

FEASIBILITY STUDY OF USING CEMENT KILN DUST AS A CHEMICAL  
CONDITIONER IN THE TREATMENT OF ACIDIC MINE EFFLUENT

by

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Submitted in partial fulfilment of the requirements  
for the degree of Master of Applied Science

at

Dalhousie University  
Halifax, Nova Scotia  
July 2010

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DALHOUSIE UNIVERSITY

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DATE: July 23, 2010

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TITLE: Feasibility Study of Using Cement Kiln Dust as a Chemical Conditioner in  
the Treatment of Acidic Mine Effluent

DEPARTMENT OR SCHOOL: Department of Civil and Resource Engineering

DEGREE: MAsc CONVOCATION: October YEAR: 2010

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*I would like to dedicate this thesis to all my friends and family who have been so supportive of me and without whom I would never have been able to complete it.*

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## List of Abbreviations and Symbols Used

AMD	acid mine drainage
ANOVA	analysis of variance
APCD	air pollution control device
ARD	acid rock drainage
ASTM	ASTM International; formerly the American Society for Testing and Materials
CAC	Cement Association of Canada
CKD	cement kiln dust
CaCO <sub>3</sub>	calcium carbonate; calcite; limestone
CaO	calcium oxide; lime
Ca(OH) <sub>2</sub>	calcium hydroxide
Ca(OH) <sub>2(s)</sub>	hydrated lime
ESP	electrostatic precipitator
g CaO/L	weight in equivalent grams of total lime added to one litre
GJ	gigajoule
ICP-OES	inductively coupled plasma-optical emission spectrometry
L	litres
LKD	lime kiln dust
LOI	loss on ignition at 1000 degrees Celsius
mg/L	milligrams per litre
MgCO <sub>3</sub>	magnesium carbonate
MgO	magnesium oxide; magnesia
mL	millilitres
PCA	Portland Cement Association

rpm	revolutions per minute
SEM	scanning electron micrograph/microscope
SI	The International System of Units
SSA	specific surface area
TRO	total reactive oxides; $TRO = [(CaO + MgO) - LOI] + (Na_2O + K_2O)$
TSS	total suspended solids
USEPA	United States Environmental Protection Agency
v/v	volume per volume
w/w	weight per weight
μm	micrometres

## Glossary

<b>Acid Rock Drainage</b>	Ground or surface water that has come into contact with sulphide minerals which introduce acidity and dissolved metals into the water (also termed acid mine drainage or AMD).
<b>Acid Mine Drainage</b>	see <b>Acid Rock Drainage</b>
<b>Available Lime</b>	see <b>Free Lime</b>
<b>Biosolids</b>	Solid material produced from treatment of municipal or commercial wastewater (i.e. sewage).
<b>Calcium Hydroxide</b>	Product of the hydration of lime; $\text{Ca(OH)}_2$ .
<b>Clinker</b>	Solid nodules of material generated in a cement kiln that are further ground to produce cement.
<b>Dolomitic Limestone</b>	Limestone with high magnesium content.
<b>Floc</b>	Aggregated precipitated particles formed during water and wastewater treatment.
<b>Free Lime</b>	The amount of material (i.e. $\text{CaO}$ ) in a sample that is available to react in solution.
<b>Lime</b>	Calcium oxide ( $\text{CaO}$ ).
<b>Milli-Q</b>	A system manufactured by Millipore that produces filtered and deionized water.
<b>Mine Water</b>	see <b>Acid Rock Drainage</b>
<b>Monofill</b>	A landfill where only one type of waste is disposed.
<b>Quicklime</b>	Product of the calcination of limestone, usually having a lime content of greater than 90 %.
<b>Slaker</b>	Specialized equipment for mixing quicklime with water to create a calcium hydroxide ( $\text{Ca(OH)}_2$ ) slurry.

## **Acknowledgements**

Firstly I would like to thank my supervisor, Dr. Margaret Walsh, for encouraging me to pursue graduate studies and allowing me to accomplish more than I had ever envisioned. Without her knowledge, confidence, and continued support I would not have been able to complete this project.

The Natural Sciences and Engineering Research Council of Canada (NSERC), the Portland Cement Association (PCA), and the Cement Association of Canada (CAC) have all provided funding that has allowed me to complete this project. Cemex, Holcim, LaFarge North America, and Ash Grove Cement all provided samples of cement kiln dust for testing. Chris Petrie's knowledge and assistance with mine water sampling was also invaluable to this project. Heather Daurie, Brian Kennedy, Brian Liekens, and Blair Nickerson have all contributed their knowledge and assistance with equipment, materials, and testing related to this study. Both Simon Boilard and Heather Farmer assisted greatly with laboratory work during this study. Catherine LeBlanc provided me with the basis to begin this project, and also helped me adjust to graduate student life smoothly.

My gratitude for the assistance of both Shelley Parker and Tanya Timmins cannot be suitably expressed here. They have continually shown genuine interest and concern and have also been invaluable in supporting me throughout my studies.

I would also like to acknowledge George Manley, without whom I would never have entered into the engineering field.

Finally, I would like to thank my parents, Thomas and Lucille Mackie, for their constant support and encouragement throughout my studies.



## Abstract

Water contaminated due to mining activities is often acidic and can contain high concentrations of dissolved metals. This mine water, or acid rock drainage, is most commonly treated in an active lime treatment plant, where quicklime is slaked with water to produce a calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) slurry that is used to neutralize the mine water and precipitate metals which can then be removed through sedimentation. Cement kiln dust (CKD) is a fine-grained, alkaline material that is generated as a by-product of cement production. Its high lime ( $\text{CaO}$ ) content makes it attractive as a substitute for quicklime in the generation of  $\text{Ca}(\text{OH})_2$  slurries for the treatment of mine water.

The first part of this study analyzed six CKD samples for several physical and chemical properties to determine their variability and to compare them to the characterization of a commercial quicklime sample. The CKDs samples were found to have smaller particle size distributions and larger surface areas than the quicklime sample. The main characteristic affecting the reactivity of CKD was found to be its free lime and reactive oxides content. The CKD samples with high free lime content (i.e. 34 and 37 % free  $\text{CaO}$ ) performed similarly to quicklime, which was found to have a free lime content of 87 %, in terms of pH achieved in slaking experiments.

Neutralization and precipitation experiments using acidic mine water containing high concentrations of zinc and iron determined that all slaked CKD slurries performed comparably to the quicklime slurry in terms of precipitation of soluble metals. However, additional material was required to be added in order to neutralize mine water to the target pH of 9.5 the lower the free lime and reactive oxides content of the CKD. Bench-scale settling experiments showed that all CKD-generated slurries were able to remove precipitated metals comparably to the quicklime-generated slurry, though the CKDs with low free lime content resulted in higher concentrations of particles and total suspended solids (TSS) in settled, treated mine water. All CKD slurry-treated mine water samples generated lower volumes of sludge after settling than those treated with quicklime slurry, even with the increased product addition required for treatment. Increasing the settling time or polymer dose in mine water samples treated with a low free lime CKD-generated slurry resulted in TSS concentrations comparable to samples treated with quicklime slurry, and also resulted in a further reduction of total metals.

The results of this research show that CKD can be effectively used to neutralize mine water and precipitate and remove dissolved metals. In addition, using CKD in lieu of quicklime could result in reduced sludge volumes which show the potential for increased dewaterability. Further testing of the impacts of CKD treatment on sludge characteristics as well as pilot scale testing should be conducted.

## Chapter 1: Introduction

Cement kiln dust (CKD) is a fine-grained alkaline material that is a by-product of cement clinker production. Cement is produced by introducing raw materials into a kiln where they are heated to a maximum temperature of approximately 1500 °C in order to change their chemical makeup. The main ingredient in cement is limestone which, along with a silica source (e.g. sand or clay), an alumina source, and an iron source (e.g. mill scale), is crushed and then introduced into a kiln, where it is heated. This transforms the raw materials into clinker, which is mainly comprised of calcium silicates and calcium aluminates. The clinker is then further processed by grinding with the addition of a small quantity of gypsum to create cement (Kosmatka et al., 2002).

Cement clinker production requires a great deal of energy. In Canada, it has been estimated that an average of 3.70 gigajoules (GJ) is required to produce each tonne of clinker (CAC, 2010a). Globally, this figure is 4.4 GJ (IEA, 2007), which is more than the amount of energy released in the detonation of one tonne of TNT. This energy is primarily needed to heat the raw materials in order to transform them chemically through the calcination process. Clinker production also releases large amounts of carbon dioxide (CO<sub>2</sub>) into the atmosphere. It has been estimated that an average of 0.83 tonnes of CO<sub>2</sub> are released for each tonne of cement produced globally (IEA, 2007). In Canada, approximately 732 kg of CO<sub>2</sub> are released per tonne of cement (CAC, 2010a). Roughly 40 % of these emissions come from the fuels that are burned to heat the raw materials and 60 % from the release of CO<sub>2</sub> from limestone during calcination. Fossil fuel consumption and industrial processes related to cement production (e.g. calcination, material extraction) account for 3 to 4 % of global CO<sub>2</sub> emissions (Raupach et al., 2007; IEA, 2007).

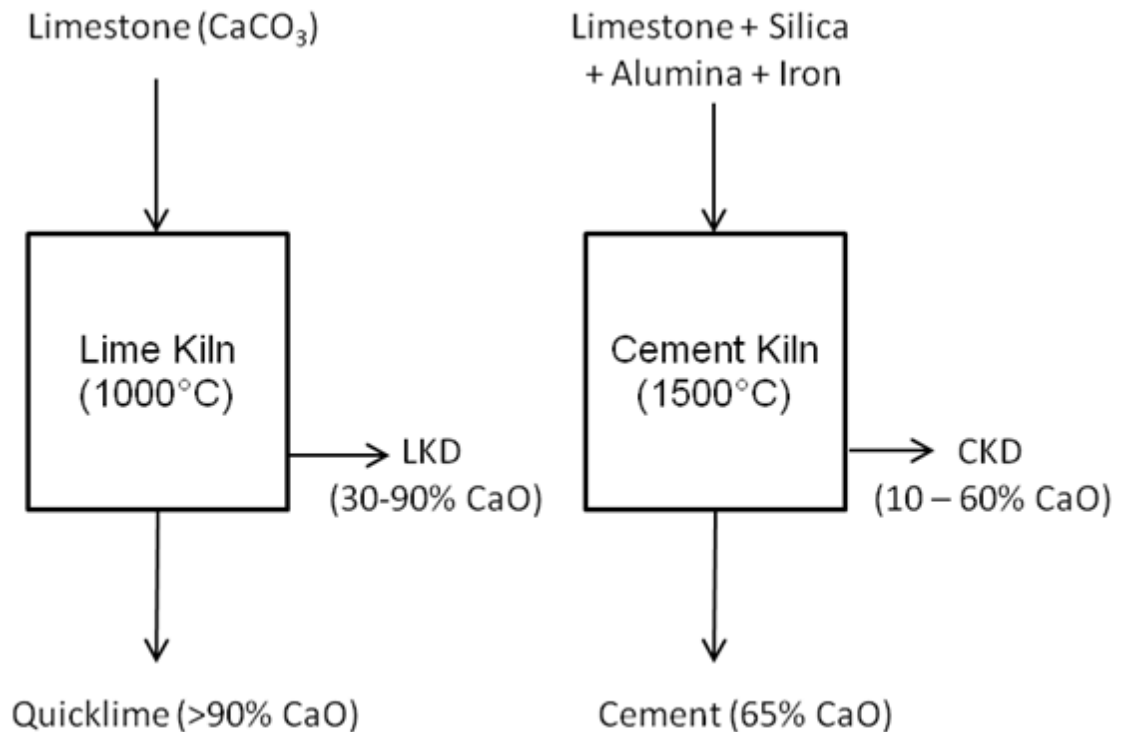
The introduction of alternative materials as raw feed for clinker production (e.g. blast furnace slag), as well as increased blending of finished cement with alternative materials (e.g. fly ash), has led to a decrease in energy consumption and CO<sub>2</sub> production (CAC, 2010a; IEA, 2007), however this can only go so far without affecting cement quality. The energy and emissions associated with cement production are also associated with CKD generation, for which at the moment there are few alternatives to land disposal

(Adaska & Taubert, 2008; Bhatta, 1995; Klemm, 1993). Finding additional alternative uses for this waste material will ensure that less of this energy is wasted and that less CKD ends up in landfills.

Mining is highly destructive to the environment, but also highly necessary to our civilization. We require metals and minerals to build our cities and towns, and to keep us connected on a global scale. Many mined materials can be reused and recycled, aluminum being an excellent example. However recycling cannot fulfill our constant demand for more and better products, or fuel our exponential growth and development. Therefore we must strive to make the extraction of minerals have the least impact possible on the natural ecosystems that contain them. Preventing contamination of water at mining operations would obviously be ideal, and in many cases is more cost effective than treating it after the contamination has occurred. The release of acidity and dissolved metals due to weathering of exposed sulphidic deposits, waste rock, and tailings is difficult to estimate and can continue for hundreds of years after mining has ceased (Lottermoser, 2007; Brown et al., 2002; Younger et al., 2002). There are many ways to treat acidic mine water, also termed acid rock drainage (ARD) or acid mine drainage (AMD), both passively and actively. However, due to the tried and true nature of active chemical treatment with quicklime, the ability of this treatment process to deal effectively with and respond quickly to changes in contaminated water quality and flow rates, and its comparatively low costs, it is and will be the main choice for dealing with these types of effluents for many years to come (Younger et al., 2002; Coulton et al., 2003a).

Quicklime is an alkaline product used in a variety of environmental and industrial applications in addition to mine water treatment. It is produced similarly to cement, by heating limestone in a kiln. The extraction of limestone and subsequent calcining process to make quicklime are destructive, energy intensive, and release greenhouse gases (e.g. CO<sub>2</sub>) into the atmosphere. The calcium carbonate (CaCO<sub>3</sub>) content present in a high-calcium limestone is converted into calcium oxide (CaO) during calcination to release carbon dioxide (CO<sub>2</sub>) (Boynton, 1980), as with cement production. Figure 1.1 illustrates the similarities and differences between the two processes, the main differences being lower kiln temperatures for lime production, and additional raw materials for cement

production. Producing quicklime also generates a byproduct called lime kiln dust (LKD), which is fine grained, like CKD, but generally has a higher lime content (Boynton, 1980). The production of magnesium oxide (MgO) can also occur during calcination if processing a dolomitic limestone that, by definition, contains 35 to 46 % magnesium carbonate ( $MgCO_3$ ). CaO and MgO are the main active ingredients in quicklime, and together make up over 90 % of the material (ASTM, 2006; Boynton, 1980).



**Figure 1.1: Comparison of the production of quicklime and cement clinker.**

The experiments and analyses performed as part of this research study were founded on the hypothesis that CKD can be used to effectively replace quicklime in the production of calcium hydroxide ( $Ca(OH)_2$ ) slurries for the active treatment of mine water to remove acidity and soluble metals. This hypothesis was based on the similarities in production and raw materials characteristics (i.e. limestone) between quicklime and cement, and thus CKD.

## **1.1 Objectives**

The main hypothesis of this research was tested using the following sub-objectives:

- to determine the physical and chemical characteristics of several CKD samples and compare to those of quicklime;
- to evaluate and compare the acid neutralization and metal precipitation capacity of calcium hydroxide slurries generated using CKD and quicklime; and
- to determine settled water quality of mine water treated with CKD-generated calcium hydroxide slurries compared to quicklime slurry treatment under variable mixing conditions, slurry concentrations, and polymer doses.

## **1.2 Thesis Organization**

Following this introduction, Chapter 2 focuses on a review of the background and relevant literature involving cement kiln dust and mine wastewater generation and treatment. A brief review of current regulations regarding CKD disposal and mine effluent discharge is also included. Chapter 3 contains a description of the materials and methods used in this study. Chapter 4 presents and discusses the results of a CKD characterization study undertaken to determine the similarities and differences in physical and chemical properties of several CKD samples and a commercial quicklime sample. Chapters 5 and 6 present the results of a bench-scale mine water treatment study. Chapter 5 discusses the acid neutralization and metals precipitation capacity of CKD versus quicklime; Chapter 6 discusses the final treated mine water quality and effects of several operating parameters on final treated effluent quality. Chapter 7 summarizes the conclusions of the study and presents recommendations for future research.

## **1.3 Originality of Research**

Previous studies have focused on the reuse of CKD in its solid, unhydrated form (Peethamparan et al., 2008; Sreekrishnavilasam et al., 2006; Miller & Zaman, 2000), or on removing various metals from synthetic solutions in small lab-scale trials (Zaki et al., 2007; Pigaga et al., 2005; El-Awady & Sami, 1997). The current study attempts to simulate the active treatment of actual mine water as closely as possible at the bench

scale. Previous studies regarding metal removal focused on one CKD sample, while this study looks at multiple CKDs from various cement plants, allowing for the determination of any relationships between CKD physicochemical properties and the level of treatment achieved.

This research is valuable in evaluating a possible alternative to quicklime in the treatment of acidic and metal contaminated effluents such as ARD. Using CKD to replace or supplement quicklime in an active lime treatment plant would reduce the need to extract and process raw materials, and reduce chemical costs. It would also ensure that the energy and materials that go into generating CKD are not wasted. In addition, this would open up a new avenue for the reuse of CKD, further diverting waste from landfills and on-site storage facilities currently used by the cement manufacturing industry. The results of this research can also be potentially applied to investigations into other environmental treatment applications where quicklime or other alkaline materials are currently used, and for treating other acidic and metal-contaminated effluents.

## **Chapter 2: Literature Review**

A comprehensive literature review was conducted in order to gather background information on the production, properties, and current management practices of both cement kiln dust (CKD) and mine water. Relevant regulations were also investigated concerning the disposal and discharge of both CKD and mine effluent. A brief summary of relevant studies concerning metal removal with CKD is also included.

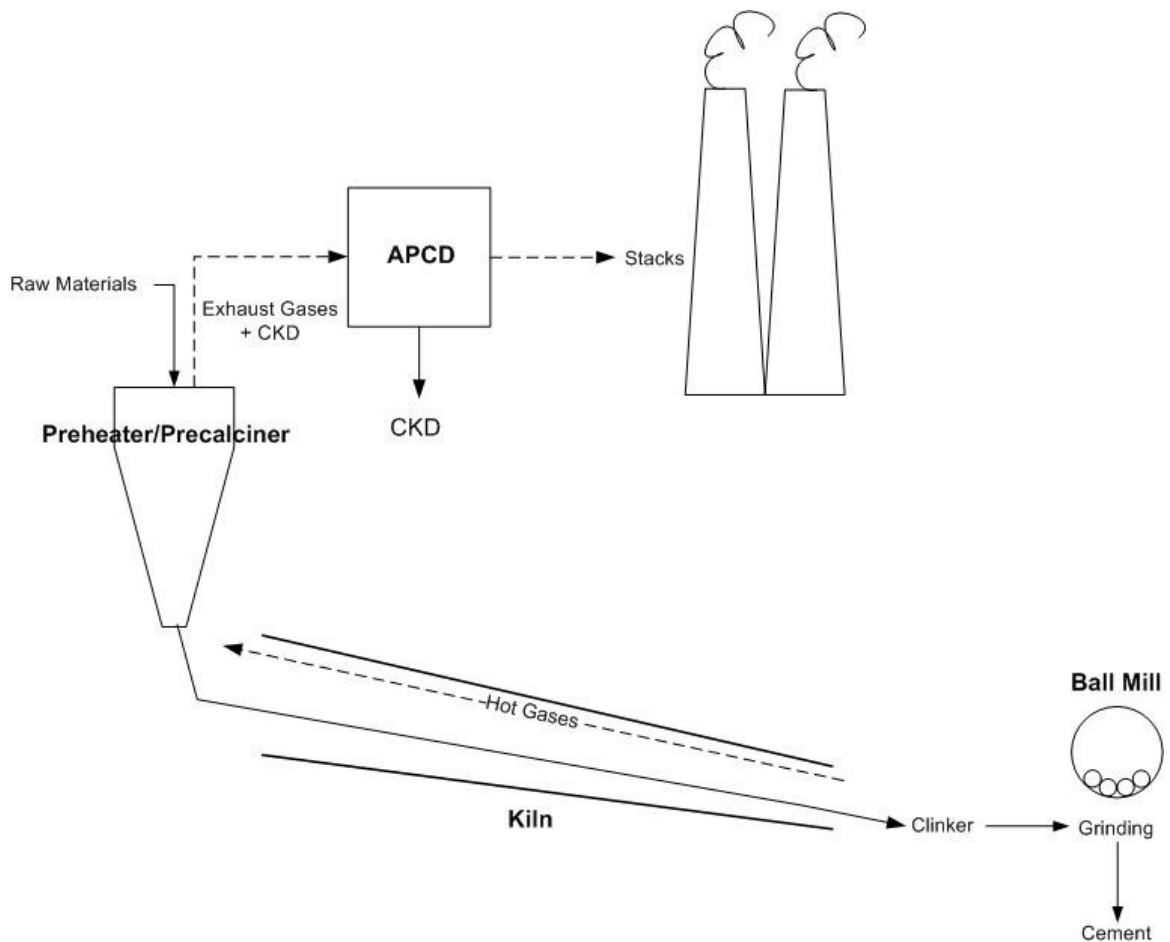
### **2.1 Cement Kiln Dust**

#### **2.1.1 Production and Characteristics**

Worldwide cement production has increased from approximately 2.5 billion tonnes in 2006 to 2.8 billion tonnes in 2009, with most of that production increase occurring in China (Oss, 2010). The same period showed a decrease in cement production in the United States from approximately 100 million tonnes to 72 million tonnes (Adaska & Taubert, 2008; PCA, 2009a; Oss, 2010). The most recent data from the Cement Association of Canada (CAC, 2010a) reports that 15 million tonnes of cement were produced by its member companies in 2008. The generation of CKD, a by-product of cement manufacturing, has been estimated to be 15 to 20 % of clinker production (USEPA, 1993), which would put worldwide CKD generation at an estimated 420 to 560 million tonnes for 2009, and American (US) production at 10 to 15 million tonnes.

Cement is produced by heating raw materials in a kiln, as shown in Figure 2.1. Cement and CKD properties vary from plant to plant, due to kiln type and process differences as well as variations in raw materials and fuel sources (Klemm, 1993; Siddique, 2008; USEPA, 1993). There are several types of cement kilns, which can be defined in a number of ways. Wet process kilns are fed raw materials in a slurry form, and dry process kilns are fed raw materials in granular form. Kilns can also be long (length/diameter  $\cong$  30) or short ( $L/D \cong$  10 to 15), and may include a preheater or precalciner (Bye, 1999). Preheaters and precalciners can reduce power consumption since they use excess hot gases from the kiln to raise the temperature of the kiln feed (preheater) or start the calcination process (precalciner).

CKD has basically the same properties as cement clinker, though it is the fine-grained portion that is captured in the air pollution control devices (APCDs) of cement kilns (see Figure 2.1). Baghouses and electrostatic precipitators (ESPs) are examples of APCDs that trap particulates prior to emission of gases from the kiln through smokestacks. In modern cement kilns, most of the CKD trapped by these devices is returned to the head of the kiln to be used as raw feed; an estimated 64 % in 1990 according to the USEPA (1993). However, due to cement quality specifications and the potential for a reduction in the effectiveness of air pollution control devices and damage to kilns, not all CKD can be recycled in this fashion (USEPA, 1993). Alkalis and chlorides are the main concern.



**Figure 2.1: Schematic of generalized cement production process.**

Numerous studies have characterized the chemical and, less often, physical properties of CKD samples from around the world (Peethamparan et al., 2008; Zaki et al.,



2007; Peethamparan, 2006; Sreekrishnavilasam et al., 2006; Pigaga et al., 2005; Duchesne & Reardon, 1998; El-Awady & Sami, 1997; Bhatta & Todres, 1996; Todres et al., 1992; Collins & Emery, 1983; Haynes & Kramer, 1982). Though CKD chemical makeup varies substantially, its main component is calcium, which is largely in the form of calcium carbonate (calcite,  $\text{CaCO}_3$ ), calcium sulphate (anhydrite,  $\text{CaSO}_4$ ), and calcium oxide (free lime,  $\text{CaO}$ ) (Peethamparan et al., 2008; Duchesne & Reardon, 1998; Haynes and Kramer, 1982). Quartz ( $\text{SiO}_2$ ), arcanite ( $\text{K}_2\text{SO}_4$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) can also be present, along with trace oxides of Al, Fe, Na, Mg, Ti, and others. Calcium oxide, also termed free lime or available lime, reacts with water to form calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), making CKD an alkaline or caustic material. The amount of free lime and other soluble oxides (e.g.  $\text{Na}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ) varies widely between CKDs, making some more reactive than others. The pH of aqueous CKD solutions, or slurries, is usually around 12 (Siddique, 2006; Collins & Emery, 1983). CKD also contains minute amounts of trace metals such as arsenic, barium, lead, and zinc, totalling less than 0.05 % by weight (Siddique, 2006; Klemm, 1993). Physically, CKD is fine-grained with a mean particle size between 1 and 100  $\mu\text{m}$ , and surface areas in the range of 0.24 to 1.39  $\text{m}^2/\text{g}$ , as measured by the Blaine method (Peethamparan, 2006; Sreekrishnavilasam et al., 2006; Collins & Emery, 1983). The specific gravity of CKD samples has been reported to be in the range of 2.48 to 2.96 (Peethamparan, 2006; Collins & Emery, 1983).

### 2.1.2 Current Management Practices

Historically, CKD has been disposed of in waste piles or landfills with little regard for the effects that this highly alkaline and reactive material can have on the environment. Due to its alkaline nature, leachate from CKD has an extremely high pH (e.g. 11 to 13) which can cause numerous detrimental effects to the receiving environment (USEPA, 1993). Trace metals in CKD can also potentially leach from CKD disposal sites and cause deleterious environmental effects (Duchesne & Reardon, 1998; USEPA, 1993). In addition, the small particles of CKD can easily become airborne and inhaled or deposited elsewhere, potentially contaminating crops with dioxins (USEPA, 1993). In the United States, CKD is classified as a special waste under Subtitle C of the Resource Conservation and Recovery Act (RCRA), and is therefore not subject to federal

hazardous waste regulations (USEPA, 1993). In 1999, the United States Environmental Protection Agency (USEPA) proposed a set of regulations specific to CKD that would keep it off the hazardous waste list as long as it is managed effectively (USEPA, 1999). The USEPA's proposed rule includes standards for landfill placement and design to control the potential release of alkalinity and heavy metals to the environment through leaching and runoff, and to control airborne particle release through covers. It also includes guidelines for continued monitoring. To date, no further action has been taken on implementing this proposed rule (USEPA, 2008a; Adaska & Taubert, 2008). According to the Portland Cement Association (PCA, 2009b), “[f]or those cement plants who use CKD monofills, proper management and closure of them is an integral part of their operations.” In Canada, industrial solid and hazardous waste disposal is regulated at the provincial level. There are no disposal regulations specific to CKD, however monofill or waste pile designs must be approved by the relevant agency.

Modern cement kilns recycle the majority of CKD produced in the United States. A PCA member company survey reported that in 2006, 1.16 million tonnes of CKD was used beneficially off site, while 1.40 million tonnes was landfilled. A further 0.26 million tonnes was reclaimed from landfills, mostly for use as kiln feed (Adaska & Taubert, 2008). There are no available data on the amount of CKD recycled into the kiln feed for this period; however, according to the USEPA (1993), approximately 65% of CKD produced in the US in 1990 was recycled to the head of the cement kiln. Using the estimate that puts CKD production at 15 to 20 % of clinker production (USEPA, 1993). The 99.8 million tonnes of cement produced in the US in 2006 (Adaska & Taubert, 2008) would have generated 15 to 20 million tonnes of CKD, with 10 to 13 million tonnes (65 %) being recycled into the kiln. Though the amount of CKD that is reused beneficially has increased by over 35 % over the past 20 years and landfilling decreased by 50 %, there is still a large amount of kiln dust waste generated (Adaska & Taubert, 2008). It can only be assumed that this estimate on CKD waste generation requiring disposal is higher in countries with older cement kilns that are unable to recycle CKD within the kiln.

There are several current reuse options for fresh and even some landfilled CKD in addition to recycling into the cement kiln, all taking advantage of its alkaline properties

(i.e. lime content). CKD can be used in blended cement products, concrete, and for soil stabilization (Peethamparan et al., 2008; Siddique, 2006). The high lime and potassium content of CKD lends well to its use as a fertilizer, either alone or after it has been used to pasteurize municipal biosolids (i.e. N-Viro process) (Adaska & Taubert, 2008; Christie et al., 2001; Bhatta, 1995; Klemm, 1993). CKD has also been used in the solidification and stabilization of hazardous wastes along with various other applications (Adaska & Taubert, 2008; Siddique, 2006; Bhatta, 1995; Klemm, 1993).

## **2.2 Mine Water**

Mine water, for the purposes of this thesis, is defined as any liquid that is discharged from a mine site, due to either mining activities or natural flows, which has become contaminated due to contact with material exposed from mining activities. This review will be focused on effluent from ferrous- and base-metal mines. Mine water can be acidic and have high amounts of dissolved metals, sulphate, and suspended particles (Lottermoser, 2007; Brown et al., 2002). With many mines, this is due to the sulphide formations that the target metals are contained within. This type of effluent is termed acid rock drainage (ARD) or acid mine drainage (AMD). ARD is formed when sulphide minerals in rocks are exposed to oxygen and water, the two components necessary to the formation of ARD (Kuyucak, 2001). Weathering of sulphide minerals can also occur naturally or due to construction activities not related to mining, making the term acid mine drainage somewhat misleading. ARD can be much cheaper to prevent than to treat; generation of ARD can continue for hundreds or even thousands of years (Lottermoser, 2007; Kalin et al., 2006; Brown et al., 2002; Younger et al., 2002).

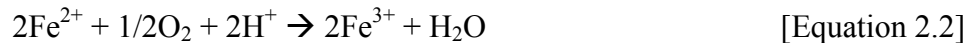
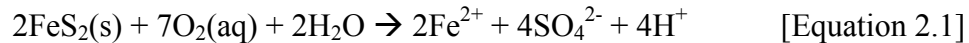
### **2.2.1 Acid Rock Drainage Generation and Characteristics**

Base metals that are of value to our economy (e.g. zinc and lead) naturally occur in the form of minerals which are found in rocks that can contain anywhere from less than one part per million (e.g. gold) to a few percent by weight (e.g. nickel and zinc) (Xstrata, 2009). These ore deposits can be located anywhere from one to over several hundred metres below Earth's surface, leaving more than an estimated 70 % of the material extracted during mining activities as waste. This waste comes mainly from surface mines that must strip off unwanted soil and rock (overburden) to get at the ores.

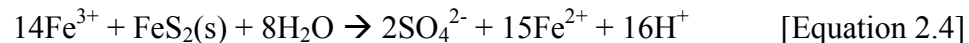
Underground mining is much more efficient in this aspect, though underground mines make up less than 20 % of mines around the world (Younger et al., 2002).

Metal deposits are found mainly in the form of minerals like pyrite (FeS<sub>2</sub>), sphalerite (ZnS), and other sulphides, which, in addition to other sulphide-containing deposits like coal seams, will generate ARD when exposed to both water and oxygen (Johnson & Hallberg, 2005; Younger et al., 2002; Kuyucak, 2001). Though this release of contaminants is caused by natural weathering processes, mining activities serve to expose these formations to oxygen and thus start or speed the generation of ARD (Ríos et al., 2008). Waste rock piles, drainage from underground mines, and runoff from open pit mines are all sources of water contamination from mining activities (Akcil & Koldas, 2006; Brown et al., 2002; Kuyucak, 2001). Sulphide minerals can also be subject to weathering due to naturally occurring surface formations or construction activities that expose sulphidic bedrock.

Equation 2.1 shows the generation of soluble ferrous iron, sulphate, and acidity from the weathering of pyrite. With sufficient oxygen available, ferrous iron (Fe<sup>2+</sup>) will oxidize to ferric iron (Fe<sup>3+</sup>), which consumes acidity following Equation 2.2.



Equation 2.2 represents the slowest reaction in this sequence. Ferric iron can then generate much greater acidity much more quickly by reacting with water (Eq. 2.3) or pyrite (Eq. 2.4) (Brown et al., 2002).



Sphalerite (ZnS) releases soluble zinc ions and sulphate upon contact with dissolved oxygen following the reaction in Equation 2.5, which can also be applied to other metal sulphides (Younger et al., 2002).



