption reactions (e.g., Guan et al. 2009; Wang et al. 2011), but oxidant consumption, and thus chemical costs, would be lower if contaminants were maximally removed prior to oxidation in a polishing step, as in the current study. The results of this study show that removal of arsenic to below current treatment standards, even from mine waters comprised of elevated arsenite concentrations, is possible with greatly reduced or even eliminated chemical oxidant doses.

6.5 Conclusions

- Single-stage treatment processes for SMW containing 60 mg As/L using current best available technology (i.e., pre-oxidation with $KMnO_4$ (for As(III) only), $Fe_2(SO_4)_3$ coagulation, and lime precipitation) coupled with ballasted flocculation and sedimentation (which has been shown to get better arsenic removal than traditional sedimentation; Smith & Edwards 2002) were unable to meet proposed future Canadian MMER discharge guidelines (i.e., 0.10 mg As/L).

- SMW with arsenic in the form of arsenite (i.e., As(III)) required higher doses of ferric coagulant and a higher operating pH (i.e., 9.5 vs 5.5) or pre-treatment with chemical oxidation in order to meet similar total arsenic concentrations in clarified water after single-stage treatment of As(V) SMW. This shows that chemical oxidation is not necessarily required as an initial pre-treatment step for arsenic removal if pH and coagulant doses are adjusted accordingly.
- Over 99.99 % of arsenic in As(V) SMW was removed during the two-stage treatment process, resulting in final total arsenic concentrations of 0.004 ± 0.002 mg/L, below the proposed MMER discharge guideline, the current drinking water guideline (i.e., 0.010 mg/L), and the CCME protection of aquatic life guideline (i.e., 0.050 mg/L).
- As(III) SMW treated in Stage 2 with upstream oxidation (5 mg $KMnO_4$/L) or downstream pH adjustment ($9 < pH < 9.5$) was able to surpass the proposed future MMER discharge guideline for arsenic with final concentrations of 0.010 ± 0.008 and 0.037 ± 0.006 mg/L, respectively.
- The coagulation, ballasted flocculation, and sedimentation treatment process evaluated was found to perform better at a colder operating temperature. The lower clarified arsenic concentrations observed at 3 vs 23 °C show that exothermic adsorption mechanisms are a prevalent pathway for arsenic removal from water using ferric coagulation.

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6.7 References

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Chapter 7 Conclusions and Recommendations

7.1 Conclusions

This thesis detailed a comparison of two high-rate mine water treatment processes, HDS and ballasted flocculation, and explored the mechanisms behind the differences and similarities in treatment outcomes between them. The impacts of replacing lime with CKD in these processes on water and sludge quality were also examined. The research presented in this thesis points to the general conclusion that solids loading has the greatest effect on precipitation mechanisms and settled sludge quality in terms of water content. More specific conclusions drawn from the research presented in this thesis are outlined presently.

In Chapter 3, a comparison between the two high-rate processes and conventional active lime treatment found that the ballasted flocculation process resulted in the lowest concentrations of As, Zn, and turbidity in treated effluent, while the HDS process resulted in the lowest sludge volumes per L of treated mine water. Further investigation of the HDS process in Chapter 4 revealed that the significantly lower sludge volumes found with HDS compared to conventional sedimentation and with CKD compared to lime were due to higher solids concentrations during treatment in both cases. The higher solids loading from either sludge recycling or CKD addition both promoted surface precipitation or contaminants and increased compression settling effects, decreasing the water content of the flocs and sludge, respectively. Using CKD in the HDS process was found to reduce final total As concentrations and sludge volumes compared to lime; however, poor coagulation and settling ability of CKD particles and flocs resulted in higher clarified water turbidity in these tests.

Further investigation into the ballasted flocculation process in Chapter 5 showed that clarified water turbidity and Fe concentrations were not affected by ballast type (i.e., microsand, glass beads, or magnetite) or ballast addition at all. It was therefore concluded that the higher flocculation mixing speed used with the ballasted flocculation process, necessary to keep the ballast material suspended during flocculation, was likely the mechanism behind increased contaminant removal found for that process, not the addition of ballast material. Ballast addition did, however, significantly reduce sludge volumes compared to no ballast addition, confirming that solids loading has a significant impact on compression settling. CKD was shown to be able to replace both lime and ballast material in this process without detrimental effects to finished water quality. Turbidity of CKD-ballasted flocculation-treated samples was significantly reduced compared to CKD-HDS treated samples, again likely due to higher flocculation speeds allowing for better flocculation.

Finally, a comparison between single- and two-stage ballasted flocculation processes for the treatment of high-As mine water was outlined in Chapter 6. The ballasted flocculation process was selected based on the outcome of the initial comparison of treatment processes which showed that this process was able to reduce As to lower concentrations than the other processes examined. However, a single-stage oxidation-ferric coagulation-ballasted flocculation process was unable to reduce the 60 mg As/L in the mine water to below the stringent targeted guideline of 0.10 mg/L, even when As was present solely as As(V). The addition of a second ballasted flocculation treatment stage with a small dose of coagulant was able to reduce As concentrations to well below 0.10 mg/L. The pre-oxidation of As(III) was found to be unnecessary if ferric coagulant doses were increased and pH was adjusted to between 9.0 and 9.5. The lower clarified effluent As concentrations observed at 3 versus 23 °C indicate that exothermic adsorption mechanisms are a prevalent pathway for both As(III) and As(V) removal from water when using ferric coagulation.

7.2 Recommendations

Chapter 5 of this thesis showed that both lime and ballast material in the ballasted flocculation process could be replaced with CKD without having an effect on finished water quality. The replacement of lime and ballast material in the ballasted flocculation process with CKD would eliminate the need for microsand recovery using hydrocyclones and allow for higher sludge solids concentrations to be generated during sedimentation. This would reduce both capital costs and sludge dewatering and storage requirements. Pilot-scale testing of CKD in the ballasted flocculation process is therefore recommended. Further investigation into flocculation mixing speed and its relation to contaminant removal should be undertaken to determine the optimum speed to both decreased powere consumption and increase contaminant removal. Further research into reducing turbidity/TSS concentrations when CKD is used in the HDS process, via modifying polymer type and dose or adding coagulant, is also suggested, due to the prevalence of sludge recycling in the wastewater treatment industry. Testing of the sludge produced when lime is replaced with CKD in mine water treatment processes in terms of leaching of regulated metals (i.e., sludge stability) also needs to be undertaken in order to determine appropriate disposal methods.

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