Water that comes into contact with these minerals that have been exposed due to mining activities becomes contaminated with sulphate, soluble metals, and acidity. Bacterial activity also plays a role in speeding up acid generation (Akcil & Koldas, 2006; Younger et al., 2002). Mine water characteristics will vary widely based on the type of mine, the distribution of minerals in the ore, and the rate of weathering (Akcil & Koldas, 2006; Kuyucak, 2001). Discharges sampled from pyrite and lead/copper/zinc mines had pH values in the range of 2.5 to 3.0, sulphate concentrations of 441 to 5110 mg/L, aluminum of 13.9 to 128 mg/L, zinc of 1.4 to 978 mg/L, and iron in the pyrite mine was measured at 1460 mg/L (Banks et al., 1997). A different sample from discharge at a copper/lead/zinc mine had a pH less than 2, a lead concentration just above 2 ppm, copper just above 30 ppm, arsenic just under 5, zinc between 7 and 80, iron between 1300 and 1400, and chromium and nickel both under 0.1 ppm (Ríos et al., 2008). These contaminated waters, if allowed to be discharged into the environment, can cause many detrimental environmental effects (Johnson & Hallberg, 2005). Dissolved metals may precipitate once in the aquatic environment due to changes in solubility with pH, coating receiving waterways with metal hydroxides and ochre from precipitating iron. This can be seen in Figure 2.2.

In addition to being unpleasing aesthetically, elevated concentrations of metal precipitates will coat benthic organisms and fish gills, smothering them (Brown et al., 2002). Metals like copper, iron, lead, and zinc, among others, are toxic to aquatic species in their bioavailable form, often replacing necessary ions in biomolecules (i.e. enzymes). Suspended and dissolved solids in mine water can also interfere with natural ecosystems by increasing turbidity and reducing light penetration (Brown et al., 2002; CCME, 1987). Contaminants released into the environment from water generated in mining operations can also affect anthropogenic activities that involve water use downstream of mining activities, as well as commercial and recreational fishing and other water-based activities.

### 2.2.2 Mine Water Treatment Options

Remediation of mine water falls into two main categories: passive and active treatment. Passive treatment involves no added mechanical energy and relies on the gravitational flow of contaminated water through the treatment media for contaminant



**Figure 2.2: Acid mine drainage (June 25, 2008; photo taken by author).**

removal. Active treatment of mine water requires the addition of mechanical energy along with chemicals for contaminant removal (Johnson & Hallberg, 2005; Brown et al., 2002; Younger et al., 2002). The main type of active treatment of ARD involves quicklime addition in a treatment plant and subsequent precipitation and removal (through settling) of contaminants (Akcil & Koldas, 2006; Coulton et al., 2003a; Kuyucak, 2001). Both active and passive treatment, when forming metal hydroxides for removal, will result in the generation of sludge which must be disposed of properly.

#### *2.2.2.1 Passive Treatment*

Passive treatment takes advantage of natural attenuation processes to treat mine water. It uses naturally available energy and requires only infrequent maintenance over the lifetime of the design. Wetlands, limestone drains, and bioreactors are examples of passive treatment systems. The advantages of using passive treatment include low

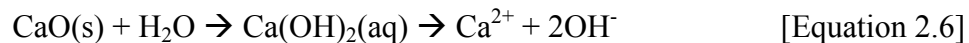
operating costs and aesthetics, while disadvantages include the large land area required and the inability to adapt to fluctuations in contaminant loading rates (Johnson & Hallberg, 2005; Younger et al., 2002).

#### 2.2.2.2 *Active Treatment*

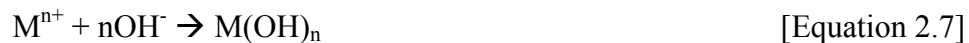
Active treatment of contaminated mine water includes all processes that are not passive treatment processes. It is the remediation of polluted water using treatments that involve the addition of energy and/or chemicals from outside the system. Most active treatment involves the use of oxidation, alkaline addition, and sedimentation to reduce acidity and precipitate and remove dissolved metals (Younger et al., 2002). The main advantages of active treatment are the smaller footprint of treatment systems when compared to passive treatment (i.e. wetlands) and the ability to respond quickly to variations in flow rates and contaminant loads. Active treatment systems are also well studied compared to the relatively recently developed passive treatment options (Younger et al., 2002; Brown et al., 2002). However, chemical costs for active treatment systems can be prohibitive (Johnson & Hallberg, 2005).

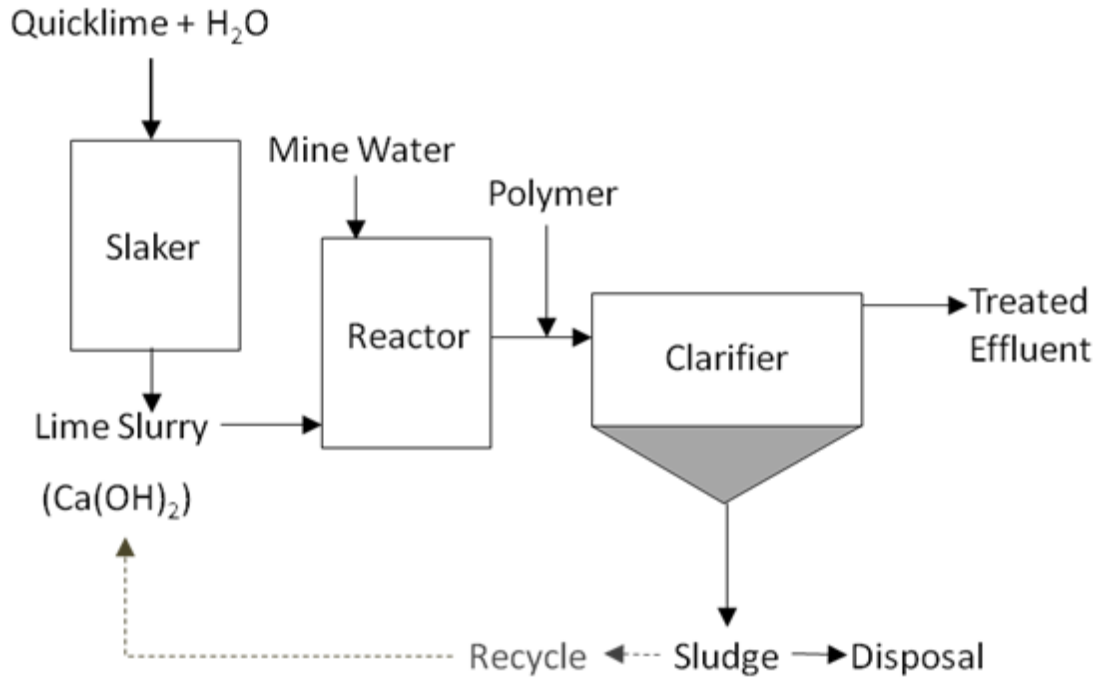
Active lime treatment plants utilize quicklime or hydrated lime as an alkaline reagent to raise the pH of mine water and thus precipitate metals. Shown in Figure 2.3 is a schematic of a typical active lime treatment plant. Process steps will vary from plant to plant.

In a lime treatment plant, quicklime is mixed with water in a slaker, hydrating the quicklime (CaO) to calcium hydroxide (Ca(OH)<sub>2</sub>), which then dissociates into hydroxide and calcium ions as shown in Equation 2.6.



This slurry is then mixed with the mine water in a reactor tank, where hydroxide ions combine with dissolved metal ions to form solid metal hydroxides following Equation 2.7, where n represents the valence of the metal species, M (e.g. 2+).



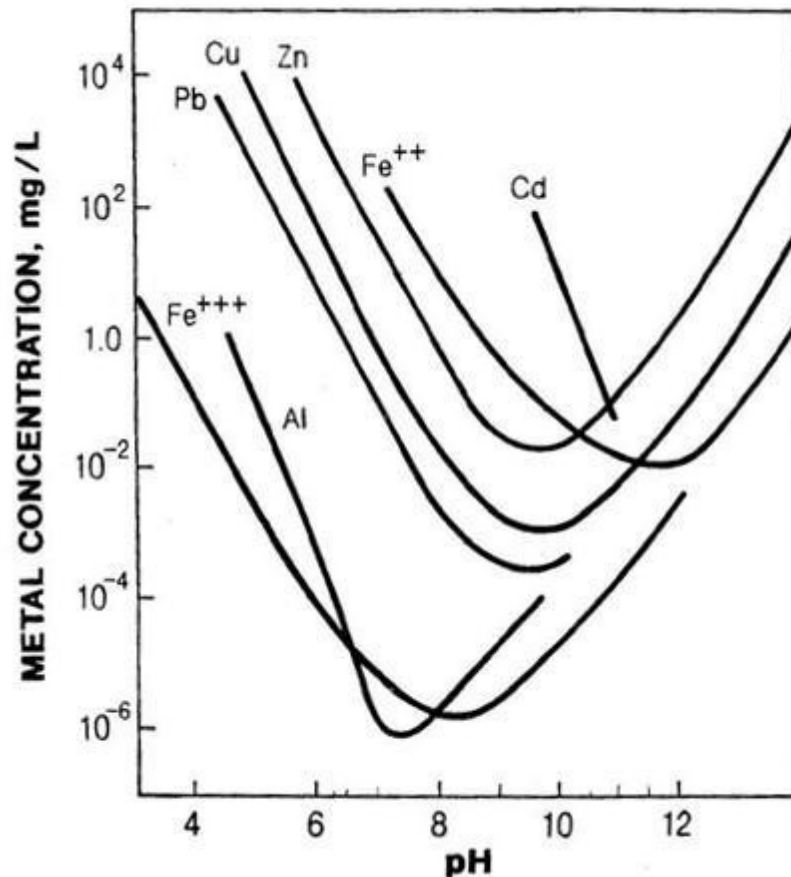


**Figure 2.3: Typical active lime treatment plant.**

These reactions are obviously pH dependent. Metals form their hydroxides at varying pH values; solubility profiles for several metals are shown in Figure 2.4. In order to target a specific metal for removal, different precipitation pH values would be required. A pH above 9.0 or 9.5 is generally considered to be effective for the removal of zinc, and potentially for cadmium, copper, manganese, and magnesium (Kurniawan et al., 2006; Charerntanyarak, 1999; Zinck and Aubé, 1999; Huck & LeClair, 1978; Huck, Murphy, Reed & LeClair, 1977).

A polymer is usually added at this point to increase floc size and speed up settling (Huck, Murphy, & LeClair, 1977). Treated water is then sent to either a clarifier or settling pond to allow particulates to settle out, resulting in a low-density sludge that contains 2 to 5 % solids (Aubé & Zinck, 1999; Brown et al., 2002). In plants that use some form of the high density sludge (HDS) process, 10 to 90 % of the sludge is returned to the slaker or mixed with the mine water coming into the treatment plant prior to fresh lime addition. The HDS process has been shown to increase sludge density to 30 % or more (Aubé & Zinck, 1999).





**Figure 2.4: Solubility profiles of several metals (Aubé and Zinck, 2003).**

### 2.2.3 Mine Water Discharge Regulations

Mine water, as outlined above, can contain harmful acidity and dissolved metals in toxic quantities. Regulations exist in order to protect the natural environment as well as human and non-human animal life and industries such as commercial fishing. Unfortunately, many countries in the world have inadequate or are completely lacking regulations to protect people and the environment from the detrimental effects of mining activities, or are unable to enforce them (Brown et al., 2002). There are also a vast number of abandoned mines worldwide whose historical and continued contamination of the surrounding environment is mostly allowed to continue unchecked. Governments in North America and the European Union, among others, are slowly implementing legislation to ensure that this contamination is dealt with (Brown et al., 2002).

### 2.2.3.1 Canada

In Canada, discharge of effluent from metal mines is regulated under the Fisheries Act. The Metal Mining Effluent Regulations (MMER) apply to both operating mines and closed mines, as long as they had not been closed prior to the registration date of the regulations (MMER, 2002). Though not the point of this review, it should be noted that the maximum concentrations of deleterious substances as laid out by the MMER were set in 1977 with the implementation of the Metal Mining Liquid Effluent Regulations (MMLER) and were not modified with the update of the regulations in 2002. In addition to the maximum total concentrations allowable for deleterious substances listed in Table 2.1, the pH of effluent must be between 6.5 and 9.5, and it must not be acutely toxic to aquatic species, namely rainbow trout (MMER, 2002).

**Table 2.1: Maximum limits for contaminants in mine discharges as regulated under the Canadian Fisheries Act (MMER, 2002).**

<b>Parameter</b>	<b>Maximum Authorized Monthly Mean Concentration</b>	<b>Maximum Authorized Concentration in a Composite Sample</b>	<b>Maximum Authorized Concentration in a Grab Sample</b>
Arsenic	0.50 mg/L	0.75 mg/L	1.00 mg/L
Copper	0.30 mg/L	0.45 mg/L	0.60 mg/L
Cyanide	1.00 mg/L	1.50 mg/L	2.00 mg/L
Lead	0.20 mg/L	0.30 mg/L	0.40 mg/L
Nickel	0.50 mg/L	0.75 mg/L	1.00 mg/L
Zinc	0.50 mg/L	0.75 mg/L	1.00 mg/L
Total Suspended Solids	15.00 mg/L	22.50 mg/L	30.00 mg/L
Radium 226	0.37 Bq/L <sup>a</sup>	0.74 Bq/L	1.11 Bq/L

<sup>a</sup>Becquerels are the SI units of radioactivity.

The Canadian Council of Ministers of the Environment (CCME) produces the Canadian Environmental Quality Guidelines (CEQG), which are objectives for maintaining the quality of the air, land, and water (CCME, 2010). The guidelines are based on the best available scientific information about the effects of these substances on the receiving ecosystems. Within the CEQG, the Canadian Water Quality Guidelines for the Protection of Aquatic Life sets limits on the concentrations of deleterious substances that can be discharged to a freshwater or marine aquatic habitat. These are guidelines only (i.e. they are not enforceable) and are included here solely in order to contrast with

the MMER maximum limits above. Those limits are much less stringent; however the mine water discharges are diluted upon release into the receiving waterways. The CCME guidelines have a maximum limit on iron, unlike the enforceable regulations above, due to its toxicity to aquatic species (CCME, 1987). In addition to the limits set out in Table 2.2, the pH of the discharged effluent must be between 6.5 and 9 (CCME, 2007). These guidelines have additional parameters to those shown in the table, only the most relevant were listed.

**Table 2.2: Maximum amounts of relevant substances as laid out in the Canadian Water Quality Guidelines for the Protection of Aquatic Life (CCME, 2007).**

<b>Parameter</b>	<b>Concentration (mg/l)</b>
Arsenic	0.005
Copper	0.002 – 0.004 <sup>a</sup>
Cyanide	0.005 (as free CN)
Iron	0.3
Lead	0.001 – 0.007 <sup>a</sup>
Nickel	0.025 – 0.150 <sup>a</sup>
Zinc	0.03

<sup>a</sup>Allowable maximum concentration depends upon hardness of water.

### 2.2.3.2 *United States*

The USEPA, under Title III of the Clean Water Act, sets effluent guidelines for industrial discharges including those from mines, which can be found in Title 40 of the Code of Federal Regulations (40 CFR 440). The guidelines listed in Table 2.3 are for effluent discharge from mines removing copper, lead, zinc, gold, or silver bearing ores from open-pit or underground operations. In addition to the guidelines listed in Table 2.3, the effluent must have a pH in the range of 6.0 to 9.0. The effluent guidelines apply to discharges to surface waters and municipally-owned sewage treatment plants, and are based on the treatment level achievable by current technology, not the risks to the receiving environment (Ore Mining and Dressing Point Source Category, 1988).

The regulated contaminants vary compared to Canadian metal mine effluent regulations, which don't include cadmium or mercury but do include arsenic, cyanide, nickel, and radium. The US discharge regulations for mines are subdivided based on ore type, unlike the Canadian ones which are for all metal mines. The US regulations have

not been updated since 1988, making them only slightly more recent than the MMER. In terms of the discharge criteria themselves, the two sets of regulations are similar, with allowable lead and zinc slightly higher in the US while the allowable copper there is half of the Canadian value.

**Table 2.3: Maximum limits for contaminants in effluent discharged from mines in the US (Part 40, Subpart J—Copper, Lead, Zinc, Gold, Silver, and Molybdenum Ores Subcategory) (Ore Mining and Dressing Point Source Category, 1988).**

<b>Parameter</b>	<b>Maximum for any 1 day (mg/L)</b>	<b>Average of Daily Values for 30 Consecutive Days (mg/L)</b>
Cadmium	0.10	0.05
Copper	0.30	0.15
Lead	0.60	0.30
Mercury	0.002	0.001
Zinc	1.50	0.75
Total Suspended Solids	30	20

### **2.3 CKD as a Lime Substitute**

Due to the similarities in composition of CKD to quicklime (i.e. lime content), it has the potential to be an effective alternative for treatment of ARD as well as other acidic wastewater. Quicklime is made the same way as cement: raw materials are crushed and then heated in a kiln in order to transform their chemical properties. Limestone ( $\text{CaCO}_3$ ) is transformed into lime ( $\text{CaO}$ ) by driving off carbon dioxide ( $\text{CO}_2$ ). This process is called calcination. The production of magnesium oxide ( $\text{MgO}$ ) can also occur if processing a dolomitic limestone that, by definition, contains 35 to 46 % magnesium carbonate ( $\text{MgCO}_3$ ) (Boynton, 1980). Unlike cement, limestone is the only raw material in quicklime manufacture, because for most applications the amount of  $\text{CaO}$  and  $\text{MgO}$  must be greater than 90 % (ASTM, 2006). Calcining temperatures are also lower for lime kilns than for cement kilns, at approximately 1000 °C (Boynton, 1980).

Several CKD characterization and reuse studies have demonstrated the presence of elevated concentrations of calcium oxide that signifies the potential for CKD to be used as a base material in the production of calcium hydroxide slurries for neutralization and precipitation treatment processes (Peethamparan et al., 2008; Zaki et al., 2007; Sreerishnavilasam et al., 2006; Pigaga et al., 2005; Todres et al., 1992; Collins &

Emery, 1983). Surveys of the reuse options for CKD also suggest that it could be used to treat industrial acidic wastes (Bhatty, 1995; Klemm, 1993). CKD has also been demonstrated to be effective at removing metal ions dissolved in aqueous solutions (Zaki et al., 2007; Pigaga et al., 2005; El-Awady & Sami, 1997). However, available information on the use of CKD for such applications is preliminary and isolated in that these studies have been done on only selected CKD samples and mainly synthetic wastewater.

Zaki et al. (2007) demonstrated that CKD leachate was effective at removing copper, nickel, and zinc ions, both individually and in combination, from synthetic wastewater by hydroxide precipitation. The CKD leachate in the study was prepared by washing varying amounts of CKD (from 2.5 to 10 grams) with 250 mL of water, then filtering out the remaining solids. Varying portions of this leachate (1 to 20 mL) were then mixed with 20 ml of synthetic metal solutions in batch tests. Mixing in an unspecified manner continued from zero to 30, 90 and 120 minutes, at which point samples were filtered and analysed for residual metals. Removal efficiencies of close to 100 % were found at varying optimal operating parameters for individual solutions containing 100 mg/L of each metal and a solution of all three at a concentration of 50 mg/l of each metal. Removal of metals increased with increasing CKD leachate concentration in the batch trials, as did pH. The CKD sample used in that study had a free lime content of 14.84 % and a total lime content of 40.65 % by weight.

Pigaga and colleagues (2005) tested the capacity of samples of dry CKD to remove copper, nickel, lead, cadmium, and cobalt from individual synthetic solutions. Metal solutions of 100 mL with concentrations varying from 60 to 9000 mg/L were poured onto 2 or 10 g of dried CKD and stirred by magnetic stirrer either continuously or for 30 second intervals four times a day. Experiments were conducted from one to sixteen days prior to analyzing for residual metals. The authors found that when Cu, Ni, and Co were at initial concentrations of 500 mg/L or less, CKD could remove those metals to below discharge targets of 1, 0.5, and 1 mg/L, respectively, with as little as half an hour of mixing at 20 grams of CKD per litre. A single CKD sample was used in that study that had a free lime content of 3 to 7 % and a total lime content of 38 to 48 %.

El-Awady and Sami (1997) showed that CKD is effective at removing chromium, iron, copper, and cobalt ions from synthetic solutions. Solutions of 100 mg/L Cr, 400 mg/L Fe, 1000 mg/L Cu, and 100 mg/L Co were prepared in 100 mL batches and added to dried CKD samples varying in amount from 0.0 to 40.0 g/L. Flasks were then stoppered and shaken at rates from zero to 200 rpm for a maximum of 2 hours prior to filtering and analysis. The researchers also treated a sample of chromium tank wastewater from a tannery in the same manner as above to evaluate removal of chromium, zinc, cadmium, copper, lead, nickel, iron, and manganese. This wastewater had a high chromium concentration (3556.2 mg/L) but low concentrations of all other metals (totalling 26 mg/L). Close to 100 % removal of target metals in tannery wastewater was achieved using 20 g/L CKD with 30 minutes of mixing at 150 rpm. The authors also showed that CKD can be effective at removing approximately half of the organics from the tannery wastewater, measured as chemical oxygen demand (COD), and all of the suspended solids. The CKD sample used in that study had an average total lime content of 43.9 %, no free lime content was given.

## **2.4 Conclusions**

CKD is a fine-grained alkaline solid waste product generated from cement manufacturing. Hundreds of millions of tonnes of CKD are generated worldwide each year, with the main disposal option being unregulated on-site storage or municipal landfills. Even with advances in technology allowing for more CKD to be recycled within the cement kiln, increased prevalence of alternative uses like agricultural liming and municipal biosolids pasteurization, and even mining of some CKD monofills for use as kiln feed, there is still a large amount of CKD being disposed of instead of reused, leaving space in the market for many more beneficial uses to be developed.

ARD has the potential to seriously damage the environment and in most jurisdictions is subject to regulations requiring treatment to remove acidity and soluble metals like zinc and iron prior to release into the environment. The most prevalent treatment for acidic mine water is in active lime treatment plants, which use quicklime to raise the pH of the effluent and precipitate metals. Chemicals like quicklime or other caustics are the largest part of the operating costs of an active lime treatment plant, and

treatment can last for hundreds of years. CKD, with its high CaO content, can potentially be used to treat ARD to reduce operating costs while protecting the environment by both avoiding disposal of the CKD and potentially removing metals and acidity from the mine water. Replacing or augmenting quicklime with CKD would also reduce the energy and raw materials required for quicklime production. Trace metals in CKD that could potentially leach into surface or ground waters also point more towards reuse in processes that already involve significant metals contamination (e.g. metal mine effluent). The use of CKD for the treatment of mine water has not been previously evaluated. However, studies have shown that CKD is effective at removing dissolved metals from synthetic solutions at concentrations at and above those found in ARD.

## **Chapter 3: Materials and Methods**

The materials, analytical methods, and data analysis methods used throughout this study are outlined below. Further explanations of bench-scale slaking and mine water treatment experiments are outlined in their respective chapters.

### **3.1 Cement Kiln Dust**

Six CKD samples were obtained from cement manufacturing plants from across North America for use in this study. In addition, a commercially available quicklime product (Graymont, Ltd.; Havelock, New Brunswick) was obtained in order to compare the performance of the CKD samples with current industry standards. Table 3.1 summarizes the raw materials and manufacturing specifications of the six cement plants. All plants that supplied CKD samples used in this study have rotary kilns that operate in the temperature range of 1370 to 1480°C. Plant C uses a wet feed process while all other plants use dry feed. Plant D has a 4-stage preheater, and Plant F has a precalciner. All of the plants except that which provided CKD B use baghouses as their dust collection system. Plant B uses an electrostatic precipitator (ESP) to collect the CKD. Two separate samples of CKD were obtained from each plant at different times to evaluate the variability of the CKD properties within each plant. Sample 1 of each CKD was obtained in November 2007 and Sample 2 in July 2008.

### **3.2 Mine Water**

Untreated mine effluent was obtained from a lead/zinc mine owned by Xstrata Zinc and located near Bathurst, New Brunswick, Canada. One of the largest zinc mines in the world, ore is mined from a massive-sulphide formation that was discovered in 1953 and put into production in 1964. The mine has produced over 120 million tonnes of ore to date, which contains lesser amounts of copper and silver in addition to lead and zinc (Xstrata, 2010). Their current water treatment process, which is an active lime treatment plant, is shown in Figure 3.1. Three wastewater streams are combined in a buffer pond prior to entering the treatment plant. Water pumped out of the current underground workings (Brunswick No. 12), leachate and runoff collected at the base of the tailings impoundment, and collected runoff from an abandoned open pit mine on the site



**Table 3.1: Cement kiln process variables of cement kiln dust (CKD) samples used in the study.**

<b>CKD ID</b>	<b>Plant Location</b>	<b>Raw materials used</b>	<b>Process</b>	<b>Kiln type</b>	<b>Kiln temperature</b>	<b>Fuels</b>
CKD-A	Alpena, MI, USA	Limestone (high CaO + high Al, Si, SO <sub>3</sub> ), fly ash, iron ore, sand	Dry	Long	1450°C	Coke/coal, plastic and broth <sup>a</sup> (up to 5%)
CKD-B	Brookfield, NS, CAN	Cement stone <sup>b</sup> , mill scale	Dry	Long	1450°C	Coal, used oil, shingles (up to 10%)
CKD-C	Clancy, MT, USA	Limestone, silica, shale, de-zincd lead slag	Wet	Long	1480°C	Coke/coal
CKD-D	Fairborn, OH, USA	Limestone, clay, coal boiler ash, mill scale	Dry, 4-stage preheater	Long	1475°C	Coke/coal
CKD-E	Joliette, QC, CAN	Limestone, sandstone, iron ore, silica, alumina	Dry	Long	1475°C	Coke/coal, tires (20%), other waste <sup>c</sup> (30%)
CKD-F	Knoxville, TN, USA	Limestone, clay, sand, mill scale	Dry, precalciner	Short	1370°C	Coke/coal, used tires (up to 5%)

<sup>a</sup>Broth is a waste product of the pesticide manufacturing industry that has a high carbon content

<sup>b</sup>Cement stone is a naturally occurring limestone whose properties are ideal for making cement, therefore no clay or sand additives are necessary

<sup>c</sup>Includes tire fluff, plastics, wood, and dried sewage sludge

(Brunswick No. 6) contribute to the influent to the treatment plant, which changes in characteristics temporally. The current mine water treatment plant on site uses quicklime (from the same source as the quicklime used in this study) which is slaked to form a calcium hydroxide slurry prior to being added to the mine water in a rapid mix tank to raise its pH to a target of 9.5. The plant treats approximately 30 000 litres of mine water per minute, with a capacity of 60 000 L/min. Since the plant uses the Conventional High Density Sludge (HDS) process, recycled sludge from the clarifier is also added to this reactor at a ratio of 20 to 30. This means that 20 to 30 kg of solids are recycled for each kg of solids precipitated, or that 95 to 97 % of solids in the reactor tank are from recycled sludge. The next reactor tank allows for further mixing and flocculation, as well as aeration of the neutralized mine water. Finally, the treated mine water is mixed with a polymer in-line (at a dose of approximately 2 ppm) and sent to a clarifier where metals are removed through settling. Clarifier overflow is then sent to a polishing pond prior to discharge.

Several large samples, approximately 100 L, of the combined mine water influent into the treatment plant were collected from the mine over the course of the study, in January, March, June, and September 2009. Samples were shipped overland and stored at room temperature (approximately 21°C). The average pH of the mine water as received was  $2.4 \pm 0.1$  except the sample collected in March, which had a pH of 6.0. This was due to the time of year it was sent; water is only pumped from the open pit mine, which is the most acidic effluent stream, during the summer. The buffer pond would be diluted by the other water streams and runoff by the time this sample was collected. The pH of the sample was adjusted to approximately 2.4 using concentrated sulphuric acid (95 to 98 % pure) at a dose of approximately 0.5 ml per litre of mine water. The total suspended solids (TSS) of the mine water was found to be low at  $70 \pm 50$  mg/L. Samples from three of the mine effluent samples collected for this study were also analyzed for a suite of metals by inductively coupled plasma-optical emission spectrometry (ICP-OES), as listed in Table 3.2. For elements with concentrations both above and below the detection limit in different samples, the value(s) below the detection limit was(were) taken to be half of the detection limit. Error terms represent one standard deviation from the mean of the three analysed samples. The elevated zinc and iron concentrations are the main concern

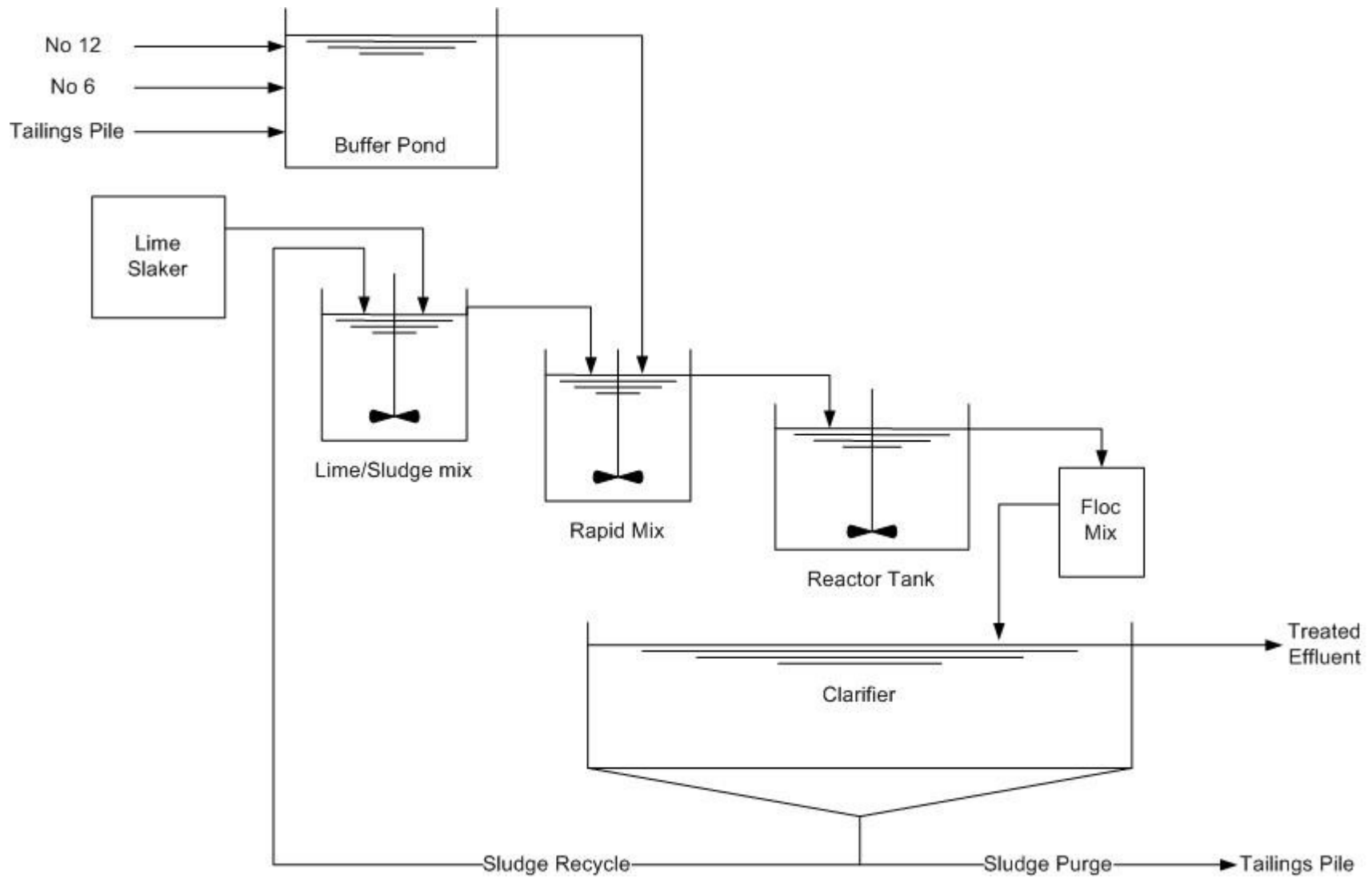


Figure 3.1: Diagram of the mine water treatment plant at Brunswick Mine.

in this mine water, along with the low pH. Further analysis of the mine water showed these metals to be mostly in their soluble form, 94 % on average for zinc and 93 % for iron. There are also high concentrations of aluminum, copper, manganese, sodium, and sulphur. In addition, the mine water has a hardness of over 1000 mg/L as CaCO<sub>3</sub>, calculated from the calcium and magnesium values in Table 3.2.

**Table 3.2: Metal concentrations in untreated mine water analysed by ICP-OES (n=3).**

Element	Symbol	Average Concentration (mg/l)	Element	Symbol	Average Concentration (mg/l)
Silver	Ag	0.01 ± 0.01	Molybdenum	Mo	< 0.01
Aluminum	Al	61 ± 8	Sodium	Na	760 ± 309
Arsenic	As	0.22 ± 0.21	Nickel	Ni	0.14 ± 0.02
Barium	Ba	< 0.01	Phosphorus	P	0.70 ± 0.43
Beryllium	Be	0.004 ± 0.001	Lead	Pb	0.36 ± 0.26
Bismuth	Bi	0.010 ± 0.005	Sulphur	S	1686 ± 442
Calcium	Ca	200 ± 26	Antimony	Sb	0.05 ± 0.00
Cadmium	Cd	0.17 ± 0.01	Selenium	Se	< 0.01
Cobalt	Co	0.71 ± 0.11	Silicon	Si	16 ± 4
Chromium	Cr	0.04 ± 0.01	Tin	Sn	< 0.1
Copper	Cu	6.48 ± 0.26	Strontium	Sr	0.32 ± 0.06
Iron	Fe	400 ± 100	Tellurium	Te	0.07 ± 0.04
Gallium	Ga	0.05 ± 0.04	Titanium	Ti	< 0.01
Potassium	K	8 ± 7	Thallium	Tl	< 0.1
Lithium	Li	0.07 ± 0.02	Vanadium	V	0.008 ± 0.006
Magnesium	Mg	150 ± 30	Zinc	Zn	108 ± 6
Manganese	Mn	55 ± 9	Zirconium	Zr	< 0.01

### 3.3 Analytical Methods

A manual Stereopycnometer™ (Quantichrome, USA) was used to measure the specific gravity of the dry CKD and quicklime samples. A laser particle size analyser (Model 2600, Malvern, UK) was used to determine the particle size distribution of the CKD samples. Dry CKD samples were suspended in an alcohol solution which was then introduced into the instrument where the solution gets passed through a laser beam. The

pattern resulting from the disruption of the laser by the suspended particles is analysed by the instrument to determine the size of the particles. An alcohol solution was used for suspension, rather than water, in order to prevent dissolution of the CKD and quicklime samples. A Hitachi S-4700 FEG Scanning Electron Microscope (SEM) was used to obtain SEM images of the CKD samples. Specific surface area measurements were made using a standard manual Blaine air permeability apparatus (Gilson, USA) following the fineness by air permeability method as outlined in ASTM C110-06. The acid neutralization potential of the CKD and quicklime samples was evaluated following ASTM standard C 400-98. The pH of solutions containing 2.5 g of dried material and varying volumes of 1.5 % sulphuric acid was measured for 30 minutes during these tests.

Major oxide analyses of dried, powdered samples was done using inductively coupled plasma-optical emission spectrometry or ICP-OES (Vista-PRO Radial, Varian). Samples were first prepared using lithium metaborate/tetraborate fusion. Sulphur content of dried samples was analyzed using a LECO Sulfur Determinator, which includes an induction furnace where the dry sample is combusted to release SO<sub>2</sub> gas and an automatic iodometric titrator that determines the amount of gas released and thus the concentration of sulphur in the original sample. The rapid sugar method was used to determine the available lime content of dry samples as outlined in ASTM standard C 25-06. Trace metals in dried CKD and quicklime, as well as treated effluent, were measured after a near total acid digestion using ICP-OES (Vista-PRO Radial, Varian).

The pH throughout the experiments was measured using variable temperature electrodes (accuFlow, Fisher Scientific), and conductivity using four cell probes (accumet, Fisher Scientific), both using XL50 meters from Fisher Scientific that were calibrated at least weekly throughout testing. Calcium, zinc, and iron concentrations in aqueous samples were measured using an atomic absorption spectrometer (AAnalyst 200, PerkinElmer). Samples were first acidified to a pH less than 2 using nitric acid following procedures outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 2005). The concentrations of the soluble form of these ions were found by filtering samples through a 0.45 µm polysulfone membrane (GE Water & Process Technologies) prior to acidification and analysis. Sulphate ion concentrations of filtered

samples were analyzed using a compact ion chromatography system (Model 761, Metrohm) with autosampler (Model 788, Metrohm).

Minimum detection limits (MDLs) for zinc and iron as measured by atomic absorption were calculated in order to ensure the validity of the value of low concentrations of these metals found in treated mine water samples. MDLs were found using the EPA method as outlined in Mac Berthouex & Brown (2002). Samples of known concentration of metal were prepared using Milli-Q water and laboratory grade standards of 1000 mg/l zinc or iron (Fisher Scientific). Seven replicates of two different concentrations near the instrument's detection limit were analysed for each metal. The minimum detection limit for zinc was found to be 0.013 mg/l and for iron, 0.049 mg/l.

The solids content of the slurries used in the bench-scale mine water treatment experiments was determined by dividing the weight of the dried solids by the weight of the slurry sample prior to drying at  $104 \pm 1^\circ\text{C}$ . The specific gravity of the slurries was calculated by dividing the weight of a sample of slurry by the weight of an equal volume of Milli-Q water at  $4^\circ\text{C}$ . The preceding tests are outlined in *Standard Methods* (APHA et al., 2005).

### **3.4 Bench-Scale Methods**

A standard six-paddle jar test apparatus (Phipps & Bird, Fisher Scientific) was used in both the bench-scale slaking experiments of Chapter 4 and the bench-scale mine water treatment experiments of Chapters 5 and 6. Specific procedures (e.g. mixing speeds, chemical doses) for each of the bench-scale experiments are outlined in their respective chapters.

### **3.5 Data Analysis**

All error terms in text and tables and error bars on graphs represent one standard deviation from the mean of at least three samples from three separate tests. Both Dunnett's method and the analysis of variance (ANOVA) were used in order to determine if the CKD samples achieved statistically comparable results to quicklime in the bench-scale slaking and mine water treatment trials. ANOVA compares the means of two or more treatments to establish if they are equivalent (Mac Berthouex & Brown, 2002). The

variance within each CKD or quicklime treatment is compared to the overall variance between all the treatments. Dunnett's method is a similar statistical analysis that compares any number of means to the mean of a control, which in this study means comparing the average results from slaking of or treatment with each CKD to the average result from slaking of, or treatment with, quicklime (Dunnett, 1964; Mac Berthouex & Brown, 2002). Unlike ANOVA, Dunnett's method also indicates whether each treatment is higher or lower than the control, if its mean is found to be significantly different. The ANOVA will only show that the treatments are similar or at least one is different, unless treatments are compared individually to the control.

Correlations between selected dry CKD properties and slaked CKD solutions, and between dry CKD properties and treated effluent characteristics, were found using Microsoft Excel. When squared, the correlation ( $r$ ) gives the coefficient of determination ( $R^2$ ) for linear regression models (Mac Berthouex & Brown, 2002). Data were also plotted to ensure validity of correlations, since a high  $R^2$  does not always indicate a useful relationship. For simple linear regression with all CKDs, i.e. a sample size of 6, an  $R^2$  of 0.66 or greater indicates statistical significance at the 5 % confidence level (or 95 % confidence interval) and an  $R^2$  of 0.84 indicates significance at the 1 % confidence level (Hahn, 1973). For experiments using only 4 samples, the coefficients of determination must be above 0.90 or 0.98 to indicate significance at the 5 % or 1 % confidence levels, respectively.

## Chapter 4: Cement Kiln Dust Characterization Study

Mackie, A, Boilard, S, Walsh, ME and CB Lake (2010) Physicochemical characterization of cement kiln dust for potential reuse in acidic wastewater treatment, *Journal of Hazardous Materials*, **173**: 283—291.

### 4.1 Introduction

This study was undertaken to compare the chemical and physical characteristics of CKD to quicklime. Quicklime is currently the most prevalent and cheapest alkaline material used to treat acidic wastewaters like ARD (Akcil & Koldas, 2006; Coulton et al., 2003a; Younger et al., 2002; Kuyucak, 2001). This study was also done to determine what characteristics of CKD may impact its ability to react with water and form calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) slurries for treatment of acidic effluents. Secondary objectives were to gauge the differences between CKD samples from different cement plants, and within cement plants at different times of the year.

CKD is a fine-grained, alkaline material that is generated as a by-product of the cement manufacturing process. In cement production, raw materials are fed into a kiln where they are heated to temperatures reaching between 1400 and 1550°C. The main raw material used to produce cement is limestone ( $\text{CaCO}_3$ ), with approximately ten percent of the raw mix made up of a silica source (e.g., sand or clay), an alumina source, and an iron source. Heating the raw materials to such high temperatures, a process called calcination, alters the chemical makeup of the materials to produce cement clinker (Kosmatka et al., 2002).

Large quantities of air used for combustion and to carry the fuel to the burning zone of a cement kiln results in an exhaust gas that is entrained with particles of clinker, raw materials, and partially calcined raw materials (i.e. CKD) (Albeln et al., 1993). CKD is separated from cement kiln exhaust gases in air pollution control devices such as baghouses or electrostatic precipitators. CKD generation has been estimated at approximately 15 to 20 % of cement clinker production (USEPA, 2008b). Most CKD currently generated in North America is returned to the head of the cement kiln for reprocessing. However, not all of the CKD generated can be reused in cement



manufacturing due to chemical specifications, a potential reduction in the effectiveness of pollution control devices, and the possibility of damage to kilns (USEPA, 1993). One study found that of the 12.9 million tonnes of CKD generated in the United States in 1990, 8.3 million tonnes (64 %) was recycled into the cement kiln, while approximately 0.4 million tonnes (3 %) was reused off site (USEPA, 1993). This leaves roughly 4.2 million tonnes (33 %) of CKD to be landfilled or disposed off-site. Results of a more recent survey showed that for the 87 million tonnes of cement clinker produced in 2006, 1.2 million tonnes of CKD were reused on or off-site (not including recycling into kiln feed) while 1.4 million tonnes were landfilled. In addition, 0.3 million tonnes of CKD was reclaimed from landfills, mainly for use as kiln feed (Adaska & Taubert, 2008).

In the United States, CKD is currently classified as a special waste that is temporarily exempt from federal hazardous waste regulations (Subtitle C of the Resource Conservation and Recovery Act (RCRA)). In 1999, the USEPA proposed a rule for the management of CKD that includes standards for landfill placement and design to control the potential release of heavy metals to the environment through leaching and runoff, and to control airborne particle release through covers, and guidelines for continued monitoring (USEPA, 1999). Any CKD that is not managed following this rule would be classified as a hazardous waste and subject to regulation under Subtitle C of the RCRA (USEPA, 1999). CKD used for beneficial purposes (i.e. recycling) is exempt from this rule. In Canada, solid and hazardous waste disposal is regulated at the provincial level. There are no disposal regulations specific to CKD, however, landfill designs must be approved by the relevant agency.

Acidic waste streams like acid rock drainage (ARD) from base metal mines contain hazardous metals that, along with high acidity, damage ecosystems (Younger et al., 2002). In practice, the neutralization of acidic wastewater streams often involves the addition of chemicals to raise pH levels and precipitate soluble metals. Elevating the pH of these waste streams causes the dissolved metals to precipitate in the form of hydroxides which can then be removed through settling or filtration processes. The most common material used in treatment of acid rock drainage from mines is quicklime in the form of lime slurries (Akcil & Koldas, 2006; Coulton et al., 2003a; Younger et al., 2002;

Kuyucak, 2001). Quicklime is an alkaline product used in a variety of environmental and industrial applications. It is produced similarly to cement, by heating limestone in a kiln. The calcium carbonate ( $\text{CaCO}_3$ ) content present in a high-calcium limestone is converted into calcium oxide ( $\text{CaO}$ ) during calcination to release carbon dioxide ( $\text{CO}_2$ ) (Boynton, 1980). The production of magnesium oxide ( $\text{MgO}$ ) can also occur if processing a dolomitic limestone that, by definition, contains 35 to 46 % magnesium carbonate ( $\text{MgCO}_3$ ). The temperatures in lime kilns are generally lower than those in cement kilns, at approximately  $1000^\circ\text{C}$  (Boynton, 1980). According to ASTM Standard C1529-06a, quicklime must contain a minimum of 90 %  $\text{CaO} + \text{MgO}$ , and therefore the only raw material in quicklime manufacture is limestone (ASTM, 2006). This is the specification for a high calcium quicklime product for environmental uses and dictates that the limestone used as raw material must have a calcium content of greater than 90 %.

There are several current reuse options for CKD. These include soil stabilization, as an additive for blended cement products, solidification/stabilization of hazardous wastes, pasteurization of municipal biosolids, and as a fertilizer (Bhatty, 1995). Several CKD characterization and reuse studies have demonstrated the presence of elevated concentrations of calcium oxide that highlights the potential for CKD to be used as a base material in the production of lime slurries for neutralization and precipitation processes (Peethamparan et al., 2008; Zaki et al., 2007; Sreekrishnavilasam et al., 2006; Pigaga et al., 2005; Todres et al., 1992; Collins & Emery, 1983). However, available information on the use of CKD for such applications is preliminary and isolated in that very few studies have been done on only selected types of wastewater and selected CKD samples. Previous studies have mainly focused on the potential reuse of CKD in a solid form, though Zaki et al. (2007) demonstrated that CKD leachate was effective at removing copper, nickel, and zinc ions from a synthetic wastewater by hydroxide precipitation. The CKD leachate in that study was prepared by washing varying amounts of CKD with water, then filtering out the remaining solids. Also, Pigaga et al. (2005) found that dry CKD was efficient in the removal of heavy metals from synthetic aqueous solutions.

The results of a study of the physicochemical characteristics of six CKD samples from cement plants across North America and one quicklime sample are presented here.

The characterization of CKDs presented in this chapter consists of (1) physical analysis including specific gravity, particle size distribution, and specific surface area, (2) chemical analysis including an analysis of major oxides and available lime, and (3) morphological analysis with scanning electron micrographs (SEMs) of unhydrated CKD samples. In addition, the chemical quality of the calcium hydroxide slurries generated using CKD samples characterized in this study were compared to those generated using a commercial quicklime product. The study focused on determining the impact of the physicochemical properties on the viability of using CKD as a raw material for the production of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) slurries for use in wastewater treatment applications. To this end, correlations between the physical and chemical properties and the reactivity in water (determined by the pH achieved, or disassociation of CaO and other alkalis in water) of the CKDs were calculated and are presented here as well. The acid neutralization potential of the hydrated lime slurries generated from CKD samples was also evaluated and compared to that of quicklime.

## 4.2 Materials and Methods

A manual Stereopycnometer<sup>TM</sup> (Quantichrome, USA) was used to measure the specific gravity of the dry CKD and quicklime samples. A laser particle size analyser (Model 2600, Malvern, UK) was used to determine their particle size distributions. Dry CKD samples were suspended in an alcohol solution which was then introduced into the instrument where the solution gets passed through a laser beam. The pattern resulting from the disruption of the laser by the suspended particles is analysed by the instrument to determine the size of the particles. An alcohol solution was used for suspension, rather than water, in order to prevent dissolution of the CKD and quicklime samples. A Hitachi S-4700 FEG Scanning Electron Microscope (SEM) was used to obtain SEM images of the CKD samples. Specific surface area measurements were made directly by using a standard manual Blaine air permeability apparatus (Gilson, USA) following the fineness by air permeability method as outlined in ASTM C110-06. Specific surface areas were also calculated from the laser particle size distributions using the measured specific gravity values. The acid neutralization potential of the CKD and quicklime samples was evaluated following ASTM standard C 400-98. The pH of solutions containing 2.5 g of

dried material and varying volumes of 1.5 % sulphuric acid was measured for 30 minutes during these tests.

Major oxide analyses of dried, powdered samples was done using inductively coupled plasma-optical emission spectrometry or ICP-OES (Vista-PRO Radial, Varian). Samples were first prepared using lithium metaborate/tetraborate fusion. Sulphur content of dried samples was analyzed using a LECO Sulfur Determinator, which includes an induction furnace where the dry sample is combusted to release SO<sub>2</sub> gas and an automatic iodometric titrator that determines the amount of gas released and thus the concentration of sulphur in the original sample. The rapid sugar method was used to determine the available lime content of dry samples as outlined in ASTM standard C 25-06. Trace metal concentrations in dried CKD and quicklime samples were measured after a near total acid digestion using ICP-OES.

Bench-scale experiments to model the lime slaking process were conducted using a standard jar test apparatus (Phipps & Bird, Fisher Scientific). The jar tester was modified using a 13 mm thick piece of Plexiglas in order to better simulate the mixing conditions in a lime slaker by raising the bottom of the jars closer to the mixing paddles. Several dosages of each CKD sample, normalized to its CaO content, were added to the jars with 750 ml of room temperature Milli-Q water (approximately 20 °C). Water was added at a slow and constant rate to avoid ‘drowning’ the CKD particles. Drowning occurs when water is added too quickly and creates an outer shell of hydrated lime (Ca(OH)<sub>2(s)</sub>) that slows or prevents the interior of the particles from hydrating (Boynton, 1980). Each sample was then rapid mixed at 200 rpm for 30 minutes, with 250 ml of cold water (4 °C) added at the end and mixed for one minute to ensure maximum dissolution of Ca(OH)<sub>2</sub>; the solubility of CaO and Ca(OH)<sub>2</sub> increases with decreasing temperature (Boynton, 1980). The temperature of the test solutions was monitored during the slaking process. The CKD doses used were 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 g CaO/L. These doses were chosen in order to include the maximum solubility of CaO in water, 1.25 g/l at 20 °C (Boynton, 1980). After mixing, samples of the slurry were collected and analyzed for pH, conductivity, and calcium (Ca<sup>2+</sup>) content. The remainder of the solution was passed through a 0.45 µm polysulfone membrane filter (GE Water & Process Technologies) and

the same analyses were performed on the filtrate. Sulphate ion concentrations were also measured on the filtrate from the jar tests.

The slaked solutions were filtered through a 1.5  $\mu\text{m}$  Whatman filter (934-AH) prior to the 0.45  $\mu\text{m}$  filter in order to determine total suspended solids (TSS) concentrations of the samples according to *Standard Methods* (APHA, 2005). In order to estimate the percent dissolution of the CKD material the filters were weighed before and after filtration and these measurements were compared to the mass of CKD that had been added at the beginning of the jar tests.

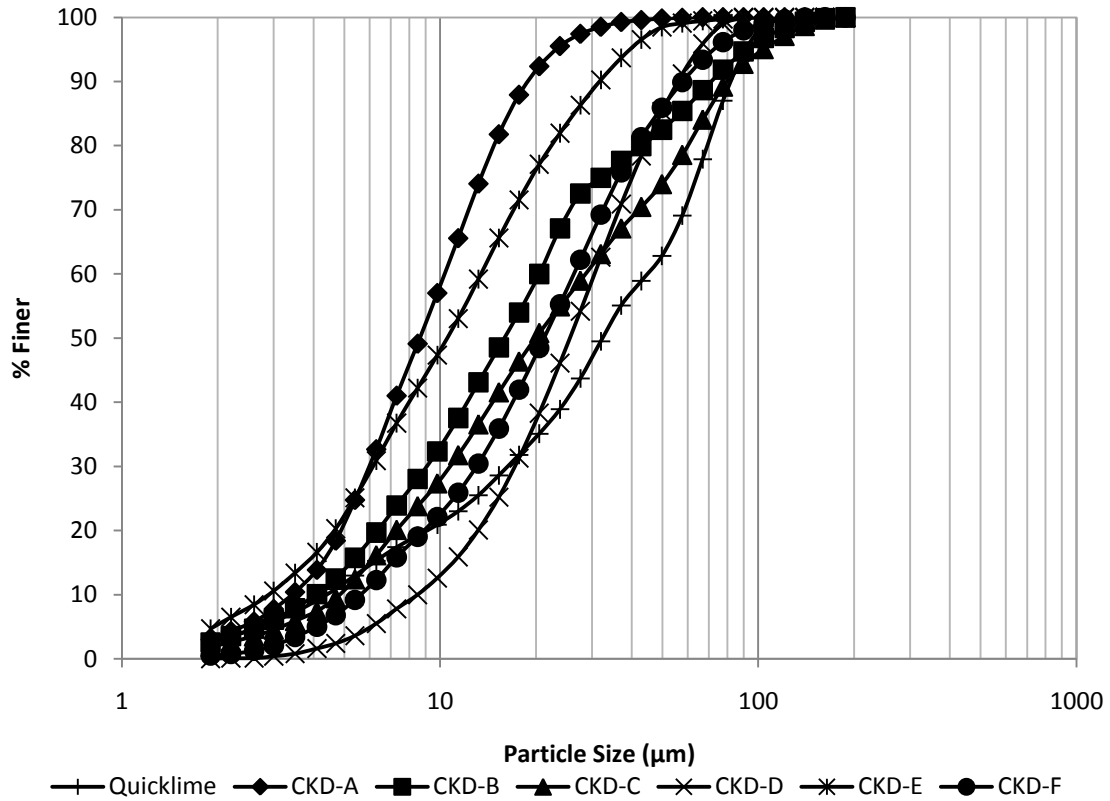
The pH was measured using variable temperature electrodes (accuFlow, Fisher Scientific), and conductivity using four cell probes (accumet, Fisher Scientific), both using an XL50 meter from Fisher Scientific. Calcium ions were measured using an atomic absorption spectrometer (AAAnalyst 200, PerkinElmer). Sulphate ion content was analyzed on the filtered samples using a compact ion chromatography system (Model 761, Metrohm) with autosampler (Model 788, Metrohm).

### **4.3 CKD and Quicklime Physicochemical Characterization**

The results of the physicochemical characterization of the CKD and quicklime samples are discussed in this section. These tests were all performed on unhydrated samples. Characteristics of the CKD samples are compared to each other, to quicklime, and to the results of previous studies.

#### **4.3.1 Particle Size and Morphology**

In the laser particle size distributions presented in Figure 4.1, it is shown that CKD-A contained the finest particles while CKD-D contained the coarsest particles. Also shown in this figure, for comparison, is the particle size distribution of the commercial quicklime product, which was found to be coarser than all the CKD samples analyzed. CKD-A and CKD-E were found to be notably finer than the quicklime sample and other CKD samples. Median particle sizes found from the distributions were 8.5  $\mu\text{m}$  for CKD-A, 15.9  $\mu\text{m}$  for CKD-B, 20.5  $\mu\text{m}$  for CKD-C, 31.6  $\mu\text{m}$  for CKD-D, 10.6  $\mu\text{m}$  for CKD-E, 21.2  $\mu\text{m}$  for CKD-F, and 32.0  $\mu\text{m}$  for quicklime.



**Figure 4.1: Particle size distributions of CKD and Quicklime Samples (n=2).**

Shown in Figure 4.2 are the SEMs that were taken of the dry, unhydrated CKD samples. The SEMs qualitatively show the relative particle sizes of the CKDs, with CKD F appearing to have the largest particle size and CKD A having the finest and most uniform particle size. It can be seen from the SEMs that CKD-A and CKD-E demonstrated the highest amounts of fine particles, which corresponds with the laser particle size data. The SEMs also show the large variability in composition and particle shape of the different CKD samples

Using results from a study performed for the Portland Cement Association (PCA) by Todres et al. (1992), the USEPA (1993) found that dry kilns with precalciners produced the largest sized CKD particles (median particle size = 22.2 µm), followed by wet kilns (9.3 µm), with long dry kilns producing the smallest CKD particles (3 µm).

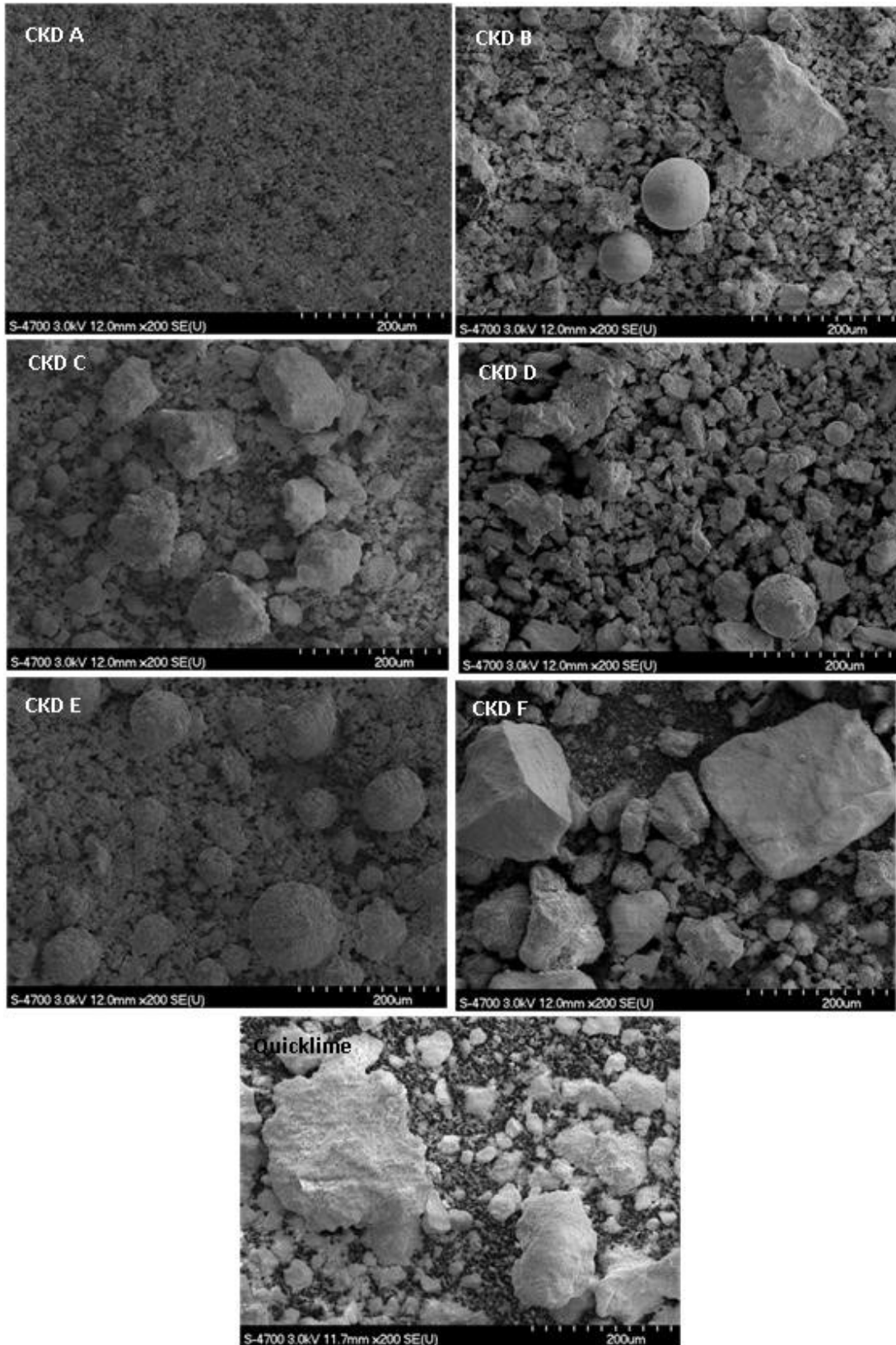


Figure 4.2: Scanning electron micrographs of CKD and quicklime samples

Similar results were found using another study conducted on four CKD samples that concluded that CKD generated in long, dry kilns had the smallest particles size while CKD generated in dry kilns with a precalciner had the largest particle sizes (Peethamparan, 2006). The results of both previous studies correspond to results found in this study (at the 50 % finer or median particle size), in that the analysis of CKD samples taken from long dry kilns (CKD-A, CKD-B, and CKD-E) found that 50 % of the particles were smaller than 8 to 16  $\mu\text{m}$ . Samples taken from the wet, long kiln (CKD-C) and dry, short kiln with precalciner (CKD-F) were found to have a slightly larger particle size distribution, with 50 % of the particles smaller than approximately 20  $\mu\text{m}$ . The CKD samples taken from the dry, long kiln with preheater were found to have the largest particle size distribution of all of the CKD samples analyzed in this study, with 50 % of the particles smaller than 25  $\mu\text{m}$ .

#### 4.3.2 Specific Gravity and Specific Surface Area

Table 4.1 presents the specific gravities and specific surface areas (SSAs) of the CKD and quicklime samples. The specific gravities were within the range reported for CKD samples from previous studies except for CKD-D, which is just above the previously reported upper limit of 2.96 (Peethamparan, 2006; Collins & Emery, 1983). All CKD samples have lower densities than the quicklime sample and are similar to each other, which can be seen in the table. The specific surface areas given by the Blaine method, also termed Blaine fineness, show that CKD-D has a SSA similar to that of quicklime, while all other CKD samples have greater SSAs. The areas calculated from the laser particle size distribution indicate that CKD-C, CKD-D, and CKD-F have similar SSAs to quicklime, with the others larger. It can also be seen from the results in Table 4.1 that the surface areas given by the Blaine method were found to be consistently lower, though by varying factors, than those calculated from the laser particle size distributions. This can be attributed to the assumption used when estimating surface area from particle size distributions that all particles are spherical in shape, which, in the case of CKD, they are not. In addition, the laser particle size method cannot penetrate the particles to measure the internal surface area as well as external, which the Blaine method does. A previous study found Blaine SSAs for CKD samples to be 1.25 times lower for one



sample and from 1.72 to 2.53 times higher than the laser SSAs for the rest (Peethamparan, 2006). This study's Blaine SSA measurements are from 5 to 20 times higher than their laser particle size distribution-calculated counterparts.

**Table 4.1: Specific gravity measurements and specific surface area measurements (n=2).**

Sample ID	Specific Gravity	Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> )	
		Blaine Method	Particle Size Method
CKD-A	2.84 ± 0.05	0.502 ± 0.008	0.10 ± 0.03
CKD-B	2.87 ± 0.06	0.350 ± 0.008	0.06 ± 0.07
CKD-C	2.83 ± 0.02	0.5 ± 0.2	0.025 ± 0.007
CKD-D	2.98 ± 0.02	0.194 ± 0.006	0.03 ± 0.02
CKD-E	2.76 ± 0.05	0.65 ± 0.06	0.061 ± 0.004
CKD-F	2.94 ± 0.05	0.4 ± 0.2	0.03 ± 0.02
Quicklime	3.28	0.164	0.021

The results demonstrate that the CKD particles have a higher specific surface area than quicklime; the specific surface area of the CKD samples was between 2 and 4 times greater than that of the quicklime product evaluated. The specific surface area measurements also agree with particle size distributions and SEMs in that CKD-A and CKD-E have the finest particle sizes as well as the highest surface areas. Due to the fineness of the CKD particles, there is a larger surface area available for the reaction of CaO with water to produce Ca(OH)<sub>2</sub>. This indicates that the oxide particles present in CKD may demonstrate greater reactivity due to the increased surface area. Increased surface area also allows more space for metal adsorption; CKD has been demonstrated to act as both a neutralizing agent and sorbent (Pigaga et al., 2005).

#### 4.3.3 Major Oxides

The results of the major oxides analysis are presented in Table 4.2. Also included in this table is the available lime, or free CaO, content of each sample. The major oxide measurement of the calcium oxide (CaO) content assumes that all calcium in the sample is in the form of CaO, however, this is not the case. Some of the calcium content may be in the form of calcium carbonate, CaCO<sub>3</sub>, (i.e. the unreacted limestone), or calcium sulphate (CaSO<sub>4</sub>). Available lime is a measure of the CaO content that is readily available for reactions (Boynton, 1980), and is of interest in this study to evaluate the amount of

CaO in each CKD that would react with water to form calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ). Previous studies have found that CKD can contain from 8.1 to 61.3 % by weight of total CaO and from zero to 30 % by weight free CaO (Peethamparan et al., 2008; Zaki et al., 2007; Sreekrishnavilasam et al., 2006; Pigaga et al., 2005; Duchesne & Reardon, 1998; El-Awady & Sami, 1997; Bhattu & Todres, 1996; Bhattu, 1995; Todres et al., 1992; Collins & Emery, 1983; Haynes & Kramer, 1982). In this study, CKD-D and CKD-F were found to contain both the highest total CaO (57 % for both) and free CaO (34 and 37 %, respectively) content, after quicklime (90 % total and 87 % free). These high free lime values are higher than the previous maximum reported in literature (Collins & Emery, 1983). In contrast, CKD-C and CKD-E demonstrated the lowest CaO content at 40 % and 35 % for total, respectively and 5 % and 3.5 % for free. High loss on ignition (LOI) indicates that the CKD is high in slow-reacting calcium carbonate and low in reactive free lime (Bhattu & Todres, 1996). The LOI values for the CKD samples further support the total and free lime analysis results, in that CKD-D, CDK-F, and quicklime were found to have LOI values less than 6.0, indicating lower  $\text{CaCO}_3$  and higher free lime content in comparison to the other CKD samples analyzed. LOI values are also in agreement with previously reported values. Table 4.2 also demonstrates the low variability within each plant at different times of the year. Error values are due to the variation between the two samples taken at each plant in November 2007 and July 2008 and represent one standard deviation from the mean of those values.

Most other major oxide percentages found in the CKD samples in this study are in agreement with previously reported values as well (Peethamparan et al., 2008; Zaki et al., 2007; Peethamparan, 2006; Sreekrishnavilasam et al., 2006; Pigaga et al., 2005; Duchesne & Reardon, 1998; El-Awady & Sami, 1997; Todres et al., 1992; Collins & Emery, 1983). The MgO content of CKD-D is slightly higher than the previously reported maximum value of 4.0 % w/w, and  $\text{SO}_3$  in CKD-B is higher at 20 % than the

**Table 4.2: Chemical composition of CKD and quicklime samples as a percentage of the total weight (n=2).**

<b>Parameter</b>	<b>CKD-A</b>	<b>CKD-B</b>	<b>CKD-C</b>	<b>CKD-D</b>	<b>CKD-E</b>	<b>CKD-F</b>	<b>Quicklime</b>
Al <sub>2</sub> O <sub>3</sub>	4.8 ± 0.7	3.9 ± 0.3	2.6 ± 0.2	3.7 ± 0.3	5.0 ± 0.8	4.7 ± 0.3	0.36
CaO	44 ± 3	47.8 ± 0.0	40 ± 3	57 ± 3	35 ± 3	57 ± 3	90.1
Free CaO <sup>a</sup>	15 ± 5	8.8 ± 0.6	5.0 ± 0.3	34 ± 3	3.5 ± 0.1	37 ± 5	87.2
Fe <sub>2</sub> O <sub>3</sub>	1.80 ± 0.09	1.39 ± 0.07	1.5 ± 0.3	2.19 ± 0.05	1.6 ± 0.2	3.1 ± 0.5	0.19
K <sub>2</sub> O	5.7 ± 0.7	2.0 ± 0.5	8 ± 2	5 ± 2	11 ± 4	2.6 ± 0.2	0.08
MgO	1.3 ± 0.04	1.0 ± 0.2	1.9 ± 0.2	4.1 ± 0.3	1.1 ± 0.2	1.2 ± 0.01	0.29
MnO	0.05 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.06 ± 0.01	0.03 ± 0.00	0.16 ± 0.03	0.42
Na <sub>2</sub> O	1.0 ± 0.3	0.25 ± 0.08	0.4 ± 0.1	0.6 ± 0.2	1.0 ± 0.4	0.2 ± 0.03	0.12
P <sub>2</sub> O <sub>5</sub>	0.11 ± 0.03	0.01 ± 0.02	0.04 ± 0.02	0.10 ± 0.01	0.08 ± 0.03	0.3 ± 0.2	0.01
SiO <sub>2</sub>	13 ± 2	15 ± 2	13 ± 2	12.9 ± 0.4	9 ± 2	20 ± 5	4
TiO <sub>2</sub>	0.23 ± 0.04	0.20 ± 0.03	0.13 ± 0.02	0.12 ± 0.00	0.15 ± 0.02	0.21 ± 0.03	0.021
SO <sub>3</sub> <sup>b</sup>	14.2 ± 0.5	20 ± 20	9.3 ± 0.2	9 ± 3	11 ± 5	4 ± 3	N/A
LOI <sup>c</sup>	13 ± 3	10 ± 20	23 ± 3	5 ± 2	22 ± 5	5.6 ± 0.6	4
TRO <sup>d</sup>	39.30	38.87	27.46	60.97	26.13	55.62	86.70
CaO + MgO - LOI	32.64	36.66	19.46	55.55	13.67	52.78	86.50
TRO - SO <sub>3</sub>	25.06	22.67	18.12	52.04	14.74	51.77	86.70

<sup>a</sup>analysis done by the rapid sugar method

<sup>b</sup>analysis done by the LECO total sulphur method

<sup>c</sup>loss on ignition at 1000°C

<sup>d</sup>total reactive oxides = [(CaO + MgO) - LOI] + (Na<sub>2</sub>O + K<sub>2</sub>O)

previously reported maximum of 17 %. The  $P_2O_5$  content of all CKD samples but CKD-E was found outside of the previously reported range of 0.08 to 0.09, and MnO was only previously reported to have a minimum value of 0.04. However the latter two oxides have only been presented in one previous study (Peethamparan et al., 2008).

The presence of particles other than calcium oxide can affect the solubility of CaO into  $Ca(OH)_2$ . Interfering oxides such as magnesium oxide (MgO), silicon dioxide ( $SiO_2$ ), aluminum oxide ( $Al_2O_3$ ), and unreacted  $CaCO_3$  particles may slow the rate of dissolution of  $Ca(OH)_2$  (Boynton, 1980). Additionally, calcium sulphate ( $CaSO_4$ ) depresses the solubility of CaO, even in small quantities. Alternatively, both magnesium oxide and potassium oxide ( $K_2O$ ) increase solubility, and will react with water to form magnesium hydroxide ( $Mg(OH)_2$ ) and potassium hydroxide (KOH), which are known for their acid neutralizing capabilities in environmental applications. In wastewater treatment,  $Mg(OH)_2$ , or milk of magnesia, has a higher basicity per unit added than either lime or caustic soda (NaOH) for equivalent neutralization (Kogel et al., 2006). However, its slower reaction rate in precipitating high concentrations of metals (e.g. > 2000 ppm) or neutralizing weak organic acids and associated longer required reactor residence times is known to be a primary disadvantage of magnesium hydroxide treatment.

The collective results of the major oxide analysis presented in Table 4.2 show that all of the CKDs analyzed demonstrated significantly higher levels of MgO,  $K_2O$ ,  $SO_3$ ,  $SiO_2$  and  $Al_2O_3$  compared to the commercial quicklime product analyzed in this study. While sulphite, silica, and alumina would present potentially interfering materials in the dissolution reactions of  $Ca(OH)_2$ , the presence of elevated magnesium and potassium oxide levels in CKD and reactions with water to produce  $Mg(OH)_2$  and KOH would potentially enhance the neutralizing capabilities of CKD slurries for acidic wastewater treatment applications.

Collins and Emery (1983) state that the reactive calcium and magnesium (i.e. free lime) in a sample can be estimated by subtracting the loss on ignition (LOI) from the total amount of their oxides (i.e.  $CaO + MgO$ ). They also suggest that the contribution from other alkalis,  $Na_2O$  and  $K_2O$ , be included, up to a value of approximately 6 % of the weight of the sample. This they termed total reactive oxides ( $TRO = CaO + MgO - LOI$

+ Na<sub>2</sub>O + K<sub>2</sub>O) and found a direct relationship between this value and the reactivity of a CKD, in terms of the 7 day compressive strength of a kiln dust/fly ash/aggregate sample. That study reported TRO values for 18 CKD samples to be in the range of 12.8 to 37.2. TRO values for the CKD samples used in this study were calculated and are included in Table 4.2, showing a range of values from 26.13 to 60.97. The TRO values of CKD-D and CKD-F are much larger values than previously reported, as is their free lime content. A more recent study also reported statistics on TRO values of 63 CKD samples, calculated from the data of previous studies, giving a range from 1.86 to 56.08. However, the alkali contribution (Na<sub>2</sub>O + K<sub>2</sub>O) was subtracted in the calculations rather than added (Sreekrishnavilasam, 2006). The values of TRO and CaO + MgO - LOI were correlated with the free lime content of the CKD samples, giving coefficients of determination (R<sup>2</sup>) of 0.9273 and 0.8733 respectively. Since the high levels of sulphite in the CKD samples could potentially affect the solubility, and thus the free lime content, of the samples by forming calcium sulphate, the SO<sub>3</sub> content of the CKDs was subtracted from the TRO values, and this was correlated to the free lime content as well. Using this value gave an R<sup>2</sup> of 0.9851, making the TRO - SO<sub>3</sub> value of CKD a good indicator of free lime content. Each of these values is significantly higher than the free lime content of the samples (Table 4.2), but the TRO - SO<sub>3</sub> value, since it gives the best correlation, could be used in lieu of free lime as an indicator of CKD reactivity.

In their 1993 report to Congress, the USEPA found that there was no apparent trend in CKD chemical composition (i.e. major oxide distribution) relating to process type, based on a limited sample for analysis (USEPA, 1993). However, other studies have demonstrated that as an industrial by-product, the composition of CKD may be linked as a function of process variables. A study by Bhatta and Todres (1996) on the use of CKD as a soil stabilizer determined that CKD can be segregated into two categories, pre-calciner kiln dust and long-wet or long-dry kiln dusts. The results of that study concluded that pre-calciner kiln dust particles were coarser and higher in free lime, while CKD particles generated in long kilns contained more CaCO<sub>3</sub> with reduced amounts of free lime. Those results are in agreement with the results of the current study with regards to CKD-F (i.e. precalciner process) which demonstrated a larger particle size distribution and higher free lime content in contrast to the other long-kiln CKD samples analyzed.

Results of the analysis of CKD-D also demonstrates that kiln dust particles generated in plants with pre-heaters are similar to those generated in precalciner kiln processes (i.e. coarser particle sizes and elevated free lime content).

#### 4.3.4 Trace Metals

Trace metals are of concern when discussing any potential reuse option for CKD as they can impact the quality of the water stream that is being treated. The USEPA (1993) compiled data from their own sampling of CKD at 15 cement plants in 1992, as well as from the 1991 PCA member company survey, the 1992 PCA report ‘An Analysis of Selected Trace Metals in Cement and Kiln Dust’, and Haynes and Kramer (1982). They concluded that several trace metals are found in CKD but at variable levels. The main trace metals found were antimony, barium, lead, manganese, strontium, thallium, and zinc. Shown in Table 4.3 are selected results of a trace metals analysis that was performed on Sample 2 of all CKDs as well as the quicklime sample used in this study. It can be seen that the values of most metals are highly variable in the CKD samples. As well, some metals are lower in the CKD samples than in quicklime, like barium and manganese, and some are higher, like chromium and nickel.

The incineration of hazardous and non-hazardous waste in cement kilns offers an effective disposal option for materials like tires and waste oil while reducing fuel costs for cement kilns (USEPA, 1993). However, the metals found in these alternative fuels could end up in cement and CKD. The only metals found by the USEPA to be statistically significantly different at the 95 % confidence level between plants burning hazardous waste and those not were lead, cadmium, and chromium. They found that those plants burning hazardous wastes had concentrations from 2.4 to 2.7 times higher of these metals. The fuels used by the cement plants supplying CKD for this study are listed in Table 3.1. CKD-E was supplied by the plant using the most waste fuel, up to 50 %, of which used tires made up approximately 20 %. The results from this study are inconclusive with regards to chromium, however, CKD-E has a cadmium content 4 to 20 times higher than the other CKDs, as well as a lead content 5 to 13 times higher. The zinc content in CKD-E, along with CKD-C, is also considerably higher than the other CKDs. The plant supplying CKD-C stated that they do not use waste fuels, however one of their

feed materials is de-zinc lead slag, which could be the source of the high zinc concentrations. The USEPA also found no correlation between plant type (i.e. wet or dry kiln) and total metals concentrations.

**Table 4.3: Trace metals analysis of unhydrated CKD and quicklime samples.**

<b>Element (mg/kg)</b>		<b>CKD-A</b>	<b>CKD-B</b>	<b>CKD-C</b>	<b>CKD-D</b>	<b>CKD-E</b>	<b>CKD-F</b>	<b>QL</b>
<b>Arsenic</b>	As	10	12	15	15	<2	18	5
<b>Barium</b>	Ba	382	175	213	183	106	105	493
<b>Beryllium</b>	Be	1.3	0.5	0.9	1.0	0.9	0.7	0.1
<b>Cadmium</b>	Cd	5	1	2	2	20	1	1
<b>Chromium</b>	Cr	38	21	45	33	40	51	11
<b>Cobalt</b>	Co	8	5	5	7	6	9	3
<b>Copper</b>	Cu	54	10	69	18	23	24	7
<b>Lead</b>	Pb	196	98	79	128	1010	101	51
<b>Lithium</b>	Li	36	22	31	31	27	20	2
<b>Molybdenum</b>	Mo	9	5	18	18	12	3	2
<b>Manganese</b>	Mn	381	410	394	517	230	931	3123
<b>Nickel</b>	Ni	25	11	17	61	24	22	6
<b>Selenium</b>	Se	<25	<25	<25	28	<25	<25	<25
<b>Silver</b>	Ag	4.6	<1	2.2	1.1	12.0	<1	<1
<b>Strontium</b>	Sr	438	425	911	150	470	265	372
<b>Thallium</b>	Tl	<25	<25	<25	<25	33	<25	<25
<b>Tin</b>	Sn	<10	<10	<10	<10	<10	<10	<10
<b>Vanadium</b>	V	63	27	59	189	80	38	11
<b>Zinc</b>	Zn	312	32	2886	59	2882	60	105
<b>Zirconium</b>	Zr	40	32	17	43	21	30	4

The elevated levels of some trace metals in the CKD samples is one of the main reasons its potential use in mine effluent treatment was chosen to be studied over other potential applications such as drinking water softening. These trace metals could be released into the water stream being treated, potentially resulting in deleterious effects to human health if ingested in large enough quantities.

#### **4.4 Slaked CKD Quality**

Slaking is the process of mixing quicklime, or in this case CKD, with water in order to create a calcium hydroxide slurry to be used in treating acidic waste streams such as mine water. The parameters used to characterize the reactivity of the CKDs when

slaked in water were pH, conductivity, and calcium ion ( $\text{Ca}^{2+}$ ) content. Both filtered and unfiltered samples were analyzed for all three water quality parameters.

#### 4.4.1 pH and Conductivity

pH was chosen as the major indicator of CKD reactivity for this experiment because of its importance in neutralizing acidic wastewater streams. Conductivity is generally a measure of the ionic strength of a solution, or how many free ions are in solution. Robinson and Burnham (2001) found in their study of dissolution rates of hydrated limes that conductivity increased close to linearly with lime dosage. Conductivity has also been directly related to the concentration of  $\text{Ca}(\text{OH})_2$  in a pure solution, although it also varies with temperature (Boynton, 1980).

Shown in Figure 4.3 are the pH results for the filtered samples and in Figure 4.4 the conductivity results for the filtered samples. The unfiltered samples had slightly higher pH and conductivity values, but follow the same trend (not shown). The data in Figure 4.3 and Figure 4.4 represent the average outcome of three trials or jars, with error bars representing one standard deviation. As can be seen from these graphs, all of the CKD samples and the quicklime sample show the same general trend of increasing pH and conductivity with increasing dosage. Zaki et al. (2007) found pH values of CKD slurries fell between 12 and 13 for solutions containing between 10 and 40 g/L CKD, increasing with increasing concentration. In terms of achieving increased pH with product addition, CKD-D and CKD-F performed the best, and do not show statistically significant differences from quicklime in this regard. This was concluded from an ANOVA test done on CKD-D, CKD-F, and quicklime ( $p$ -value = 0.24), and can be seen from the overlapping error bars on Figure 4.3 for these three samples.



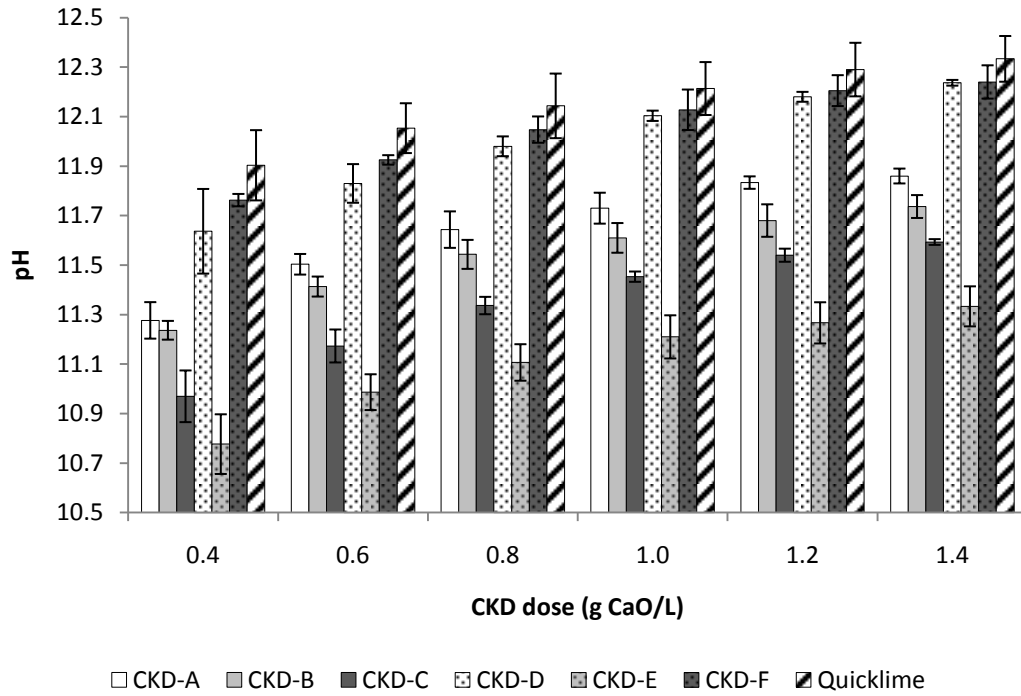


Figure 4.3: Slurry pH versus CKD and quicklime dose (n=3).

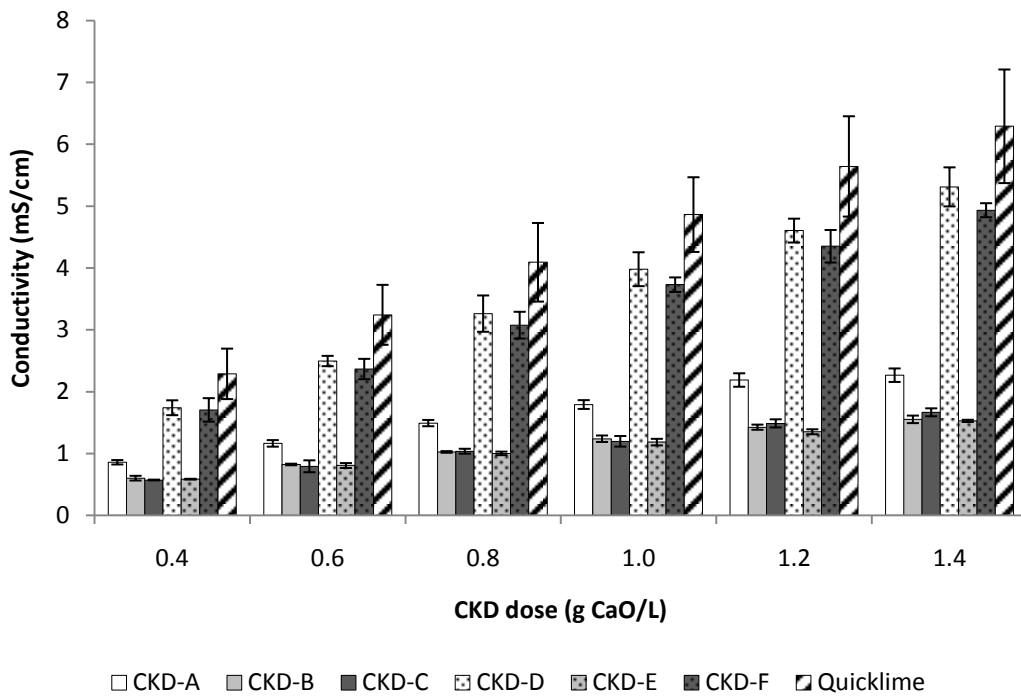
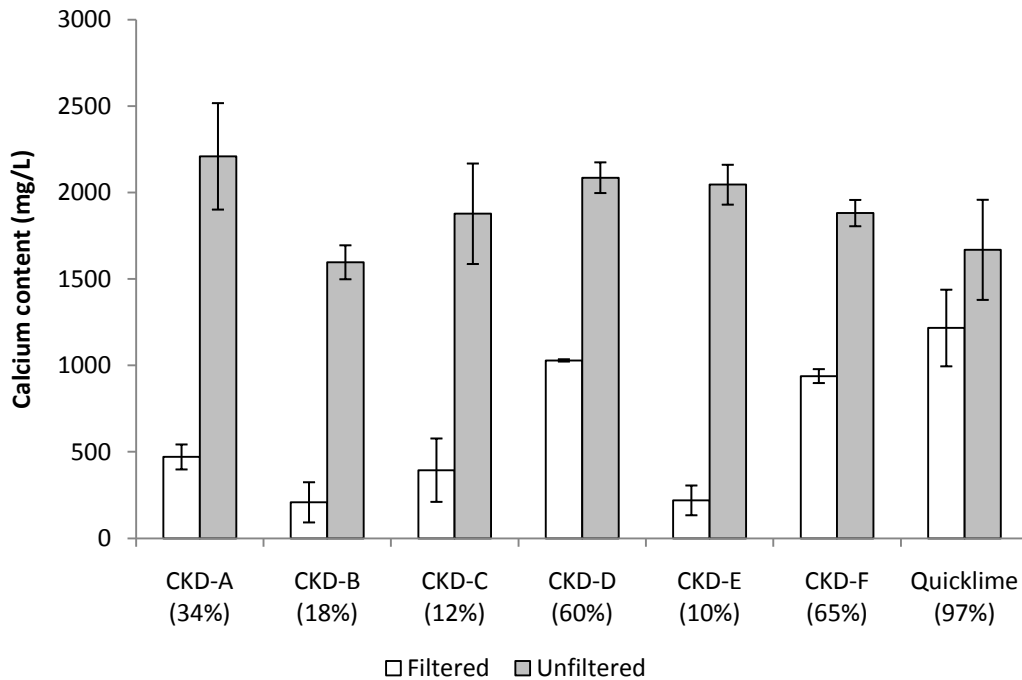


Figure 4.4: Slurry conductivity versus CKD and quicklime dose (n=3).

#### 4.4.2 Calcium

Figure 4.5 presents the calcium concentrations of the slaked solutions, which were found to be much greater in the unfiltered samples than the filtered samples of both the CKD and quicklime slurries. This suggests that there remains a large amount of unreacted calcium in the solids after the slaking period. This is most likely due to the high calcium content but relatively low free lime (i.e. CaO available for reactions) content of the samples, as presented in Table 4.2, above. The percentages in brackets beneath the CKD labels on Figure 4.5 represent the percentage of total CaO content that is as free lime. As seen on this graph, there are smaller differences between the calcium concentration in the filtered and unfiltered slaked samples from CKD-F and quicklime, which have high free lime contents, compared to those of CKD-B, CKD-C, and CKD-E, which have large differences between total and free CaO content.



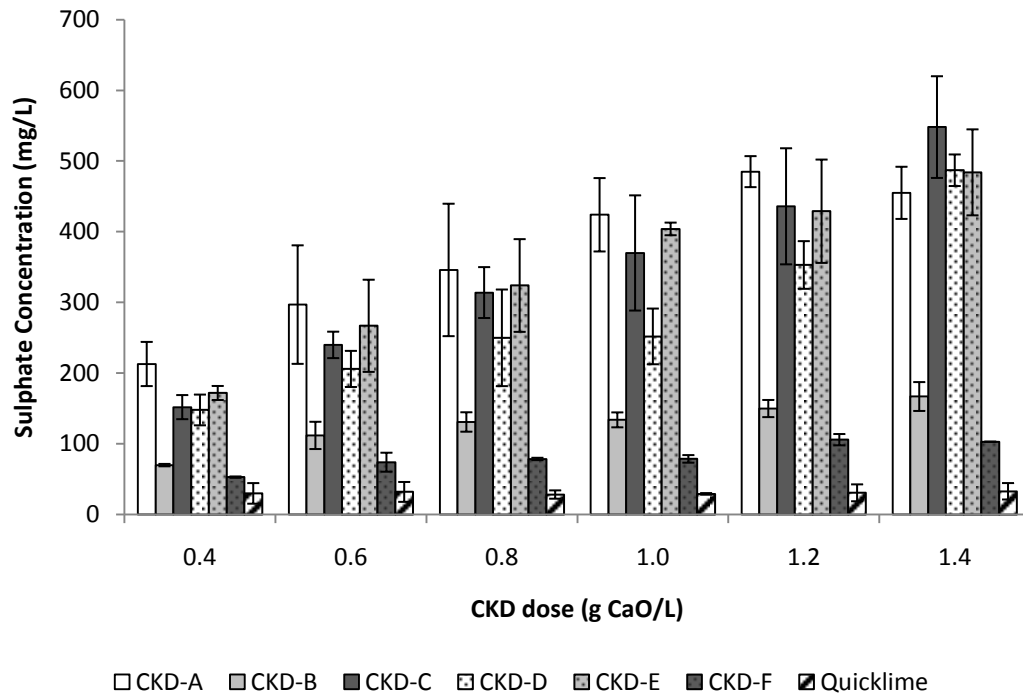
**Figure 4.5: Slurry calcium concentration versus CKD and quicklime dose (n=3). Percentages in brackets represent their percentage of total CaO that is as free CaO.**

#### 4.4.3 Sulphate

Calcium sulphate ( $\text{CaSO}_4$ ) interferes with the solubility of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) in solution, even at very low levels (Boynton, 1980). For this reason, sulphate ( $\text{SO}_4^{2-}$ ) levels were measured in the solutions to determine if this could lower the effectiveness of the treatment. Sulphate measurements were only performed on test slurries made with the second set of CKD samples used in this study. The results in Figure 4.6 show that sulphate ions measured in the filtrate of the CKD slurries were consistently 1.8 to 16 times higher than those measured in the filtrate of the quicklime slurry sample. Overall, the sulphate concentrations in the filtrate from the slaked CKD samples were found to be less than 500 mg/l, and it is important to note that most countries in the world recommend a drinking water standard for sulphate between 250 and 500 mg/l. Sulphate ions have the potential to negatively affect the performance of CKD by reacting with the calcium that it contains and depressing the solubility of CaO. Sulphate ions could also indicate the potential for scaling of infrastructure due to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) precipitation. However, in environmental applications such as neutralization of acid rock drainage (ARD), the feed streams can have  $\text{SO}_4^{2-}$  concentrations in excess of 5000 mg/l; the added sulphate from the CKD would be minimal in comparison.

#### 4.4.4 Dissolved Solids

The amount of solids dissolved in each of the slaking trials was calculated by measuring the total suspended solids (TSS) of the slaked CKD and quicklime solutions and subtracting this from the initial amount of dry material added. The amount of slurry lost (100 mL) due to sampling was accounted for by dividing the TSS of the slaked sample by 0.9. The percent of solids dissolved during the slaking trials for each of the CKDs was less than that of quicklime. The average dissolved solids were 29, 26, 31, 52, 30, and 47 % for CKDs A, B, C, D, E, and F, respectively, while for quicklime it was 65 %. This again shows that more of the CKDs with higher free lime contents (i.e. CKD-D and CKD-F) is reacting in solution, as well as for quicklime. In addition, a sample of the solids remaining after filtering the slurry produced from slaking CKD-F was analyzed for major oxides content. Results showed that total CaO content decreased by 37 %, which



**Figure 4.6: Slurry sulphate concentrations versus CKD and quicklime dose (n=3).**

was the initial free lime content of the sample. Other major oxide weight percentages that decreased were:  $K_2O$  by 12 %,  $Na_2O$  by 13 %, and  $SO_3$  by 25%, verifying that these oxides will dissolve during slaking and affect the solubility of the CKD. All other major oxide species increased in weight percentage after slaking.

#### 4.4.5 Correlations to Physicochemical Characteristics

Statistical comparisons were performed in order to determine if there is a physical or chemical characteristic of CKD that can be used to estimate its reactivity during slaking, or how effective it will potentially be in treating acidic effluents. The pH achieved at a CaO dose of 1.2 g/l for each of the CKDs was compared to several physical and chemical characteristics: CaO content, free CaO content, specific surface area by the Blaine Method, and the 50 % finer or median particle size. Seen in Table 4.4, the total and free lime content as well as the TRO and TRO -  $SO_3$  values all show a strong correlation to the reactivity of CKD as pH achieved in solution. Additionally, coefficients

of determination indicate an *inverse* relationship between pH achieved and surface area, and no correlation between pH and particle size.

**Table 4.4: Coefficients of determination for several CKD characteristics compared with the pH of slaked solutions at a total CaO dose of 1.2 g/l.**

	Free CaO	Total CaO	Surface Area	Particle Size	TRO	TRO - SO <sub>3</sub>
R <sup>2</sup>	0.9041	0.9300	0.7174	0.4307	0.9228	0.9002

Moropoulou and colleagues (2001) found in their study on limestone and quicklime properties that the specific surface area can be an indicator of quicklime reactivity. That study found that the greater the specific surface area, the more reactive the quicklime, based on temperature increase when mixed with water. It can be assumed that these properties would translate to CKD particles as well. However, the results presented above indicate otherwise. It seems counterintuitive that CKD samples that have particles with larger surface areas would give lower pH values. However, it is important to note that all of the slaked CKD samples demonstrated pH levels greater than 11.0, and that particle size distribution and specific surface size analysis were conducted on bulk CKD samples that were not specific to the type of particles present in the CKD samples (e.g., CaO particles versus SiO<sub>2</sub> particles). This, in combination with the strong relationship found between the free lime content of CKD on pH achieved, would potentially influence any impact surface area may have on CaO dissolution and CKD reactivity during the experiments.

#### **4.5 Acid Neutralization Potential**

Acid neutralization tests were performed as part of this study using each of the CKD samples to determine the viability of using CKDs with different properties to treat acidic wastewater. Figure 4.7 shows the results of the acid neutralization trials, in grams of CKD per 1000 ml of sulphuric acid versus pH achieved after 30 minutes. The results show that CKD-D and CKD-F, the two CKD samples with the highest free CaO content and those that responded best in the slaking trials, achieved the highest pH at the lowest CKD dosage, and were closest to the results from the quicklime sample. Specifically, CKD-D required 56.6 g to achieve a pH of 10, while CKD-F required 39.0 g, and quicklime, 23.3g. However, all CKD samples achieved pH values greater than 10, at

varying doses of CKD for each. CKD-E, which has the lowest free lime content, required 287 g to achieve a pH of 10. Blends of either 25 % CKD with 75 % quicklime or 75 % CKD with 25 % quicklime were also tested. Results from these tests showed that the 25 % CKD blends responded similarly to quicklime, while the 75 % CKD blends responded similarly to the pure CKD samples. These results show potential application for even CKD samples with low free lime contents to be effective at neutralizing acidic wastewater.

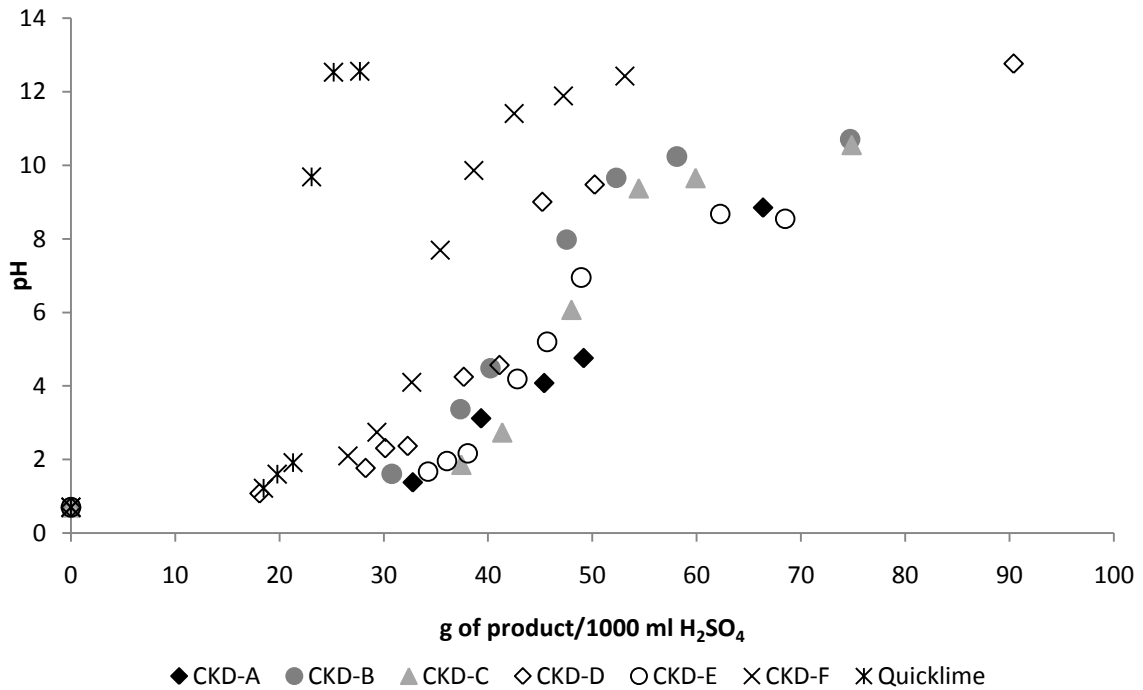


Figure 4.7: pH versus CKD and quicklime dose in 1L of concentrated sulphuric acid.

#### 4.6 Conclusions

Physico-chemical characteristics of the six CKD samples analyzed for this study were comparable to other previously published studies on CKD. The main characteristics of the CKD samples were found to vary widely from plant to plant, just as cement does. However, CKD samples were found to have low variability within each plant. This was determined by comparing the physico-chemical characteristics of two separate samples taken from each plant, one in November of 2007 and one in July 2008. The low

variability can be seen from the low deviations in particle size and specific gravity (Table 4.1) and major oxides distribution (Table 4.2).

It was found that the CKD samples tested have smaller particle sizes and higher specific surface areas than a commercial quicklime sample, which is the industry standard for treating acidic effluents like ARD. The kiln with a precalciner (Plant F), and that with a preheater (Plant D), produced CKD samples with larger particle sizes than those from the long dry kilns (Plants A, B, and E), confirming earlier studies (Peethamparan, 2006; USEPA, 1993; Todres et al., 1992). The one wet kiln (Plant C) gave a median CKD particle size between that of the long dry kilns and the kilns with a preheater or precalciner, validating the USEPA's conclusions.

The main oxides present in the tested CKDs are those of calcium, aluminum, silicon, sulphur, potassium, and magnesium. The quicklime sample tested contains only traces of oxides other than calcium. Total and free lime contents were found to be significantly lower in the CKD samples than in quicklime. The total reactive oxides value (TRO) proposed by Collins and Emery (1983) was modified to include the effect of reactions involving sulphur on the reactivity of CKD. This new value (TRO - SO<sub>3</sub>) correlated linearly to free lime content more strongly than the other values proposed (CaO + MgO - LOI and TRO).

Samples of CKD-D and CKD-F, which were found to have the highest free lime contents, showed statistically comparable results to the commercial quicklime sample when slaked, in terms of pH achieved, conductivity, and calcium ion (Ca<sup>2+</sup>) content. The main factors affecting the reactivity of CKD were found to be total and free lime content, and as a consequence also the TRO, CaO + MgO - LOI, and TRO - SO<sub>3</sub> values. These values could potentially be used as an indicator of how reactive a CKD to be used in neutralizing acidic wastewaters will be when slaked with water. Collectively, the results of the slaking experiments and acid neutralization tests show that even the CKD samples with low free lime contents achieved high pH values, demonstrating the viability of the reuse of CKD in acidic wastewater neutralization applications.

## **Chapter 5: Evaluation of Cement Kiln Dust Slurries for Neutralization and Precipitation of Metals from Mine Water**

Bench-scale experiments were performed in order to determine the effectiveness of using calcium hydroxide slurries made from CKD to treat acidic mine water contaminated with high concentrations of metals, specifically zinc and iron. This chapter looks at the neutralizing capability of four CKD samples as well as several properties of the calcium hydroxide slurries used for treatment. The capacity of the CKD slurries to precipitate zinc and iron from the mine water was also tested and is discussed here. The performance of the CKD slurries was compared to that of a standard lime slurry and also correlated to several dry CKD properties. Full data sets for bench-scale mine water treatment experiments are included in the Appendix.

### **5.1 Introduction**

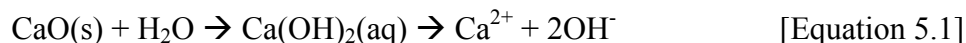
Mine water from ferrous- and base-metal mines is often contaminated with acidity and dissolved metals due to weathering of sulphide formations that the ore occurs as (Johnson & Hallberg, 2005; Younger et al., 2002; Kuyucak, 2001). This acidic effluent is termed acid rock drainage (ARD) or acid mine drainage (AMD), though the issue is not confined to the mining industry. Acidity is generated from sulphide minerals like pyrite ( $\text{FeS}_2$ ) and sphalerite ( $\text{ZnS}$ ) that are exposed to oxygen and water either naturally or due to mining or other anthropogenic activities (Johnson & Hallberg, 2005; Younger et al., 2002; Brown et al. 2002; Kuyucak, 2001). Contaminated water from mining operations can have numerous detrimental effects on the receiving ecosystems (Johnson & Hallberg, 2005).

Many jurisdictions have regulations in place to ensure that contaminated waters from mining operations are treated effectively prior to discharge. The current most widely used and reliable treatment for ARD is active treatment using alkaline addition, with the most cost effective alkaline material being quicklime or hydrated lime (Johnson & Hallberg, 2005; Younger et al., 2002; Brown et al., 2002). In addition to being cost effective in most cases, active treatment with lime has the advantage of being able to treat large volumes of water with a compact footprint as well as being able to rapidly adapt to



changes in influent contaminant concentrations. This type of treatment plant uses lime in the form of a slurry to raise the pH of the mine water and precipitate soluble metals as hydroxides, which can then be removed through settling or other clarification processes (Johnson & Hallberg, 2005; Younger et al., 2002; Brown et al., 2002).

In an active lime treatment plant, quicklime is mixed with water to generate a slurry in a process called slaking. As defined by Boynton (1980) a lime slurry is a colloidal suspension that has the consistency of thick cream. Lime slurries used in active lime treatment processes typically have a solids content between 25 and 35 % (Boynton, 1980). Other sources report slurry concentrations of 6 % w/w (Couton et al., 2003), 10 % (Huck, Murphy, & LeClair, 1977), and 16 to 40 % w/v (Hassibi, 2009). The slaking of lime with water hydrates CaO to form calcium hydroxide (Ca(OH)<sub>2</sub>), which dissociates into calcium and hydroxide ions in solution, following Equation 5.1. Hydroxide ions (OH<sup>-</sup>) can then combine with dissolved metal ions in mine water to precipitate solid metal hydroxides following Equation 5.2 which are then removed through settling or filtration mechanisms (Younger et al., 2002; Brown et al., 2002).



The dose of lime slurry added to the mine water depends on which metals are present, their concentrations, and legal discharge requirements. Because the pH of minimum solubility of metal hydroxides varies by metal species, a different pH is required depending on the type and extent of metal contamination. It has been found that a pH above 9.0 or 9.5 is effective for precipitation of metals such as zinc, cadmium, copper, manganese, and magnesium (Kurniawan et al., 2006; Chareerntanyarak, 1999; Zinck and Aubé, 1999; Huck & LeClair, 1978; Huck Murphy, & LeClair., 1977; Huck Murphy, Reed, & LeClair., 1977).

## 5.2 Materials and Methods

Four of the CKD samples characterized in Chapter 4 were selected for the bench-scale mine water treatment tests: CKD-A, CKD-B, CKD-C, and CKD-F. These samples were chosen in order to evaluate CKDs with varying particle sizes, surface areas, and free

lime contents, as outlined in Table 5.1. The properties of the commercial quicklime sample used in the study (Graymont, Inc., Havelock, NB, CA) are also included in Table 5.1 for comparison.

**Table 5.1: Physicochemical properties of CKD samples.**

<b>Sample ID</b>	<b>Specific Surface Area (m<sup>2</sup>/g)</b>	<b>Particle Size (50 % finer)</b>	<b>Total Lime (wt %)</b>	<b>Free Lime (wt %)</b>
CKD-A	0.502	8.5	44	15
CKD-B	0.350	15.9	48	9
CKD-C	0.471	20.5	40	5
CKD-F	0.393	21.2	57	37
Quicklime	0.164	32.0	90	87

Mine water samples were collected from Xstrata Zinc’s Brunswick Mine near Bathurst, New Brunswick, Canada. Key characteristics of the mine water are listed in Table 5.2. The low pH combined with high concentrations of iron and zinc in their dissolved form signifies that the mine water requires treatment prior to discharge from the site. A complete trace metal scan is included in Chapter 3, Table 3.2.

**Table 5.2: Mine water characteristics (n=24).**

<b>Parameter</b>	<b>Mine Water</b>
pH	2.4 ± 0.1
TSS (mg/L)	70 ± 50
Total Zinc (mg/L)	122 ± 15
Dissolved Zinc (mg/L)	115 ± 18
Total Iron (mg/L)	429 ± 78
Dissolved Iron (mg/L)	399 ± 78

The Brunswick lead/zinc mine uses the Conventional High Density Sludge (HDS) process to treat their mine water. The treatment plant uses quicklime slaked onsite and mixed with recycled sludge to neutralize the mine water to a pH setpoint of 9.4 to 9.5. Treated water is then dosed with a polymer at a concentration of 2 ppm and sent to a clarifier where the metal hydroxides are removed through settling. Clarifier overflow is sent to a polishing pond prior to being discharged. Effluent discharged from this pond must meet the guidelines of the Metal Mine Effluent Regulations (MMER, 2002). This includes having a discharge pH of between 6.5 and 9.5 and a total zinc concentration in effluent of less than 1.0 mg/L in a single grab sample and less than 0.5 mg/L averaged

over 30 days. Treated mine water also cannot be acutely toxic to aquatic species like rainbow trout.

The capacity of the CKD and quicklime samples to neutralize mine water was evaluated following a modified version of ASTM standard C 400-98. The pH of solutions containing 2.5 g of CKD and varying volumes of mine water were measured for 30 minutes during these tests. The ASTM standard, used in Chapter 4 to determine neutralization capabilities of the CKD samples with a standard acid solution, was modified by using mine water samples in place of sulphuric acid.

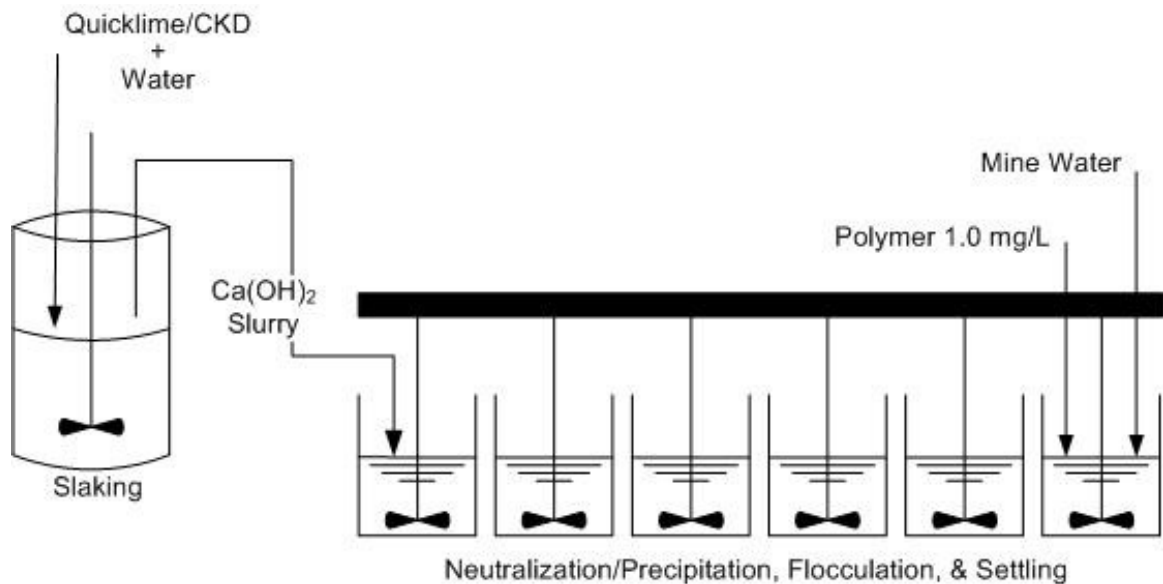
Calcium hydroxide slurries were prepared from each CKD and quicklime sample using Milli-Q water in order to eliminate the potential for interference from ions in tap water. In order to determine the effect of calcium hydroxide slurry concentration on the precipitation of metals in mine water samples with CKD and quicklime, a 5 % solids content slurry was tested in addition to a 25 % slurry. Specifically, 250 grams of CKD or quicklime were added per litre of Milli-Q water to generate the 25 % slurries and 50 g/l of CKD or quicklime for the 5 % slurries. A magnetic stir bar was effective for simulating slaking of the 5 % slurries but it could not mix the 25 % slurries. Therefore, an electric stirrer (Model 1750, Arrow Engineering, USA) was used with a 10 cm diameter circular PVC mixing vessel to simulate slaking of the 25 % CKD and quicklime samples. Slurries were mixed for a minimum of 5 minutes prior to testing to ensure dissolution of soluble oxides.

Several tests were performed in order to characterize the CKD slurries that were used in the bench-scale mine effluent treatment trials. The solids content of the slurries was determined by dividing the weight of the dried solids by the weight of the slurry sample prior to drying at  $104 \pm 1^\circ\text{C}$ . The specific gravity of the slurries was calculated by dividing the weight of a sample of slurry by the weight of an equal volume of Milli-Q water at  $4^\circ\text{C}$ . The preceding tests are outlined in *Standard Methods* (APHA et al., 2005). The TSS concentrations were also determined using *Standard Methods*. Calcium concentrations were measured using atomic absorption spectrometry (AAAnalyst 200, PerkinElmer) and pH was measured with variable temperature electrodes (accuFlow,

Fisher Scientific) using an XL50 meter from Fisher Scientific. All tests were performed in triplicate.

A schematic of the bench scale experimental set up is shown in Figure 5.1. A standard jar tester (Phipps & Bird, Fisher Scientific), was used to simulate the active treatment of the mine water (i.e. neutralization and precipitation) in batch tests. One litre of mine water was added to each of the six 2 L capacity jars and then dosed with  $\text{Ca}(\text{OH})_2$  slurry generated from either one of the test CKDs or quicklime. The volume of slurry used necessary to bring the mine water sample to a pH of 9.5 varied by CKD sample used. It was first estimated from the mine water neutralization experiments and then refined by trial and error. The pH setpoint of 9.5 was chosen to target the minimum solubility of zinc (Kurniawan et al., 2006; Charerntanyarak, 1999; Zinck and Aubé, 1999; Huck & LeClair, 1978; Huck et al., 1977), and is also the target pH of the active lime treatment plant for the mine water used in this study. The mine water samples were then rapid mixed for one minute at 150 rpm, or a velocity gradient (G-value) of approximately  $140 \text{ s}^{-1}$ , after which 50 ml samples were taken from the sample ports on the jars to determine the precipitation performance of the slurries. These samples were analyzed for total (unfiltered) and soluble (filtered) zinc and iron concentrations, in addition to pH. Four replicates of the batch jar tests were performed for each of the 25 % slurries, and three replicates were conducted using the 5 % slurry treatments. All experiments were performed at room temperature, approximately  $22^\circ\text{C}$ .

The total and soluble zinc and iron concentrations of the samples were measured by atomic absorption spectrometry (AAAnalyst 200, PerkinElmer). Samples to be analysed for soluble metals were filtered through a  $0.45 \mu\text{m}$  polysulfone membrane (GE Water & Process Technologies) filter prior to being acidified to a pH less than 2 using nitric acid for analysis (APHA, 2005). In order to accurately calculate the percent precipitation of metals from the treated mine water, samples of the untreated mine water were also analysed at the time of each jar test and analyzed for zinc and iron as well as pH and total suspended solids (TSS). The average of these results is presented in Table 5.2. The total zinc and iron in the samples does not change before settling begins, so the percent



**Figure 5.1: Diagram of experimental setup.**

precipitation was calculated as the amount of soluble metal ion (i.e. that passing through a 0.45  $\mu\text{m}$  membrane filter) decrease from the mine water analysis to the treated sample taken after the one minute rapid mix stage of the jar tests. Error bars on graphs and error terms in text and tables represent one standard deviation from the mean.

### 5.3 Mine Water Neutralization

The potential for the CKD samples to neutralize acidic mine water used for this part of the study was found following the same methods as for the synthetic acid solution in the previous chapter. Figure 5.2 presents the results of these tests, in pH achieved after 30 minutes of mixing various amounts of dry material with one litre of mine water. The horizontal line represents the target pH of 9.5, and is how approximate doses of CKD and quicklime slurries were found for the bench-scale treatment experiments. The graph shows that CKD-F, with the highest free lime content, required the addition of only slightly more material than quicklime to reach the same pH target. This is in contrast to the remaining CKD samples (i.e. CKD-A, CKD-B, and CKD-C), which all required significantly more product addition than quicklime to reach the target pH.

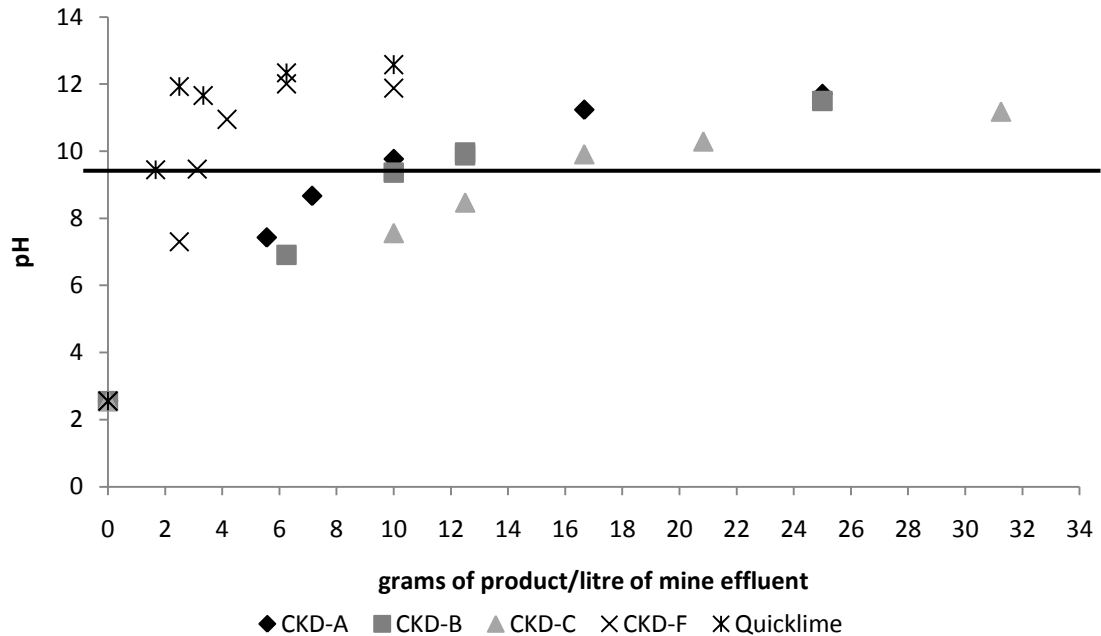


Figure 5.2: pH versus CKD and quicklime dose in 1L of mine water.

#### 5.4 Calcium Hydroxide Slurries

The slurries to be used for the bench-scale treatment of mine effluent were analyzed for their percent solids, pH, TSS concentration, and calcium concentration. The percent solids of the 5 % and 25 % slurries used in the study are shown in Figure 5.3. The measurements from the test can be seen to be below the actual concentrations of solids added (i.e. 25 % and 5 %), most likely due to experimental error. The pH of all CKD and quicklime slurries at both concentrations were found to be between 12 and 13, indicating high potential for neutralization of acidic mine water.

The total calcium and total suspended solids concentrations measured in the slurries are shown in Figure 5.4. The results show that CKD-C had the lowest TSS concentrations of all samples of both the 5 and 25 % slurries. Other CKDs have TSS concentrations near but below the initially added amounts of 250 and 50 g/L. The quicklime slurries had average TSS concentrations of  $277 \pm 7$  and  $46 \pm 7$  g/L. Quicklime had the highest calcium concentrations of both the 5 and 25 % slurries.

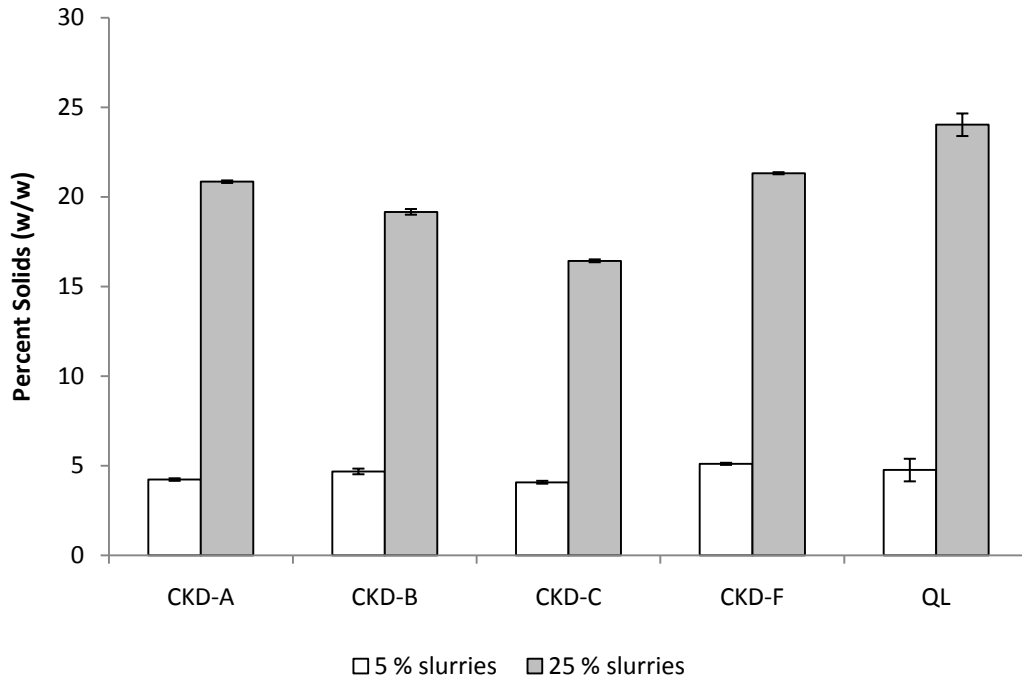


Figure 5.3: Percent solids in prepared calcium hydroxide slurries.

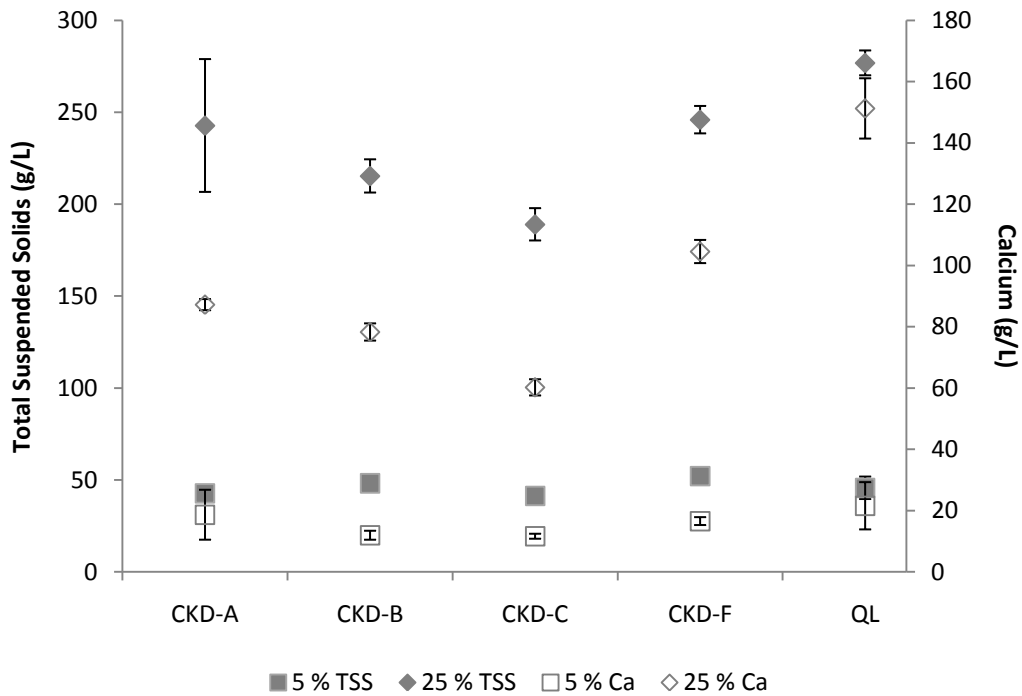


Figure 5.4: Calcium and TSS concentrations in calcium hydroxide slurries versus CKD or quicklime.

These tests were performed mainly to determine the variability of these characteristics within each of the slurries. This was determined to be low due to the small variation between values found in repeated samples of each slurry for all parameters measured, as indicated by the error bars on Figures Figure 5.3 and Figure 5.4. Correlations between the parameters analysed on the CKD slurries to several characteristics of the dry CKD samples were also calculated. No strong correlations were found between the percent solids of the slurries or their TSS concentrations and any physicochemical properties of the dry CKD samples. The coefficients of determination found for linear regressions of pH and calcium with several CKD physicochemical properties are shown in Table 5.3.

**Table 5.3: Coefficients of determination ( $R^2$ ) for linear regressions with pH and  $Ca^{2+}$ .**

Property Correlated	pH		Calcium	
	5 %	25 %	5 %	25 %
Median Particle Size	0.3321	0.0523	0.3021	0.0041
Surface Area	0.1154	0.4042	0.1448	0.0984
Total Lime	0.1706	0.9873	0.1209	0.7956
Free Lime	0.3765	0.8055	0.3574	0.8572
TRO*	0.3860	0.9604	0.3196	0.9495
TRO - SO <sub>3</sub>	0.2636	0.8379	0.2435	0.8005

\*total reactive oxides = (CaO + MgO) - LOI + (K<sub>2</sub>O + Na<sub>2</sub>O)

The strongest correlations found for the pH of the slurries was for the 25 % slurries with the total lime and TRO values, followed by TRO - SO<sub>3</sub> and free lime, values which are all strongly interrelated. The calcium concentration of the 25 % slurries showed a strong linear relationship to TRO, with the total and free lime content and TRO - SO<sub>3</sub> value correlating less strongly. The pH and calcium concentration of the 5 % slurries did not indicate any linear relationships to dry CKD characteristics.

## 5.5 Neutralization of Mine Water and Precipitation of Metals

The results of the bench-scale precipitation experiments using the 25 % slurries are presented here. The performance of each of the four CKD slurry samples tested is compared to that of the remaining three CKD slurries and the quicklime slurry. To this end, the dose of each material required to raise the pH of the mine water to the target of 9.5 was evaluated. In addition, the extent of precipitation for each CKD was examined in



terms of coagulated particle characteristics as well as the precipitation of zinc and iron. The effect of lowering the slurry concentration to 5 % is also discussed.

### 5.5.1 Calcium Hydroxide Slurry Dose

The actual volumes of the 25 % slurry used in the mine water treatment experiments are tabulated below, along with the corresponding equivalent weight of dry material present within these volumes. The mass of material that was required to achieve a pH target of 9.5 in the 1 L mine water samples (Table 5.4) is much higher than what was estimated from the neutralization tests (Figure 5.2) for the CKDs with lower free lime contents (i.e. CKD-A, CKD-B, and CKD-C). This is most likely due to the longer reaction time between the CKD and water in the neutralization tests. Those samples were mixed for 30 minutes prior to testing the pH, while the experiments discussed here had only one minute of mixing. Additionally, CKDs with lower lime contents invariably have higher amounts of other oxides, some of which are known to slow the dissolution of CaO in water (Boynton, 1980).

**Table 5.4: Slurry volume (25 % solids) and equivalent amount of dry material added to 1 L mine water samples (n=4).**

Sample ID	Slurry Added (ml)	Material Added (g)
CKD-A	53.8 ± 2.5	13.4 ± 0.7
CKD-B	70.0 ± 0.0	17.5 ± 0.0
CKD-C	115 ± 10	28.7 ± 2.5
CKD-F	13.0 ± 0.0	3.2 ± 0.0
Quicklime	8.0 ± 0.0	2.0 ± 0.0

An inverse relationship was found between the reactive oxides values of the dry CKD samples and the amount of material required to raise the pH to 9.5 in the jar tests. To achieve the pH target of 9.5, additional dry material was required to be added the lower the percentage of reactive oxides the CKD contains, and this varied linearly. The strongest correlation was found between the amount of material added and TRO, which gave an  $R^2 = 0.96$ . The correlation to CaO + MgO - LOI had an  $R^2$  of 0.92, the correlation to free lime an  $R^2$  of 0.84, and to TRO - SO<sub>3</sub>, 0.79. These regressions are

shown in Figure 5.5, which plots the mass of material added for the four CKDs tested against the weight percentage of the various reactive oxides values.

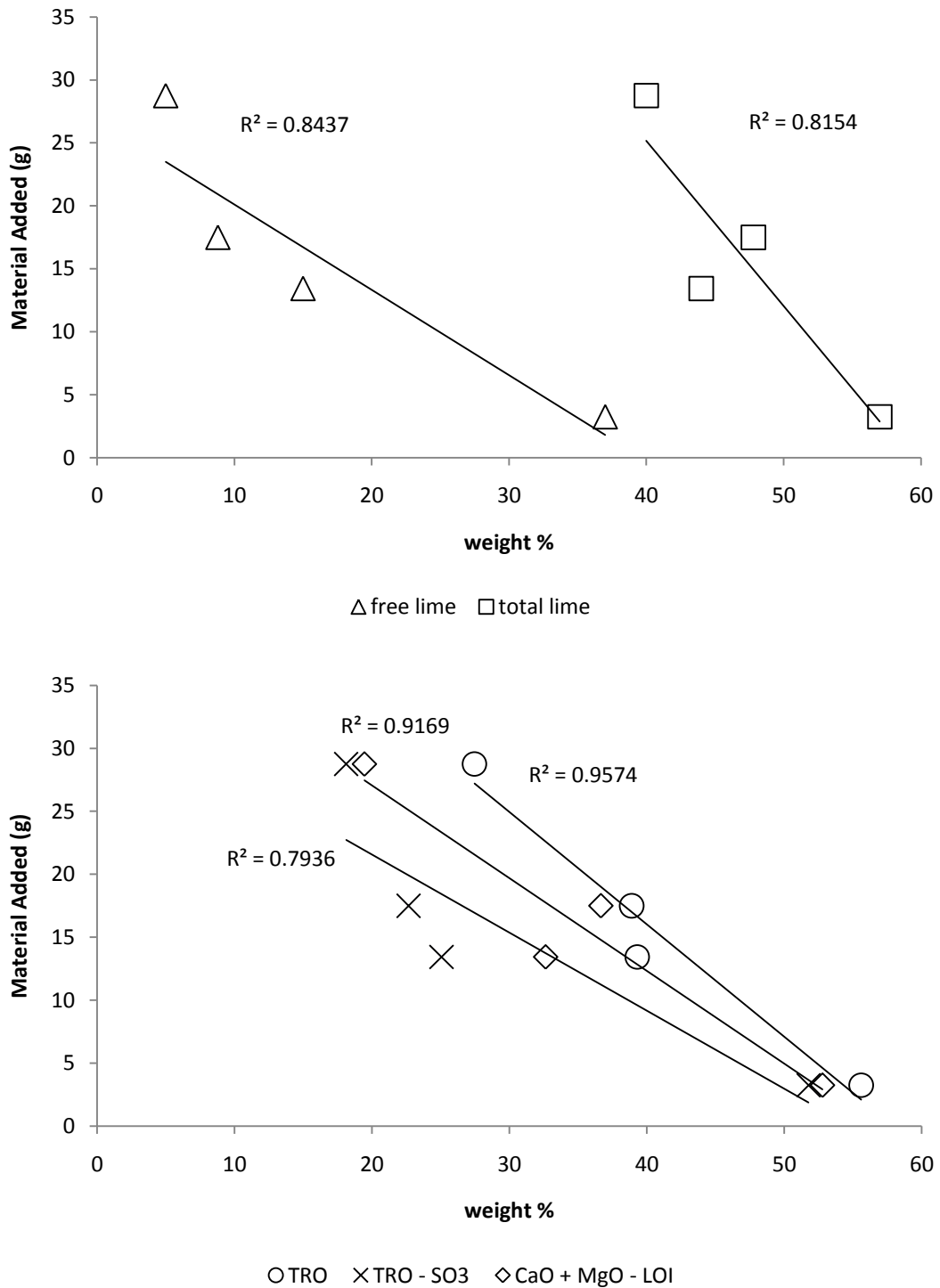
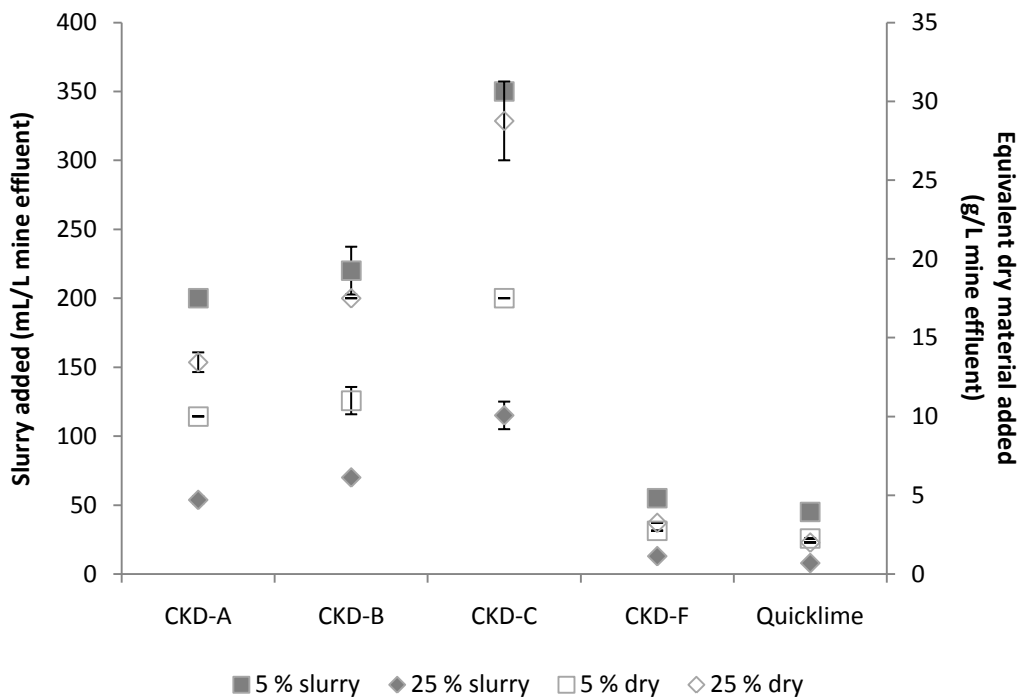


Figure 5.5: Linear regressions for dry alkaline material added to reach pH 9.5.

### 5.5.1.1 Effect of Slurry Concentration

A 5 % solids concentration slurry was tested in addition to the 25 % slurry to determine if a lower slurry solids concentration would have an effect on treatment efficacy. In terms of the amount of CKD or quicklime required to achieve the target pH of 9.5, Figure 5.6 shows that while the lower solids concentration slurry required the addition of much higher volumes of slurry, it actually translated to less dry material being used. In other words, treatment with the 25 % slurries required lower volumes of slurry, but higher amounts of dry alkaline material to achieve the same pH target as the 5 % slurries. This finding was more pronounced in the lower free lime content CKDs, and again is most likely mainly due to the higher concentration of interfering oxides in these samples.

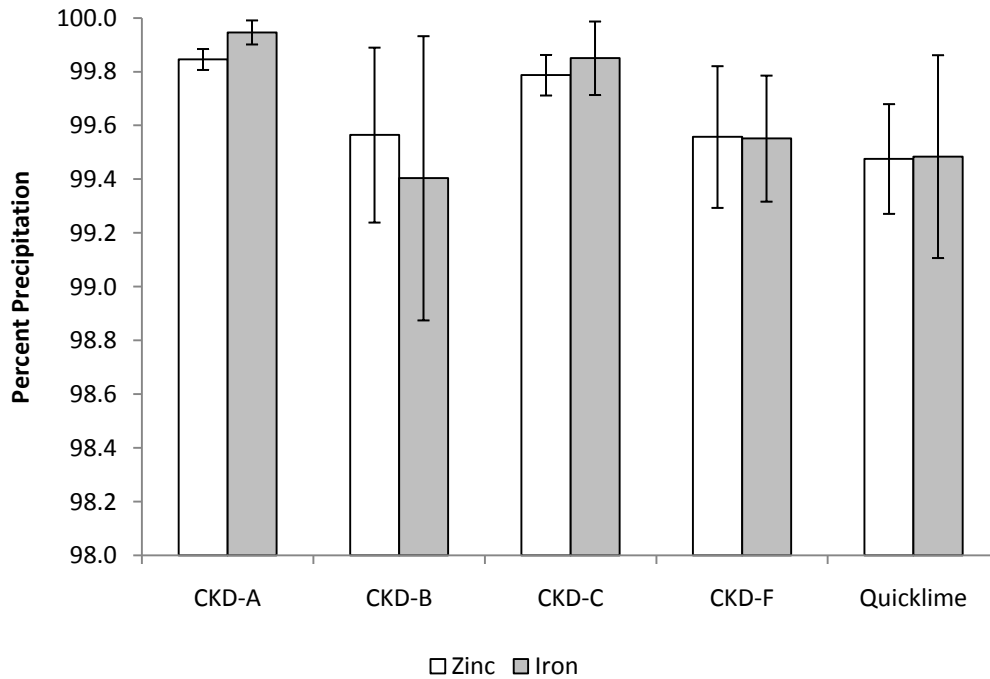


**Figure 5.6: Slurry volume and equivalent amount of dry material added to 1 L of mine water for both 5 % (n=3) and 25 % (n=4) solids slurries.**

### 5.5.2 Precipitation of Metals

The mine water samples treated with the 25 % CKD and quicklime slurries were found to result in more than 99 % precipitation of the soluble zinc and iron contained in

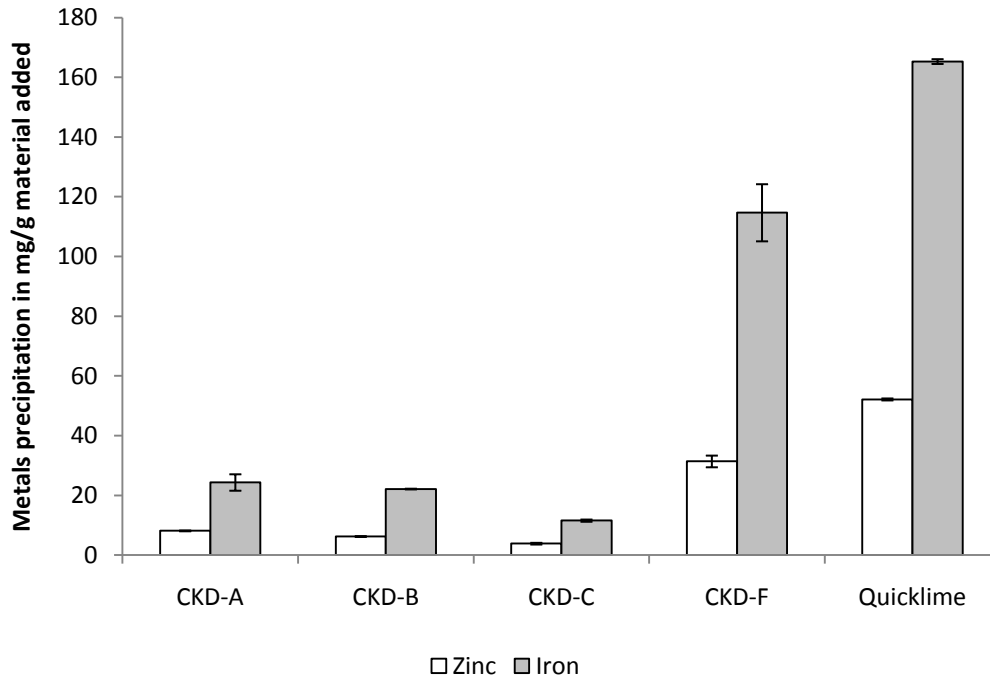
the untreated mine water, as shown in Figure 5.7. This is in agreement with results from previous studies that found greater than 99 % removal of metal ions in synthetic solutions at optimal mixing conditions after filtration of samples treated with either solid CKD or its leachate (Zaki et al., 2007; El-Awady & Sami, 1997). One of those studies used a larger pore size filter (1.5  $\mu\text{m}$ ), however, and the other one of unspecified pore size. Additionally, none of the samples treated with CKD in this study gave statistically significantly different precipitation percentages from those treated with quicklime.



**Figure 5.7: Precipitation of zinc and iron (n=4).**

No correlations were performed on the percent precipitation of the samples because the treatment of mine water samples with all 25 % CKD and quicklime slurries resulted in close to 100 % precipitation of target metals. The degree of precipitation appears to depend solely on pH, which is achieved based on the volume of CKD or quicklime slurry that is added to the mine water. This slurry volume added in turn depends on the free lime and reactive oxide content of the samples, as discussed in the preceding chapter. CKDs with low free lime and reactive oxide content required that more solid material, and therefore more slurry, be added to mine water to achieve the same pH and level of precipitation as quicklime than those with high free lime. Figure 5.8

shows that the percentage of metal precipitation achieved per gram of material added was much lower for CKD-A, CKD-B, and CKD-C than for CKD-F and quicklime.

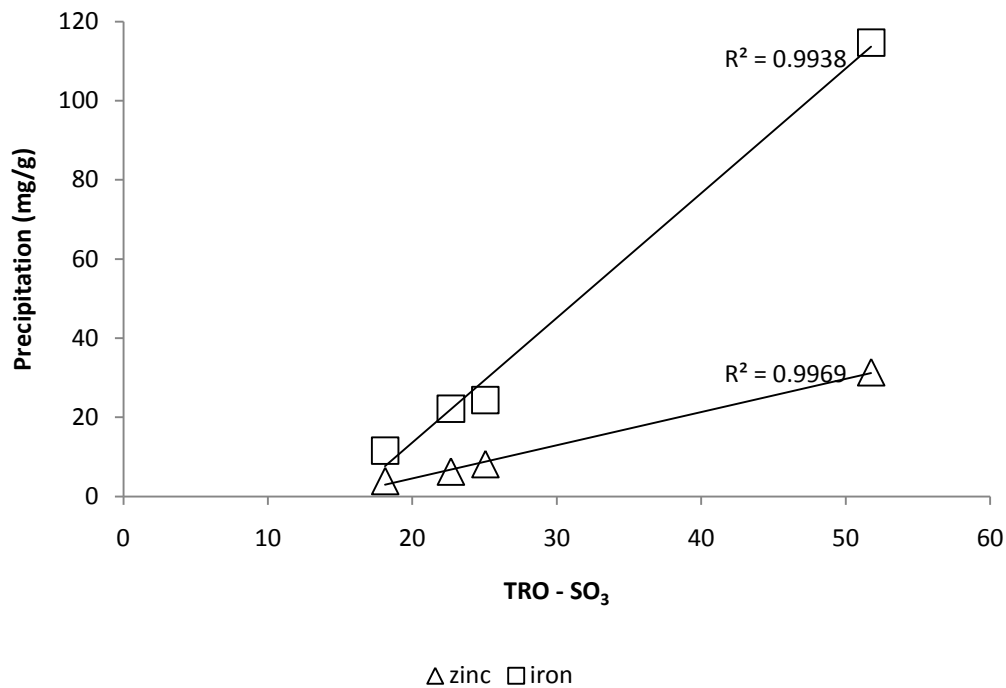


**Figure 5.8: Precipitation of metals per gram of material added (n=4).**

The relationship between reactive oxide content of the dry CKD samples and precipitation is again demonstrated in the correlations between precipitation per gram of material added and TRO - SO<sub>3</sub>, with an R<sup>2</sup> of 0.9968 for zinc and 0.9938 for iron. The graph of these linear relationships is shown in Figure 5.9. The R<sup>2</sup> for this correlation with free lime is 0.9746 for zinc and 0.9614 for iron, also pointing out, again, the strong correlation between free lime and TRO - SO<sub>3</sub>. Correlations to particle size, surface area, total lime, TRO, and CaO + MgO - LOI all gave R<sup>2</sup> values less than 0.90, the threshold for the 95 % confidence level.

#### 5.5.2.1 Effect of Slurry Concentration

The mine water samples treated with the 25 % CKD and quicklime slurries all resulted in better precipitation of both zinc and iron than those treated with the 5 % slurries, as is apparent from Figure 5.10. Addition of the 5 % slurries introduced less



**Figure 5.9: Linear regressions for TRO - SO<sub>3</sub>.**

solids to the mine water to be treated to reach the same pH target as the 25 % slurries, as discussed above. These results indicate that the higher solids density of the 25 % slurries will give better removal of metals as well, since metal ions must be precipitated in order to be removed efficiently through settling.

All mine water samples treated with CKD and quicklime slurries showed a statistically significant difference in metals precipitation per gram of material added between the 5 % and 25 % concentration slurries except for CKD-A with iron, which showed no difference (Figure 5.11). More CKD was added with the higher concentration slurries to reach the same pH. The low free lime content CKDs achieved better precipitation per gram added with the lower 5 % slurries; CKD-F and quicklime the opposite. It should be noted that the 5 % quicklime slurry treated samples actually received more quicklime by weight than the 25 %, unlike with the CKD samples, though the difference was only 0.25 grams.

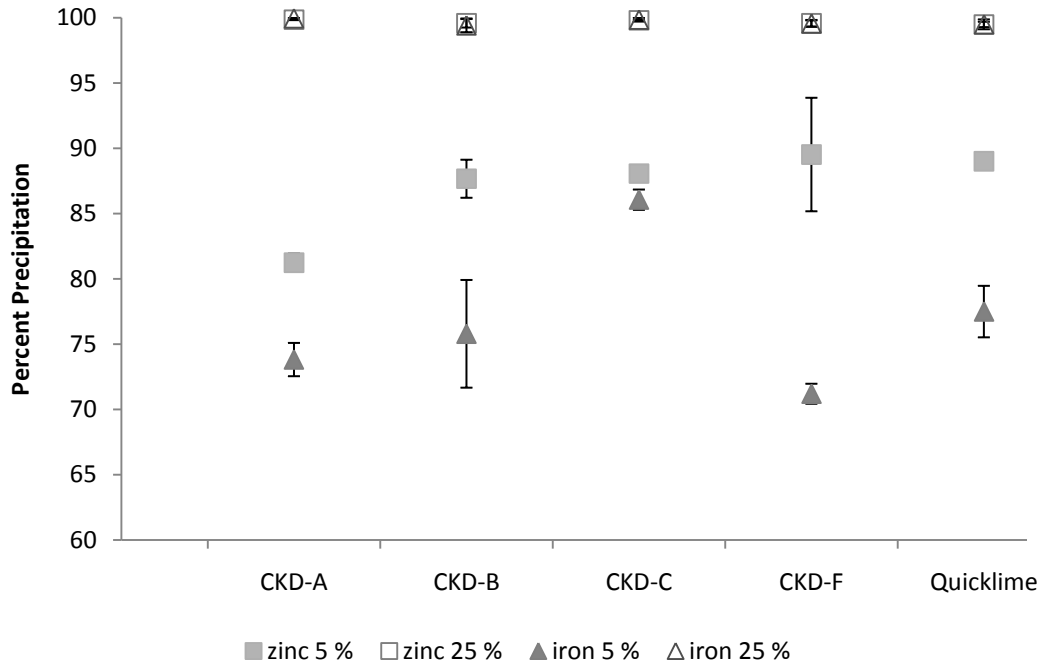


Figure 5.10: Precipitation of metals with 5 % (n=3) and 25 % (n=4) slurries.

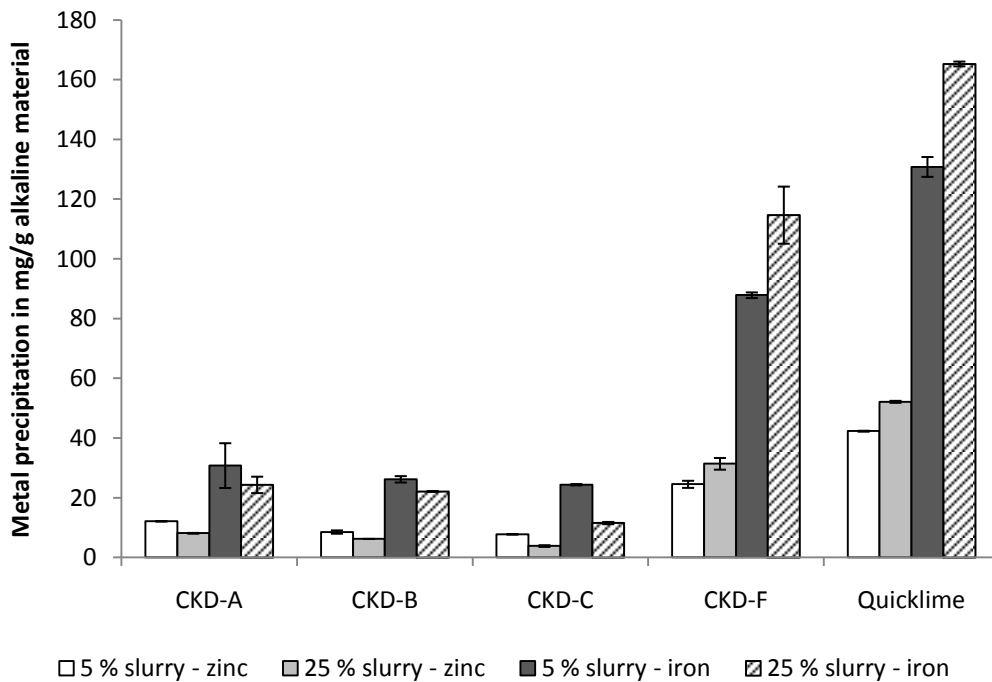


Figure 5.11: Precipitation of metals per gram material added for 5 % (n=3) and 25 % (n=4) slurries.

## 5.6 Conclusions

Overall, the performance of the CKD slurries used to neutralize samples of mine water in batch tests was comparable to that of quicklime when using a high solids density slurry (i.e. 25 %). All CKDs tested, CKD-A, CKD-B, CKD-C, and CKD-F, were able to precipitate more than 99 % of the soluble zinc and iron in the mine water samples. However, treatment of mine water with the CKD slurries required that higher volumes, translating to higher weights of dry material, be added than with quicklime to reach the target pH of 9.5. This amount varied linearly with the reactive oxide content of the base alkali material used to generate the calcium hydroxide slurries. The increased amount of material required ranged from 1.6 times that required for treatment with quicklime for CKD-F, which had the highest free lime content, to 14.3 times the amount of quicklime required for CKD-C, which had the lowest free lime content. Reducing the % solids of the slurries from 25 % to 5 % reduced the metal precipitation capabilities of the CKD- and quicklime-generated  $\text{Ca}(\text{OH})_2$  slurries from over 99 % to between 70 and 90 %, respectively.



## **Chapter 6: Evaluation of Cement Kiln Dust Slurries for Removal of Metals through Settling**

The previous chapter summarized the results of the precipitation of metals using calcium hydroxide slurries made from CKD and compared them to the capabilities of quicklime, the current commercial standard in active lime treatment plants. This chapter presents the water quality results of the batch jar tests after settling with respect to variable slurry concentration, settling time, and polymer dose. Full data sets for bench-scale mine water treatment experiments are included in the Appendix.

### **6.1 Introduction**

In an active lime treatment plant, mine water is treated by neutralization with a hydrated lime ( $\text{Ca}(\text{OH})_2$ ) slurry made by slaking quicklime with water, which causes dissolved metals to precipitate as hydroxides (Younger et al., 2002; Brown et al., 2002; Aubé & Zinck, 1999). The results of the neutralization experiments discussed in the previous chapter indicate that cement kiln dust (CKD) can be used to replace quicklime to achieve the same level of metal precipitation. The CKD-treated mine water samples required higher slurry doses to achieve the same pH target of 9.5, with the amount of slurry added varying depending on free lime and reactive oxide content of the dry CKD.

After the neutralization stage in an active lime treatment plant, polymer is added to the mine water and mixed slowly to allow continued precipitation, adsorption, and aggregation of particles into flocs which will settle out more quickly in the clarification step. A polymer is added to help increase the size of flocs and the settling efficiency of the precipitated metals (Huck, Murphy, & LeClair, 1977). Anionic polymers have been shown to work best in mine effluent treatment plants (Huck & LeClair, 1974). Polymer doses used for flocculation of mine water typically range from 0.5 to 1.5 mg/L, though doses as high as 10 mg/L have been reported (Huck, Murphy, Reed, & LeClair, 1977; Bratby, 2006). The flocculated mine water is then sent to a clarifier or settling pond to remove flocs through sedimentation prior to discharge of the clarified overflow. Sedimentation takes advantage of the action of gravity to separate out suspended particles from water (Droste, 1997). Settling basins or tanks are designed to allow for removal of

particles that settle faster than the overflow rate of the basin. Discrete particles settle according to Stokes' law (Equation 6.1). This equation shows that the settling velocity of a particle,  $v_s$ , depends on the particle's diameter and density,  $d$  and  $\rho_p$ , assuming the values for gravity, water density ( $\rho_w$ ), and water viscosity ( $\mu$ ) do not change. As particles agglomerate, their diameter and density become larger, increasing settling velocity (Droste, 1997).

$$v_s = \frac{g \cdot d^2 (\rho_p - \rho_w)}{18 \cdot \mu} \quad \text{[Equation 6.1]}$$

Previous studies examining the use of CKD in powder form or CKD leachate for removal of metal ions from synthetic solutions found reductions in metals of close to 100 % at optimal conditions (e.g. pH, mixing time) (Zaki et al., 2007; Pigaga et al., 2005; El-Awady & Sami, 1997). The earliest study looked at the removal capability of dry CKD added to synthetic solutions of chromium (Cr), cobalt (Co), copper (Cu), and iron (Fe) (El-Awady & Sami, 1997). That study found optimal removal of those metals after mixing at 150 rpm within a pH range of 2.5 to 4.5. A contact time longer than 30 minutes for Cr and Co and 60 minutes for Cu did not appreciably increase removal of those metals. The removal of iron was found to increase more gradually and complete removal was achieved after 2 hours. This indicates that the hydroxylation of iron is a slower reaction than that of the other studied metals. Another study looked at removal of Co, Cu, cadmium (Cd), nickel (Ni), and lead (Pb) from synthetic solutions using dry CKD samples (Pigaga et al., 2005). That study found that treatment through continuous stirring compared to stirring at intervals reduced the necessary contact time for removal, which was found to be between 30 minutes and 7 hours depending on the metal. Exact mixing conditions were not specified. A more recent study only looked at the effect of CKD leachate strength and dose on removal of metals, without specifying experimental conditions (Zaki et al., 2007).

## 6.2 Materials and Methods

The first stage of the bench-scale mine water treatment experiments was discussed in the preceding chapter. One litre mine water samples were added to each of the six jars

of a standard jar tester then dosed with a volume of  $\text{Ca}(\text{OH})_2$  slurry, generated with either one of the test CKDs or quicklime, necessary to bring the mine water sample to a pH of 9.5. The neutralized mine water was then rapid mixed for one minute at 150 rpm ( $G = 140 \text{ s}^{-1}$ ), after which 50 ml samples were taken from the sample ports on the jars to determine the degree of metal precipitation. After this initial neutralization and precipitation, anionic polymer (POLYFLOC AE1138, GE Water and Process Technologies) was added at a dose of 1 mg/L and the samples continued to be rapid mixed for an additional 30 seconds. The mixing speed was then reduced to 50 rpm, which translates to a velocity gradient of approximately  $44 \text{ s}^{-1}$ , and run for 2 minutes flocculation time. Samples were taken at this point for analysis of flocculated particles. The flocculated mine water was then allowed to settle quiescently for 30 minutes or 60 minutes, after which settled water samples were taken in order to characterize the quality of the final treated effluent. Four replicates of the batch jar tests were performed for each of the 25 % slurries, and three replicates were conducted with the 5 % slurry treatments. Mixing speeds and times and settling times were chosen based on previous work with similar mine effluents (Huck, Murphy, Reed, & LeClair, 1977; Huck, Murphy, & LeClair, 1977; Huck & LeClair, 1978) and with CKD treatment of metal-laden effluents (El-Awady and Sami, 1997). The effect of settling time and polymer dose was also investigated for mine water treated with CKD-B, CKD-F, and quicklime slurries.

The total and soluble zinc and iron concentrations of the samples were measured by atomic absorption spectrometry (AAAnalyst 200, PerkinElmer). Particle size analysis and images of treated mine water samples were analyzed using a Brightwell MicroFlow Imaging system (MFI). This system measures particles greater in diameter than  $2.00 \mu\text{m}$  when at the low magnification set point, which is 5 times magnification. Trace metal concentrations of settled mine water that had been treated with CKD-B, CKD-F, and quicklime slurries were determined by ICP-OES (Vista-PRO Radial, Varian). Wet sludge volumes generated in each of the jar tests were estimated from gradations on the jars of the jar tester (Amuda & Amoo, 2007; Tatsi et al., 2003). The major oxides content of dried sludge samples were determined for CKD-B, CKD-F, and quicklime using ICO-OES.

In order to accurately calculate the percent removal of metals from the treated mine water, samples of the untreated mine water were taken at the time of each jar test and analyzed for total and soluble zinc and iron as well as pH and total suspended solids (TSS). The final metal removal was calculated as the difference in total metal ion (i.e. acidification with no filtration) from the untreated mine water sample to the final settled water sample. Error bars on graphs and error terms in text and tables represent one standard deviation from the mean.

### 6.3 Flocculation of Neutralized Mine Water

Samples of flocculated mine water treated with slurries made using CKD-B, CKD-F, and quicklime were analysed using MicroFlow Imaging (MFI). These samples were taken just prior to the beginning of the settling period. Results from the analysis are presented in Table 6.1, along with the analysis of a sample of untreated mine water for comparison.

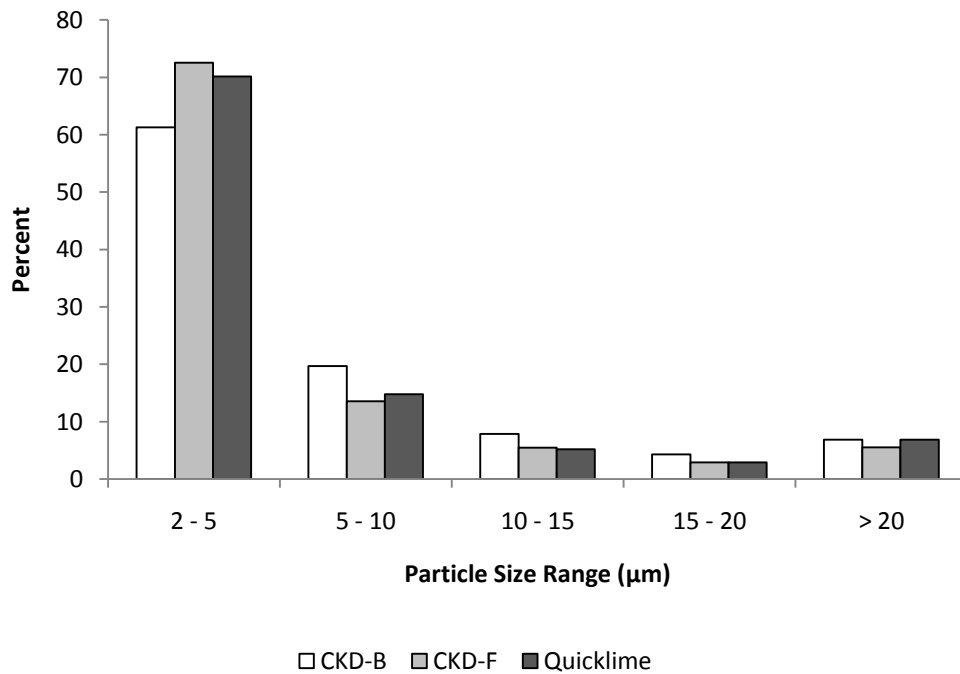
**Table 6.1: Results of particle analysis on flocculated mine water (n=1).**

Sample ID	Particle Concentration (#/mL)	Mode Particle Size Range (µm)	Mode Particle Size Concentration (#/mL)	Mean Particle Size (µm)	Largest Particle Detected (µm)
CKD-B	$3.47 \times 10^5$	2.00 – 2.25	$0.66 \times 10^5$	$7.41 \pm 11.10$	364.25
CKD-F	$3.58 \times 10^5$	2.00 – 2.25	$1.02 \times 10^5$	$8.43 \pm 25.55$	739.50
Quicklime	$0.70 \times 10^5$	2.00 – 2.25	$0.19 \times 10^5$	$10.63 \pm 37.41$	864.25
Mine Water	$0.05 \times 10^5$	2.00 – 2.25	$0.02 \times 10^5$	$3.63 \pm 3.73$	75.00

Particle concentration results show that the two mine water samples treated with CKD-generated slurries have considerably more particles after flocculation than those treated with the quicklime-generated slurry. There were also much higher concentrations of particles at the smallest size range, from 2.00 to 2.25 µm, than any other size range for all three treatments, as indicated by the mode particle size and concentration. These smallest detectable particles (2.00 to 2.25 µm) were also found in much higher concentrations in the CKD-treated mine water samples than in the quicklime-treated samples.

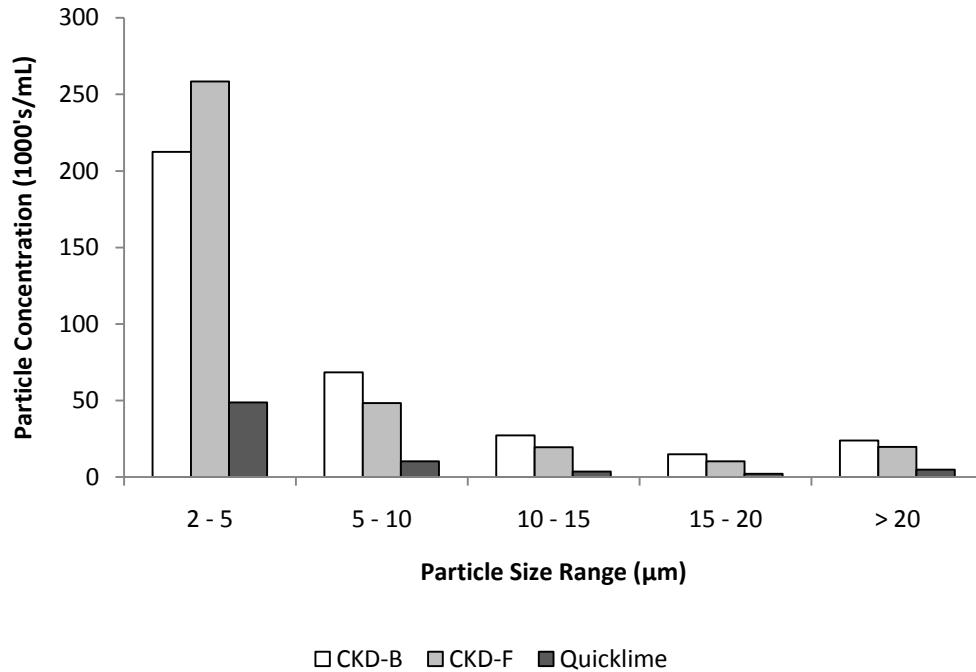
The mean particle size of the flocculated mine water sample that had been treated with the CKD-B slurry was slightly smaller than that of mine water treated with the CKD-F slurry, which in turn was smaller than that of the quicklime slurry-treated samples. The final data in Table 6.1 show that the largest particle detected in the mine water sample treated with CKD-B is half the size of the largest particle detected in mine water treated with CKD-F. The mine water sample treated with quicklime had the largest overall particle detected.

Figure 6.1 shows that the particle size distributions of the flocculated CKD-treated and quicklime-treated mine water are quite similar. However, the CKD-treated mine water samples were found to contain much higher concentrations of particles in all size ranges (Figure 6.2).



**Figure 6.1: Particle size distributions of flocculated mine water samples (n=1).**

Analysis of the particle data indicates that the particles generated in mine water samples after neutralization and flocculation with slurries made from CKD are found in higher concentrations than those in mine water treated with the quicklime slurries. CKD,

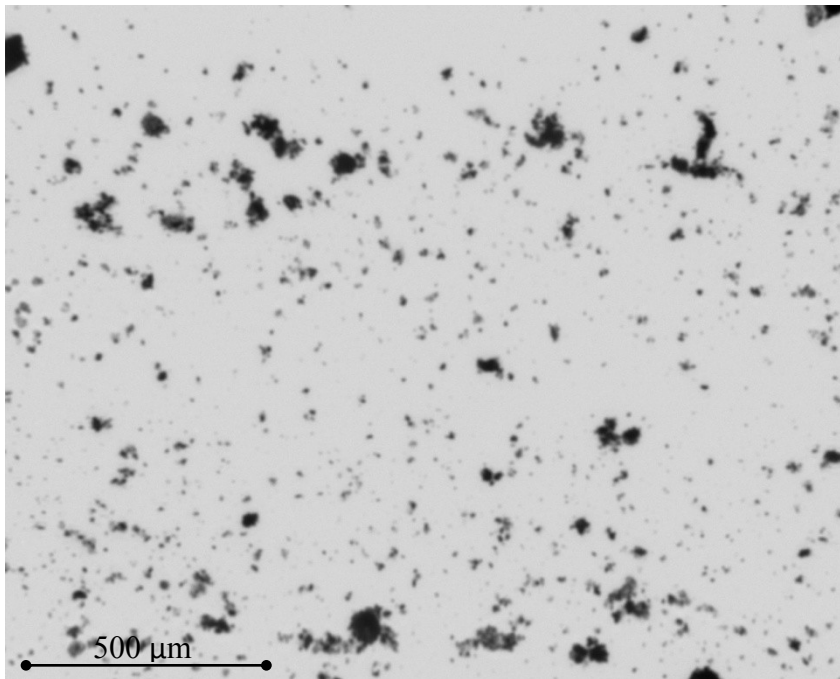


**Figure 6.2: Particle concentrations by size range in flocculated mine water (n=1).**

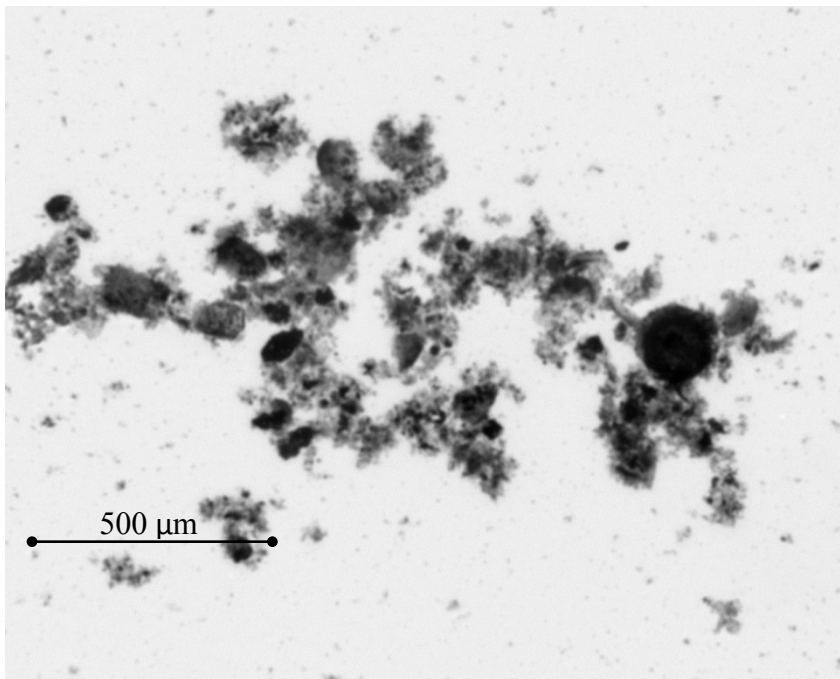
which has lower free and total lime than quicklime, contains higher amounts of other oxides. Many of these other oxides are not soluble (e.g.  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ) and therefore would precipitate as well, potentially remaining as small, discrete particles unless attracted by the polymer. The anionic polymer used in this study would also act to repel any particles having a negative charge. Particle size, density, and shape influence the settling properties of treated samples as well as settled sludge characteristics such as density and dewaterability. The smaller particles seen in the CKD-treated samples could take longer to settle than those treated with quicklime, but may be able to pack closer together, creating a denser and less voluminous sludge.

Figure 6.3 to Figure 6.5 show some of the largest particles detected during testing. These images were taken from the MFI particle analyses. Figure 6.3 illustrates that the CKD-B treated mine water samples contained many small particles and small, dense flocs. The relative density of the flocs can be seen from the variations in their transparency. The CKD-F treated mine water samples seen in Figure 6.4 have large flocs with visibly denser particles than the larger and more amorphous quicklime flocs (Figure

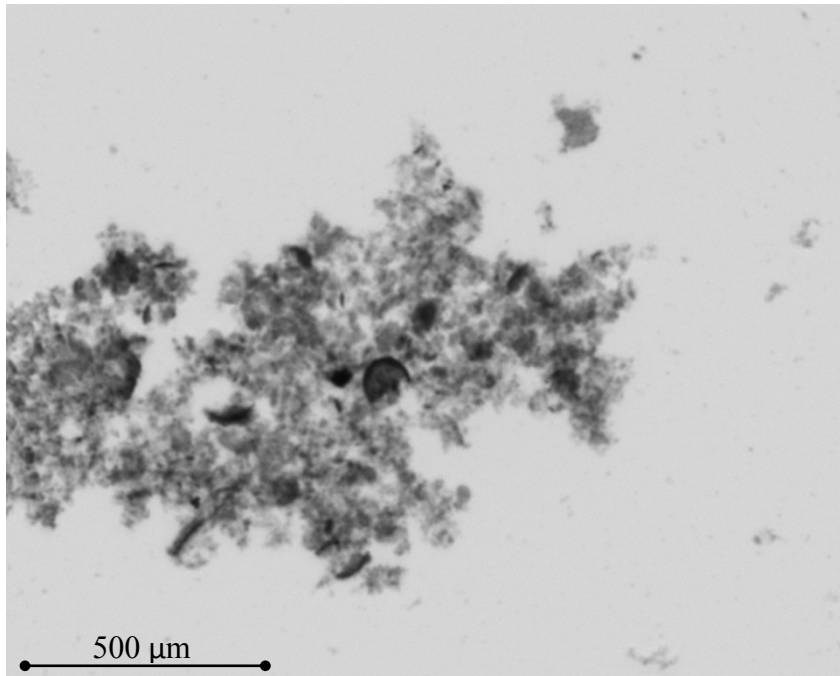
6.5). However, particles greater in size than 100  $\mu\text{m}$  account for less than 2 % of all particles detected.



**Figure 6.3: Image of flocculated mine water treated with CKD-B slurry.**



**Figure 6.4: Image of flocculated mine water treated with CKD-F slurry.**



**Figure 6.5: Image of flocculated mine water treated with quicklime slurry.**

## **6.4 Settled Water Quality**

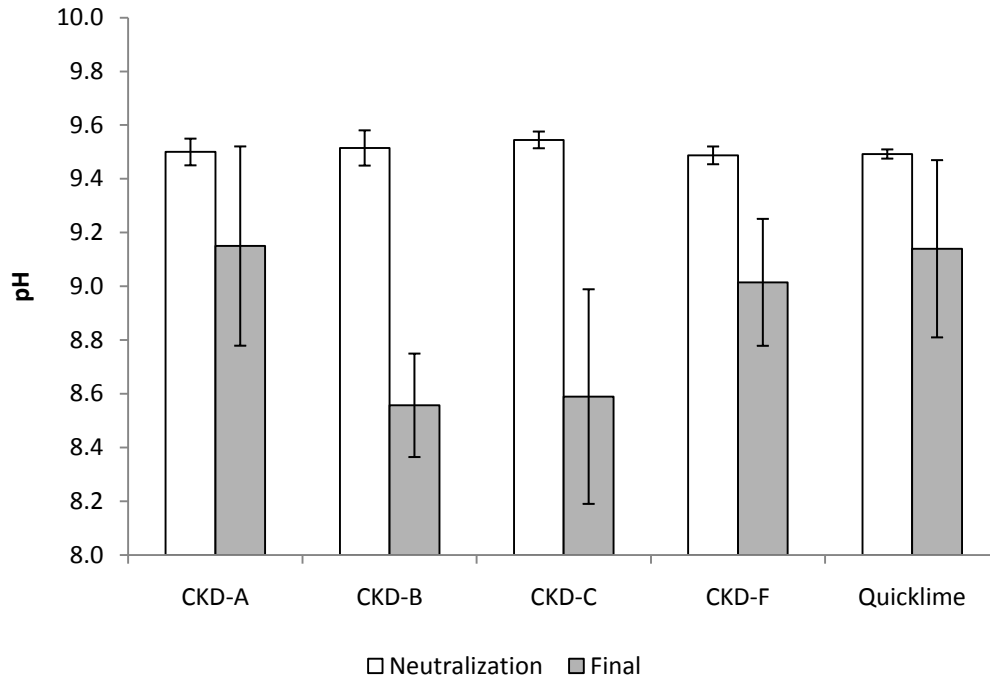
The results presented and discussed in this section are from bench tests using the 25 % solids calcium hydroxide slurries, a polymer dose of 1.0 mg/L, and settling time of 30 minutes. The effects of changing the slurry concentration, settling time, and polymer dose are discussed in following sections.

### **6.4.1 pH**

As discussed in the previous chapter, the mine water samples were dosed with enough of each calcium hydroxide slurry to raise the 1 L mine water samples to a pH of 9.5. Seen in Figure 6.6, the pH of all treated samples was found to decrease slightly with further mixing and settling after initial neutralization, with average final pH values found to be in the range of 8.6 to 9.1.

A pH drop was expected to occur as dissolved metals form hydroxides and settle out, removing  $\text{OH}^-$  ions. Statistical analysis of the data from the figure above showed that only the CKD samples with low free lime content (CKD-B and CKD-C, with 8.8 and 5.0 % w/w free CaO, respectively) had a significantly lower pH after 30 minutes of settling





**Figure 6.6: pH of treated mine water samples (n=4).**

than that during initial neutralization (i.e. 9.5). This may also indicate that the CKDs with higher free lime contents, as well as quicklime, continue to generate alkalinity after neutralization, at least more so than the other CKD samples. Further analysis using Dunnett’s method showed that all final pH values for the CKD treated samples were comparable with 95 % confidence to that of quicklime. However according to the ANOVA settled samples that had been treated with CKD-B did have a significantly different final pH from that of quicklime (p-value = 0.022). Again, all samples retained a fairly high pH throughout treatment and settling. The final pH was not found to correlate to any dry CKD physicochemical characteristics. All coefficients of determination, or  $R^2$ , for linear regressions were less than 0.50.

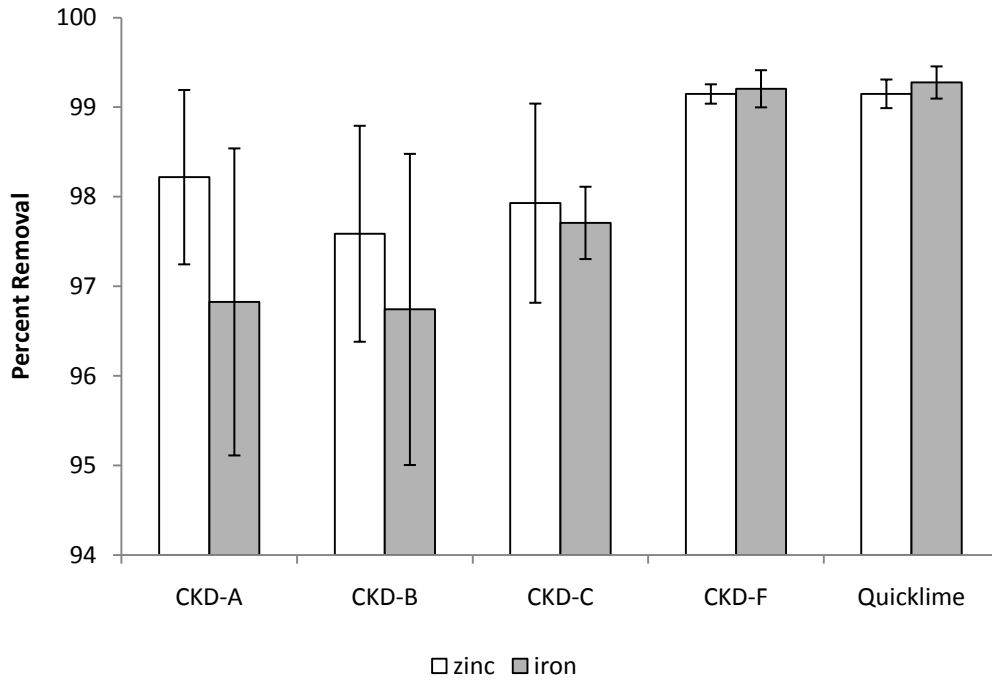
#### 6.4.2 Removal of Target Metals

The percent removal of zinc and iron after treatment are shown in Figure 6.7. Zinc removal of 98 % or greater and iron removal of 97 % or greater was achieved in all mine water samples treated with the 25 % CKD and quicklime slurries. Further, statistical analyses (Dunnett’s method and ANOVA) confirm that there is likely no difference

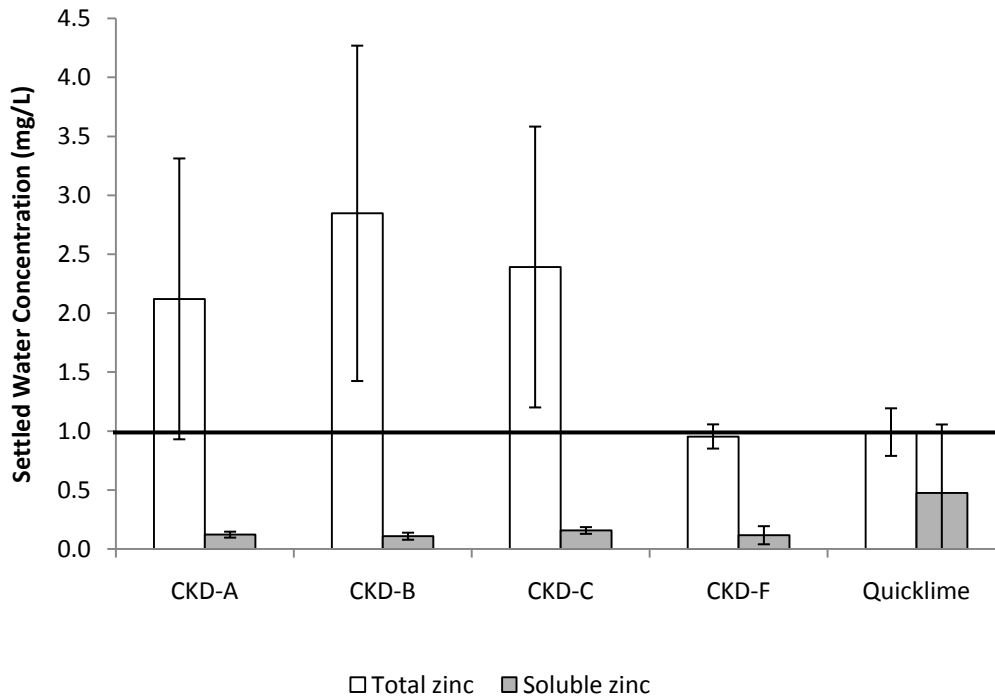
between the average zinc removal percentages of the CKD-treated and quicklime-treated mine water (95% confidence level). For iron, only the mine water samples treated with the CKD-C and CKD-F slurries showed no statistical difference in removal percentage to those treated with the quicklime slurry at the 95 % CI, however all slurry treatments were found to be equivalent at the 99 % percent confidence interval.

The removal percentages of the target metals were lower than the precipitation percentages, presented in the last chapter, for all treated mine water samples. This difference was greater for the samples treated with the low free lime CKD slurries than for those treated with the CKD-F and quicklime slurries. ANOVA tests conducted on average percent precipitation versus average percent removal of zinc for each treated sample showed statistically significant differences between these amounts for all CKDs and quicklime. The p-values from the ANOVA analysis ranged from 0.0156 for CKD-A to 0.0454 for quicklime. For iron, only the mine water samples treated with CKD-A, CKD-B, and CKD-C slurries resulted in statistically significantly more precipitation than removal. CKD-F- and quicklime-treated mine water samples removed as much iron as they precipitated, with p-values of 0.0955 and 0.3526 respectively. The lower removal percentages as compared to precipitation indicate that further settling may be required to achieve more complete removal of target metals from the treated mine water samples.

The final total zinc concentrations shown in Figure 6.8 visually confirm that treatment with CKD-F slurry, which contains the highest free lime content of all of the CKD samples evaluated in this study, performed equivalently to treatment with quicklime-generated slurry for removal of zinc from mine water. Statistical analysis of the final total zinc values indicates that there is no significant difference between the average final total zinc concentration of any of the samples (Dunnett's Method and ANOVA). This is due mainly to the large variance within the results from samples treated with CKD-A, CKD-B, and CKD-C, as indicated by the large error bars on the graph. The samples treated with CKD-A, CKD-B, and CKD-C had final zinc concentrations slightly above the current MMER guideline of 1.0 mg/L, which is indicated by the solid horizontal line on Figure 6.8.



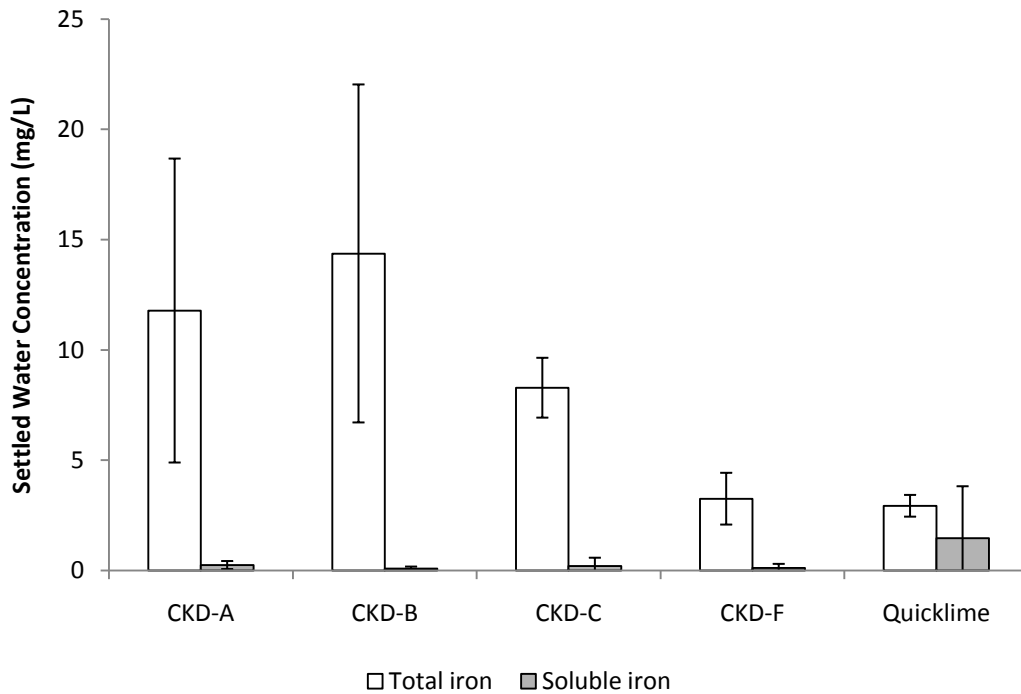
**Figure 6.7: Removal percentages of target metals zinc and iron.**



**Figure 6.8: Final zinc concentrations of treated mine water samples.**

The soluble zinc concentrations in the settled mine water samples are also shown in Figure 6.8. The results of the soluble zinc analysis point out that the vast majority of remaining zinc in treated mine water is not dissolved but mostly in the form of particles greater in size than 0.45  $\mu\text{m}$ . This indicates the potential for better removal of precipitates with increased settling time or polymer dose.

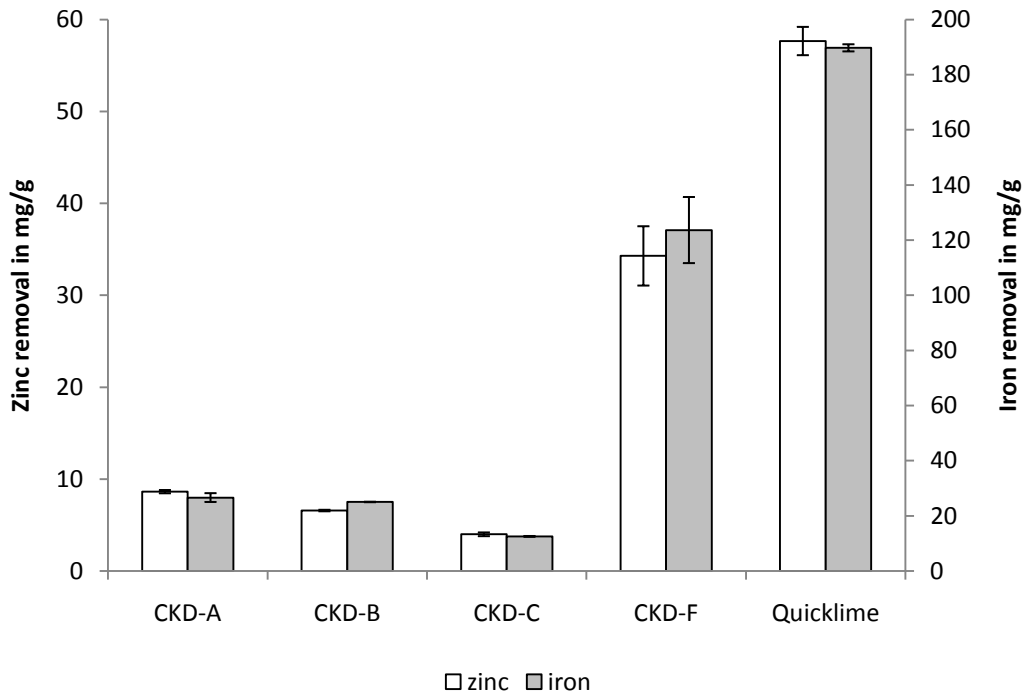
The average total iron concentrations remaining in the treated and settled mine water samples are given in Figure 6.9, below. Currently, there is no limit on iron in discharged effluent as regulated by the MMER, though iron remaining in mine water discharges can be directly toxic to aquatic life or precipitate downstream, coating waterways with ochre (Brown et al., 2002; CCME, 1987). Statistical analysis at the 95% confidence level indicates that the average total iron concentration in the settled mine water was only significantly different for those samples treated with CKD-B. They are all equal at the 99% confidence level.



**Figure 6.9: Final iron concentrations of treated mine water samples.**

The concentration of soluble iron found remaining in the treated effluent was minimal, and below the method detection limit (mdl) of 0.05 mg/L for many of the individual samples of treated mine water. This again indicates that further removal of iron would require physical removal of particulates, since iron remains in an insoluble form after precipitation.

Figure 6.10, below, was generated by dividing the total amount of zinc or iron removed from the sample (in milligrams) by the amount of alkaline reagent (in grams of CKD or quicklime) that was added by the slurry in that trial. This was done to account for the different amounts of dry material added with different CKD samples. The figure shows that there was less removal per gram of material added for the low free lime CKDs, CKD-A, CKD-B, and CKD-C, than for CKD-F and quicklime. This again shows that more material needs to be added when treating with some CKD-generated slurries to achieve the same removal percentages as with those treated with quicklime slurries.



**Figure 6.10: Milligrams of total zinc removed per gram of CKD or quicklime added to one litre of mine water.**

The coefficients of determination for linear regressions of zinc and iron removal correlated with several dry CKD and treated mine water properties are listed in Table 6.2. In order to achieve the 95 % confidence level, the  $R^2$  values must be above 0.90, and above 0.98 for 99 % confidence (Hahn, 1973). The percent removal of zinc was found to correlate most strongly with the free lime content in the dry CKD sample and the final treated and settled mine water TSS, and both are at or above the threshold for 95 % confidence. These correlations are not as strong when performed with the percent removal of iron. When metal removal is looked at in terms of milligrams of metal removed per equivalent gram of CKD added to the mine water sample, the relation between removal of zinc or iron and the free lime content of the CKD is strengthened. An even stronger relation is found, with 99 % confidence, between removal per gram CKD added and the TRO -  $SO_3$  value for the dry CKDs. The TRO -  $SO_3$  value has the strongest correlation to free lime of all the reactive oxides values investigated in Chapter 4. It can also be said with 99 % confidence that the removal of both zinc and iron per gram CKD added correlates linearly to the final TSS of the treated, settled mine water samples. The more TSS remaining in the treated, settled mine water samples, the lower the removal of zinc and iron. Again, this indicates that increasing the settling time or polymer dose is necessary in order to increase removal of the precipitated metals.

**Table 6.2: Coefficients of determination ( $R^2$ ) for linear regressions with metal removal.**

Property Correlated	Removal (%)		Removal (mg/g)	
	Zinc	Iron	Zinc	Iron
Median Particle Size	0.0930	0.5365	0.1735	0.1948
Surface Area	0.0002	0.0120	0.1150	0.1433
Total Lime	0.5481	0.4603	0.8543	0.8761
Free Lime	0.8980	0.6458	0.9740	0.9610
TRO	0.6548	0.4010	0.8659	0.8678
TRO - $SO_3$	0.8602	0.7078	0.9966	0.9940
Final Settled Water pH	0.4737	0.0628	0.2613	0.2248
Final Settled Water TSS	0.9172	0.7645	0.9948	0.9860

#### 6.4.3 Trace Metals

A trace metals analysis was done on the settled mine water samples that had been treated with slurries made from CKD-B, CKD-F, and quicklime. The trace metals remaining in the settled mine water samples treated with the CKD-B and CKD-F slurries

**Table 6.3: Trace metals in treated mine water samples compared to untreated mine water.**

Element (mg/L)		CKD-B	CKD-F	Quicklime	Mine Water
Silver	Ag	< 0.01	< 0.01	< 0.01	< 0.01
Aluminum	Al	1.4	1.4	0.3	66
Arsenic	As	0.02	0.04	0.02	0.45
Barium	Ba	0.13	0.03	0.04	< 0.01
Beryllium	Be	< 0.001	< 0.001	< 0.001	0.004
Bismuth	Bi	< 0.01	< 0.01	0.01	< 0.01
Calcium	Ca	569	590	541	219
Cadmium	Cd	< 0.01	< 0.01	< 0.01	0.18
Cesium	Ce	< 0.01	< 0.01	< 0.01	0.13
Cobalt	Co	< 0.01	< 0.01	< 0.01	0.78
Chromium	Cr	< 0.01	< 0.01	< 0.01	0.05
Copper	Cu	0.02	0.03	0.01	6.72
Iron	Fe	2.10	2.35	1.14	509
Gallium	Ga	0.03	0.02	0.02	0.07
Potassium	K	166	50	13	13
Lithium	Li	0.11	0.08	0.07	0.08
Magnesium	Mg	115	70	2.93	167
Manganese	Mn	3.26	1.38	0.10	61
Molybdenum	Mo	0.03	< 0.01	< 0.01	< 0.01
Sodium	Na	918	943	953	950
Nickel	Ni	< 0.01	< 0.01	0.02	0.16
Phosphorus	P	< 0.1	< 0.1	< 0.1	1.2
Lead	Pb	0.01	0.03	0.02	0.52
Sulphur	S	1585	1522	1356	2001
Antimony	Sb	< 0.1	< 0.1	< 0.1	< 0.1
Selenium	Se	< 0.1	< 0.1	< 0.1	< 0.1
Silicon	Si	3	1	1	18
Strontium	Sr	0.99	0.54	0.56	0.37
Tellurium	Te	< 0.1	< 0.1	< 0.1	0.1
Titanium	Ti	< 0.01	< 0.01	< 0.01	< 0.01
Thallium	Tl	< 0.1	< 0.1	< 0.1	< 0.1
Vanadium	V	< 0.01	< 0.01	< 0.01	0.01
Zinc	Zn	0.12	0.42	0.19	106

were found to be similar to or slightly higher than those measured in the quicklime-treated mine water sample. This can be seen in Table 6.3, which also includes the analysis of a sample of untreated mine water for comparison. The concentrations of metals regulated under the MMER (i.e. As, Cu, Pb, Ni, and Zn) were all below the

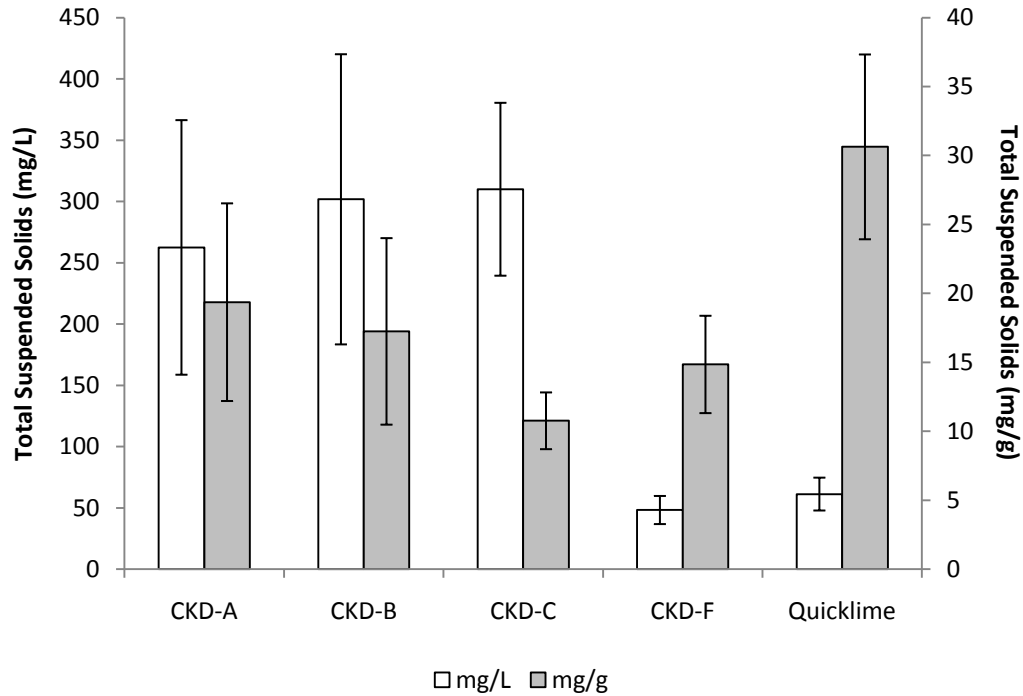
maximum value guidelines listed in Chapter 2 for all three treated samples. The final total zinc and iron concentrations measured in this analysis were lower than the averages found by the atomic absorption analysis discussed above. In addition to zinc and iron, aluminum was also present in high concentrations in the untreated mine water and removed to less than 2.0 mg/L with treatment by all three slurries. Copper was also removed to very low concentrations (i.e. < 0.1 mg/ L) from an initial concentration of 6.7 mg/L. All samples removed trace amounts of cadmium, cobalt, chromium, and phosphorus to less than the detection limits. Magnesium and sulphur were found to be at higher concentrations in the CKD-B and CKD-F treated samples compared to the quicklime-treated samples, although both CKD-treated samples showed a reduction from the initial concentrations of these metals in the untreated mine water.

#### 6.4.4 Total Suspended Solids

The total suspended solids (TSS) concentrations for settled mine water samples treated with CKD or quicklime generated slurries are shown in Figure 6.11. The TSS data are also presented in this figure as the amount of TSS in milligrams generated per gram of CKD or quicklime added to neutralize the mine water sample.

The mine water samples treated with the low free lime content CKD slurries (i.e. CKD-A, CKD-B, and CKD-C) result in higher overall concentrations of TSS than those treated with CKD-F and quicklime slurries. However, it is clear from this figure that although treatment with the quicklime slurry resulted in lower concentrations of TSS in settled mine water samples, it resulted in much higher TSS per gram of alkaline material added than treatment with the CKD slurries. Statistical analyses by Dunnett's method and ANOVA support these conclusions as well. Treatment with the slurry generated using CKD-F, which has the highest free lime content of the CKD samples tested, resulted in both low overall TSS, comparable to treatment with quicklime slurry, and low TSS per gram of equivalent dry CKD added, comparable to the other CKD treatments. None of the samples treated at the bench-scale met the maximum 20 mg/l guideline set by the MMR, though again mine water samples treated with the CKD-F slurry are comparable to those treated by the quicklime slurry.





**Figure 6.11: Final TSS concentrations of treated mine water samples (n=4).**

#### 6.4.5 Particle Size

The settled mine water samples were analysed using MFI to determine particle concentrations and sizes in the settled water after treatment. The particle size distributions in Figure 6.12 show that all treated samples have the majority of their remaining particles in the smallest size ranges (i.e. 2 to 5  $\mu\text{m}$ ). The largest particles detected in samples treated by each slurry were less than 200  $\mu\text{m}$  in diameter. This shows that the larger particles have all been removed through settling.

Though the size distributions of all three samples analysed were quite similar between the different CKD and quicklime treated samples, the concentrations of particles remaining were not. Figure 6.13 shows that the mine water sample that had been treated with CKD-B had higher concentrations of remaining particles in the smallest two size ranges presented than those treated with CKD-F or quicklime. CKD-B-treated samples also had the highest concentration of small particles after neutralization and flocculation, as discussed above. These small particles take longer to settle, according to Stokes' law. The overall mean particle sizes for the three samples analysed were  $4.94 \pm 6.10$ ,  $6.20 \pm$

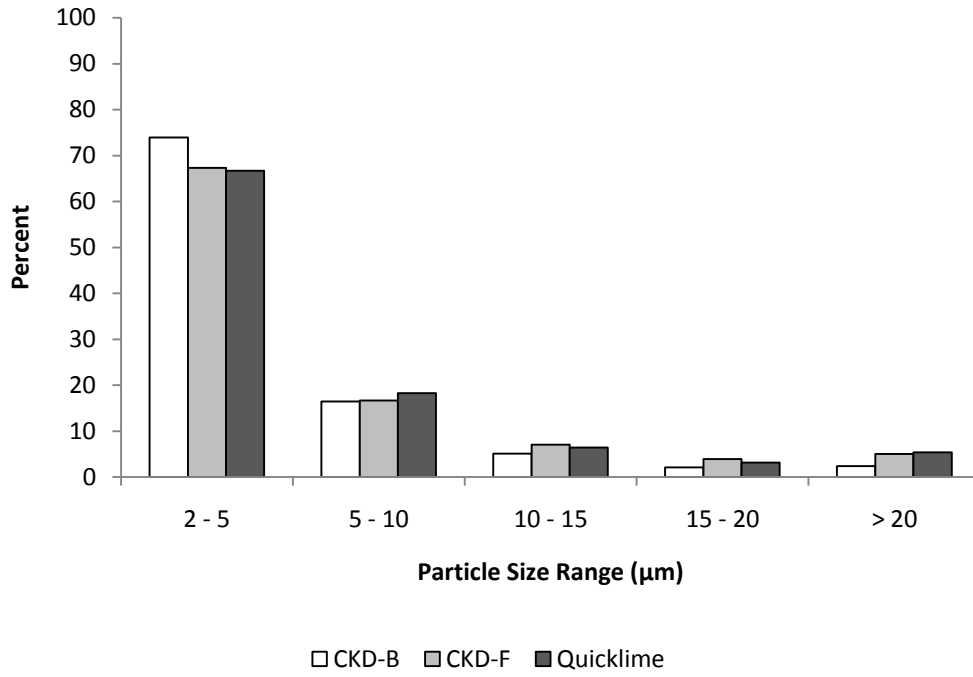


Figure 6.12: Particle size distributions in treated, settled mine water (n=1).

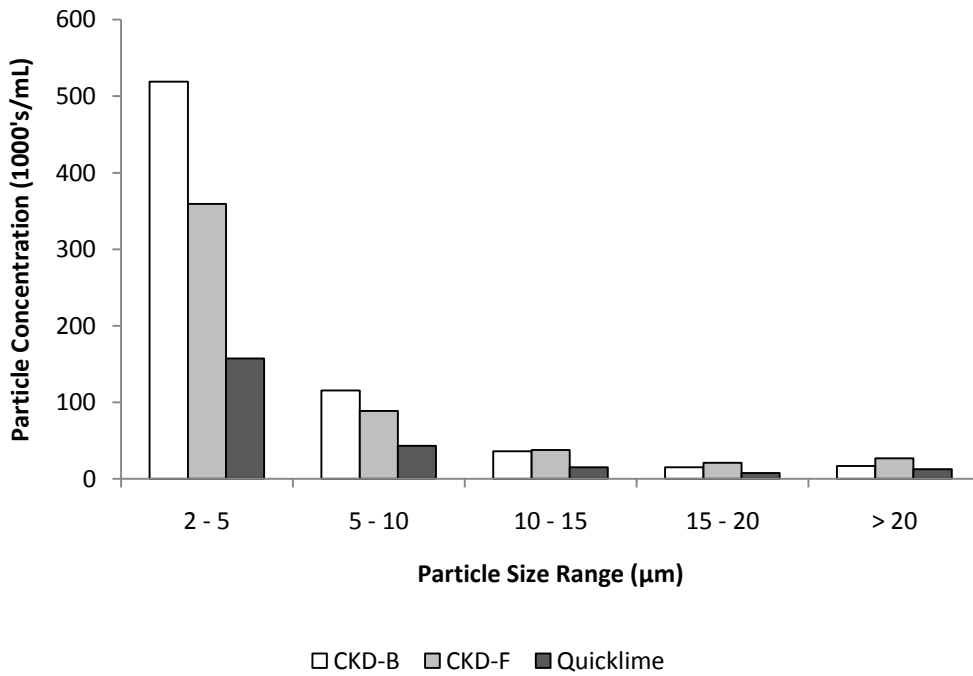


Figure 6.13: Particle concentrations by size range in treated, settled mine water (n=1).

8.04, and  $6.23 \pm 8.07 \mu\text{m}$  for mine water treated with CKD-B, CKD-F, and quicklime slurries, respectively, again showing that the CKD-B treatment resulted in the smallest particles in the settled water samples.

### 6.5 Settled Sludge Quality

As can be seen in Figure 6.14, below, the mine water samples treated with the CKD slurries generated significantly less total sludge in the 1 L batch experiments than the quicklime slurry-treated sample ( $p\text{-value} = 1.56 \times 10^{-5}$ ). This confirms that the smaller and denser particles generated from treatment of mine water with CKD slurries result in less sludge generation. The volume of sludge generated per gram of dry alkaline material added, also shown in Figure 6.14, demonstrates the difference between sludge volume generated by CKD and quicklime slurry treatments even more clearly. Statistical analysis using Dunnett’s method confirms that all treatments using CKD slurries generated less sludge per gram material added than the quicklime slurry treatments.

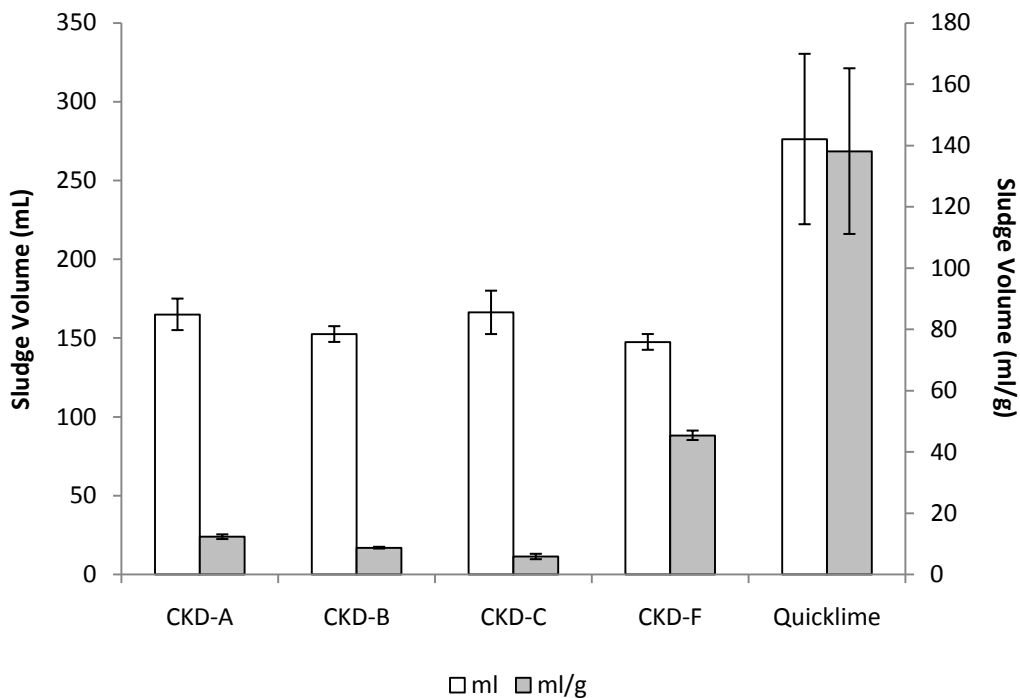


Figure 6.14: Sludge volumes generated in treated, settled mine water samples (n=4).

Further analysis showed no significant correlations between total sludge volume generated in the mine water treatment experiments and several dry CKD and treated mine water properties at either the 95 % ( $R^2 > 0.90$ ) or 99 % ( $R^2 > 0.98$ ) confidence level, as shown in Table 6.4. There is a slight negative correlation between total lime content and total sludge volume generated ( $R^2 = 0.87$ ), suggesting that a higher lime content in the dry CKD may result in decreased generation of sludge during treatment of mine water samples with the CKD slurry.

**Table 6.4: Coefficients of determination ( $R^2$ ) for linear regressions with sludge volume.**

<b>Property Correlated</b>	<b>Sludge Volume (mL)</b>
Sludge Volume (mL)	1
Material Added (g)	0.5266
Final Settled Water pH	0.0005
Final Settled Water TSS	0.4909
Total Lime	0.8663
Free Lime	0.4900
Surface Area	0.7699
Median Particle Size	0.1807

Sludge samples generated from neutralization of mine water samples treated with CKD-B, CKD-F, and quicklime slurries were dried and analyzed for major oxides. Reactive oxide values were also calculated and are included with the major oxides analysis in Table 6.5. This table also includes the average values of these oxides present in the dry CKD and quicklime samples (e.g., Dry Alkali Material), discussed in Chapter 4, for comparison.

Higher concentrations of most oxides were found in the sludge generated from treatment and settling of mine water with CKD and quicklime slurries than in the dry alkaline material used to make the slurries. The oxides of calcium, potassium, and silica however were all found in lower concentrations in the generated sludge than in the dry material, along with the reactive oxides values. This would indicate that these oxides were dissolved during slaking of the CKD and quicklime samples as expected but not precipitated or removed completely during treatment of the mine water samples. This can also be seen in the trace metals analysis of the final treated and settled mine water

samples in Table 6.3, which showed higher concentrations of calcium and potassium than were present in the untreated mine water.

**Table 6.5: Major and reactive oxides in settled sludge compared to unreacted alkaline material.**

Parameter (wt %)	CKD-B		CKD-F		Quicklime	
	Sludge	<i>Dry Alkali Material</i>	Sludge	<i>Dry Alkali Material</i>	Sludge	<i>Dry Alkali Material</i>
Al <sub>2</sub> O <sub>3</sub>	4.20	4.10	4.99	4.87	2.37	0.36
CaO	39.27	47.79	19.55	58.76	17.56	90.15
Fe <sub>2</sub> O <sub>3</sub>	5.24	1.44	14.87	2.81	14.58	0.19
K <sub>2</sub> O	1.10	2.26	0.89	2.70	0.13	0.08
MgO	1.65	1.18	4.58	1.19	5.34	0.29
MnO	0.42	0.05	1.49	0.14	1.62	0.42
Na <sub>2</sub> O	1.13	0.20	4.77	0.22	9.15	0.12
P <sub>2</sub> O <sub>5</sub>	0.04	0.01	0.15	0.17	0.06	0.01
SiO <sub>2</sub>	13.87	15.76	11.05	17.17	2.70	4.24
TiO <sub>2</sub>	0.18	0.22	0.14	0.23	0.01	0.021
SO <sub>3</sub>	7.73	5.23	20.63	5.30	34.97	N/A
LOI*	24.64	21.15	14.53	5.20	10.53	3.94
TRO <sup>†</sup>	18.51	30.29	15.25	57.68	21.65	86.70
CaO + MgO - LOI	16.28	27.83	9.59	54.75	12.36	86.50
TRO - SO <sub>3</sub>	10.79	25.05	-	52.38	-	86.70

\*loss on ignition at 1000 °C

<sup>†</sup>total reactive oxides = (CaO + MgO) - LOI - (K<sub>2</sub>O + Na<sub>2</sub>O)

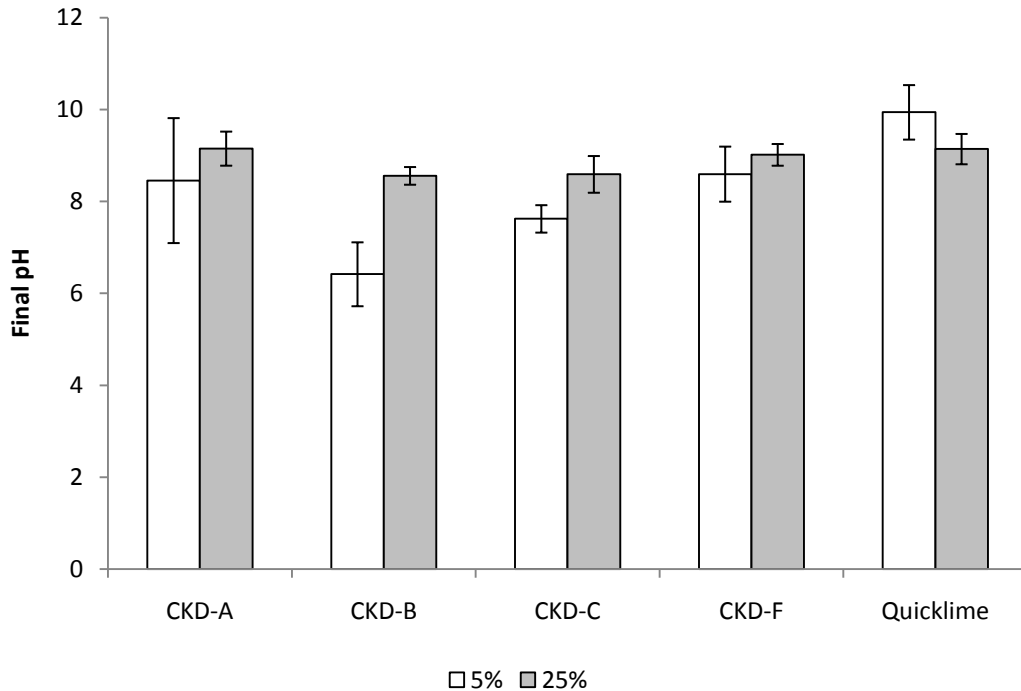
## 6.6 Effect of Slurry Concentration on Settled Water Quality

The results in the previous section were from effluent samples treated using slurries of CKD or quicklime with a target solids content of 25 %. Batch jar tests were also performed using slurries with a 5 % solids content target, in order to determine if slurry solids content has an effect on final treated effluent quality.

### 6.6.1 pH

The final pH of the settled mine water samples is shown in Figure 6.15. The higher final pH for the 25 % slurries observed on this graph for the CKDs is only statistically significant for CKD-B and CKD-C. This indicates that CKD and quicklime

slurry concentration had little to no effect on the pH of the final treated effluent, and relies more on the initial pH or slurry volume added.

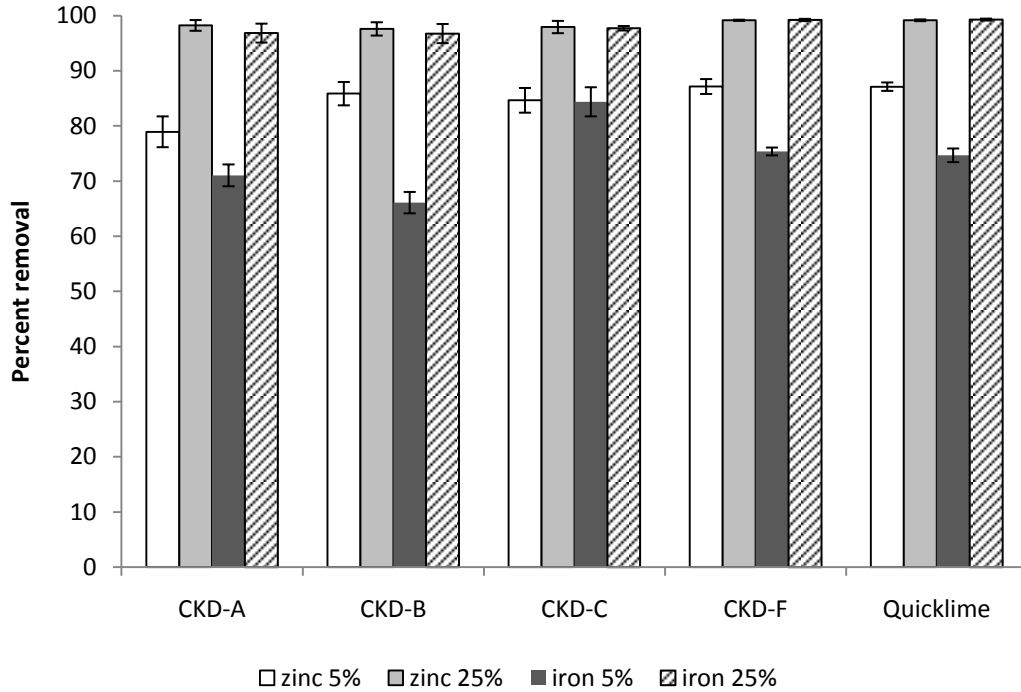


**Figure 6.15: Comparison between the final pH of mine water samples treated with 5 % (n=3) and 25 % (n=4) slurries.**

### 6.6.2 Removal of Target Metals

Figure 6.16 shows the percent removal of zinc and iron from mine water samples treated using the low (5 %) and high (25 %) solids content slurries. As is apparent from the graph, and was confirmed from ANOVA tests, the 25 % slurries provided greater metal removal than the 5 % slurries. This could be due to the higher amount of material added for neutralization with the higher concentration slurries to achieve the target pH of 9.5, as discussed in Chapter 5.

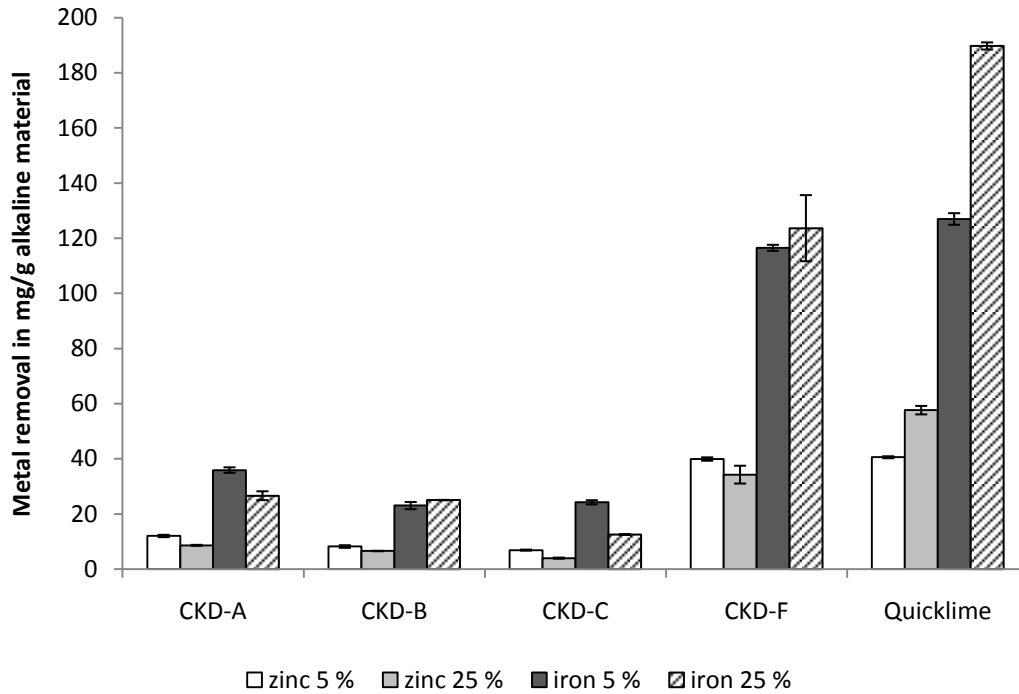
Figure 6.17 demonstrates that zinc removal from mine water per gram of alkaline material added during neutralization was actually slightly higher for the 5 % slurry for all CKD samples evaluated. Statistical analysis determined that the average iron removal per gram CKD added, also shown in Figure 6.17, is the same at both slurry concentrations for CKD-B and CKD-F. For CKD-A and CKD-C, more iron was removed per gram material



**Figure 6.16: Comparison between the percent removals of target metals from mine water samples treated with 5 % (n=3) and 25 % (n=4) slurries.**

added with the 5 % slurry, as with zinc. For quicklime, removal of both zinc and iron per gram dry material added was higher when samples were treated with the 25 % slurry than with the 5 % slurry.

Final total zinc concentrations of settled mine water that had been treated with the 5 % slurries were well above current regulatory guidelines for all samples tested, including quicklime, with a combined average of  $18 \pm 6$  mg/L. Iron concentrations remaining in the settled, treated mine water samples were also quite high after treatment with the 5 % slurries with a combined average of  $111 \pm 26$  mg/L. For comparison, the combined average final total values for the mine water samples treated with the 25 % CKD and quicklime slurries were  $1.9 \pm 1.2$  mg/L for zinc and  $8.4 \pm 6.3$  mg/L for iron. So although in most cases more metals were removed per gram CKD added when treating mine water with the 5 % slurries, the overall removal of metals was higher when using the 25 % slurries.



**Figure 6.17: Comparison between removals of target metals per gram of alkaline material added with 5 % (n=3) and 25 % (n=4) slurries.**

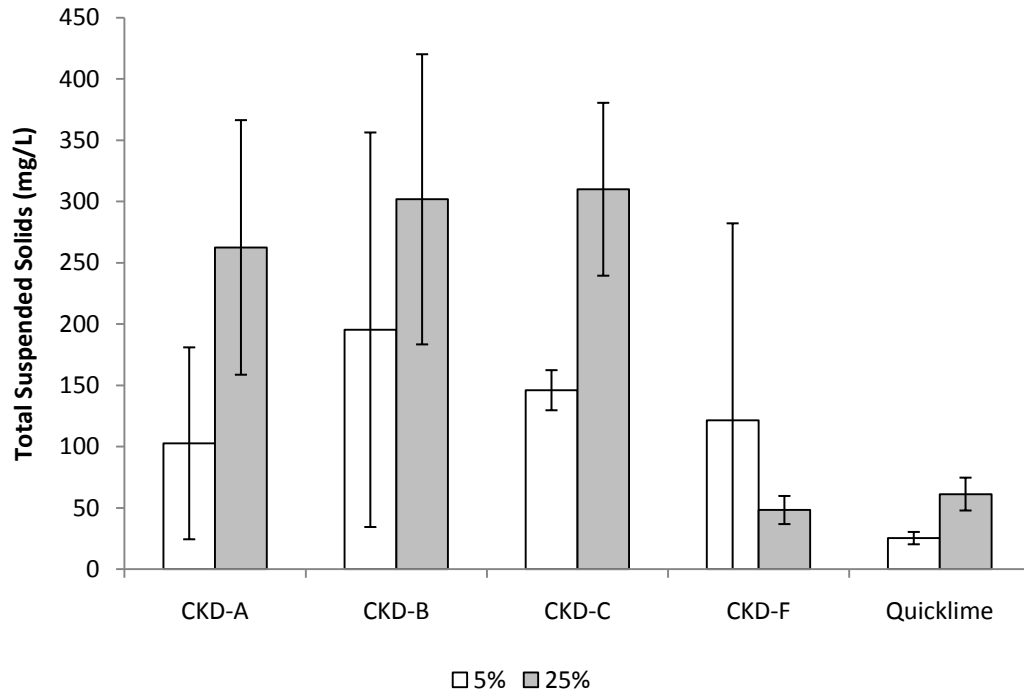
### 6.6.3 Total Suspended Solids

The TSS results presented in Figure 6.18 seem to indicate that there were higher concentrations of solids remaining in the settled mine water samples treated with the 25 % slurries than in those treated with the 5 % slurries. However this was only significant for CKD-C (P-value = 0.009) and quicklime (P-value = 0.176), likely due to the large variance in TSS concentrations from multiple samples in the CKD trials.

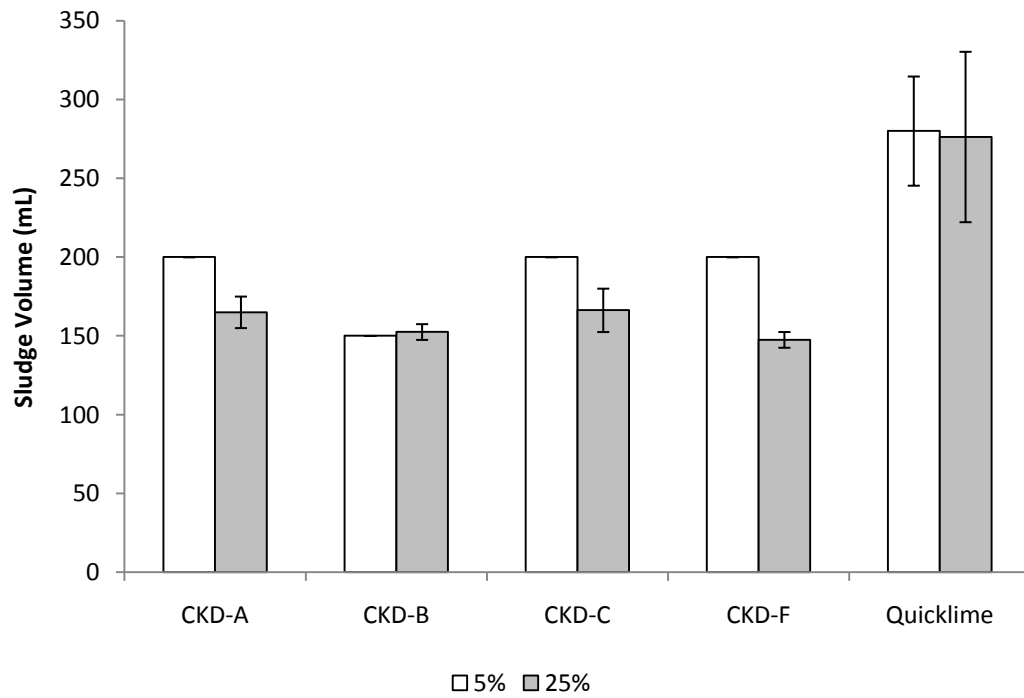
### 6.6.4 Sludge Volume

Shown in Figure 6.19 are the sludge volumes that were generated after treatment of the 1 L mine water samples. Statistical analysis determined that the sludge volume generated in mine water samples treated with the CKD-B and quicklime slurries was not affected by the solids concentration of the slurry used, which is indicated in the figure. All other treatments showed statistically significant differences in sludge volume generated when using low solids slurries versus high solids ones. More specifically, higher solids concentrations slurries (25 % solids) generated less sludge during treatment





**Figure 6.18: Comparison between TSS concentrations of mine water treated with 5 % (n=3) and 25 % (n=4) slurries.**



**Figure 6.19: Comparison of sludge volumes generated in mine water treated with 5 % (n=3) and 25 % (n=4) slurries.**

than low solids ones (5 %). Again, this was only true for CKD-A, CKD-C, and CKD-F. These results further indicate that higher solids concentration slurries are better suited to the treatment of mine water than low solids concentration slurries.

## **6.7 Effect of Settling Time on Settled Water Quality**

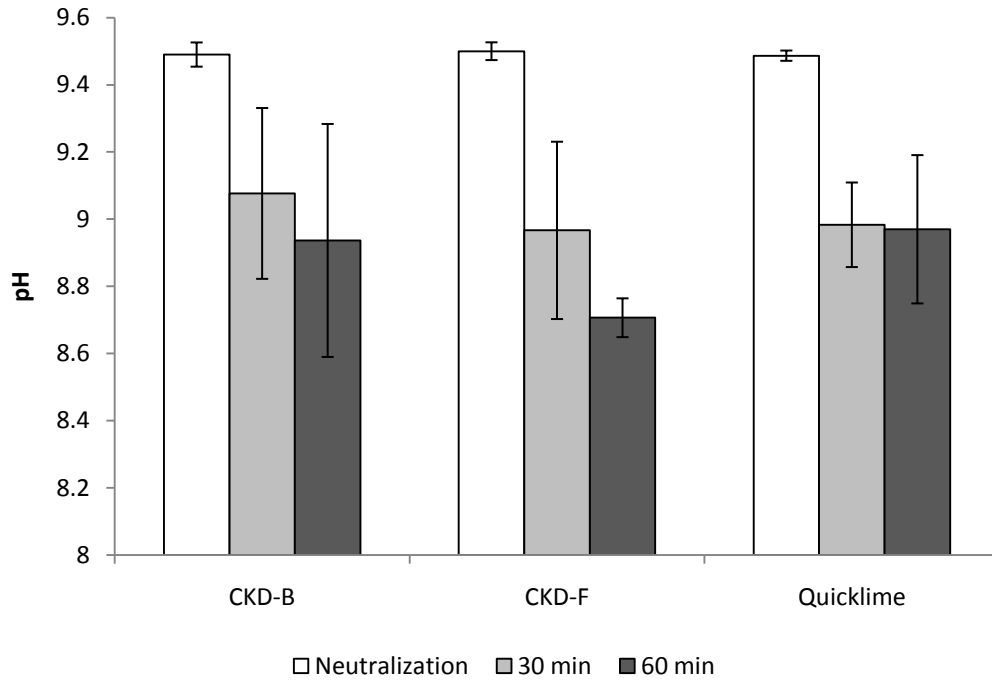
Results of experiments treating mine water samples with CKD-generated slurries with 25 % solids content indicated that further reductions in total metals may be possible with increased settling time. This was inferred from higher TSS and total metals concentrations in mine water samples treated with CKD-A, CKD-B, and CKD-C versus those in samples treated with CKD-F and quicklime, as discussed previously. The effect of increasing the settling time from 30 minutes to 60 minutes is discussed here.

### **6.7.1 pH**

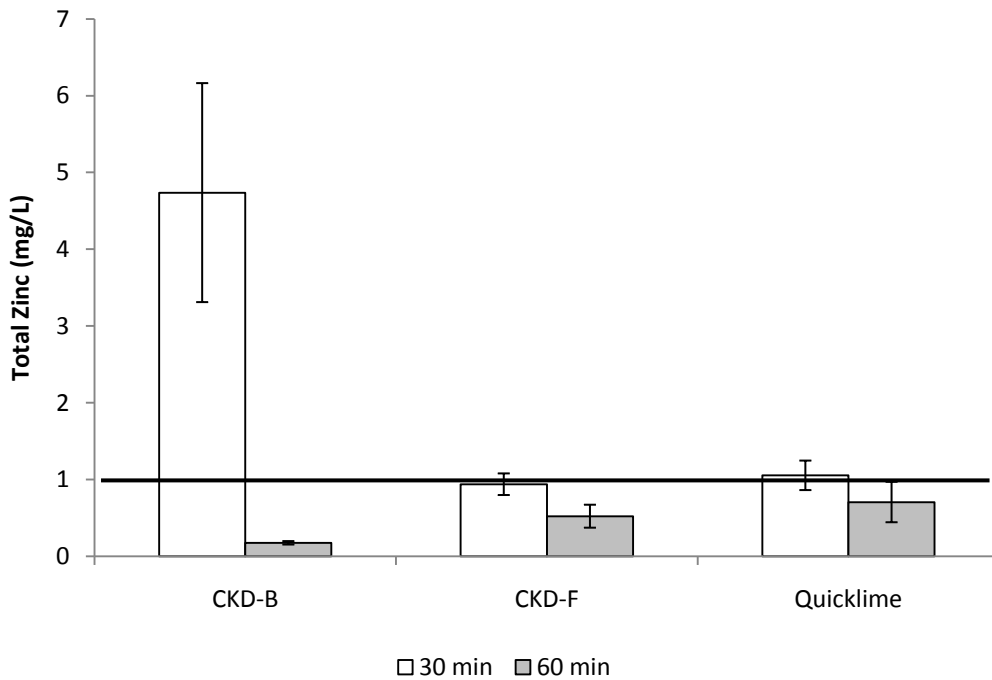
The final pH of mine water samples treated with slurries made using CKD-B, CKD-F, and quicklime and settled for 30 and 60 minutes is shown in Figure 6.20. The results presented in the figure show that pH did not drop significantly with the increased settling time. In addition, the results show that final pH values of the CKD-treated mine water samples were not significantly different from those treated using quicklime after 30 or 60 minutes of settling.

### **6.7.2 Target Metals**

As shown in Figure 6.21, increasing the settling time from 30 to 60 minutes decreased the amount of zinc remaining in the mine water samples treated with CKD slurries. This effect was more notable for the low free lime content CKD-B than for CKD-F. The difference in removal of zinc with increased settling time is not statistically significant for the quicklime treated mine water samples. The figure also clearly shows that the increased settling time reduced the zinc content of the mine water treated with CKD-B to below current treatment standards, as indicated by the solid line at 1.00 mg/l. Figure 6.21 also demonstrates that the increased zinc removal with increased settling time actually reduced zinc in those samples treated with CKD-B to an average below that of the quicklime treated samples. This difference is statistically significant at the 95 %



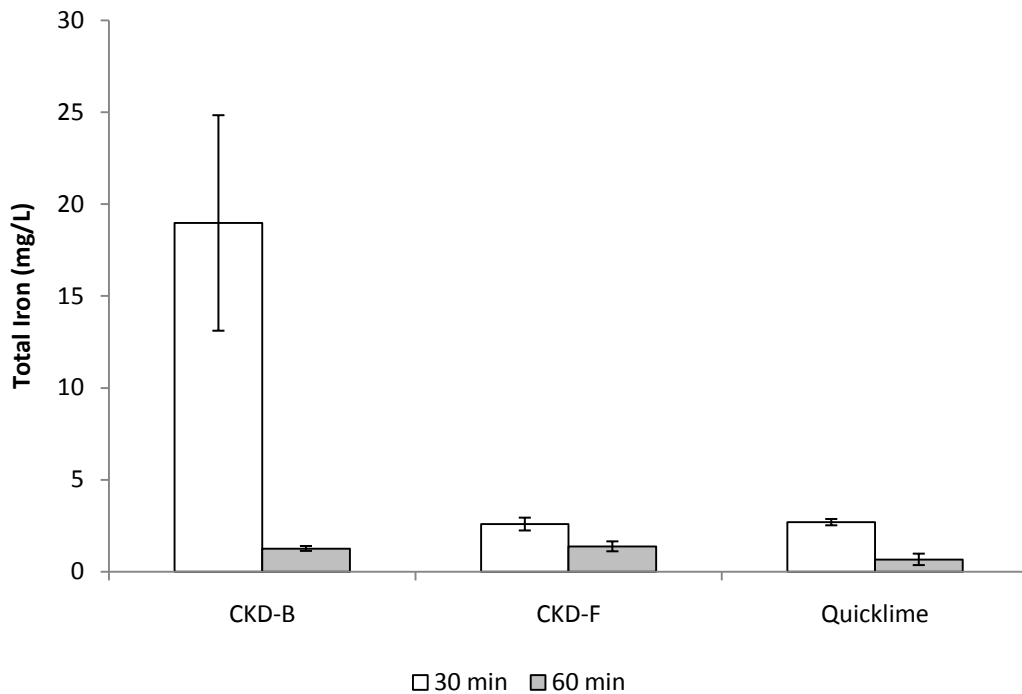
**Figure 6.20: Comparison between the final pH of treated mine water samples settled for 30 and 60 minutes (n=3).**



**Figure 6.21: Comparison between the total zinc of treated mine water samples settled for 30 and 60 minutes (n=3).**

CI, however the final total zinc concentrations resulting from treatment with all three alkaline materials were equivalent at the 99 % CI.

As seen in Figure 6.22, below, iron levels were only significantly reduced with increased settling in the CKD-B and quicklime treated mine water samples. The average removal of iron after 60 minutes of settling was the same for all three treatments at the 95% confidence interval.



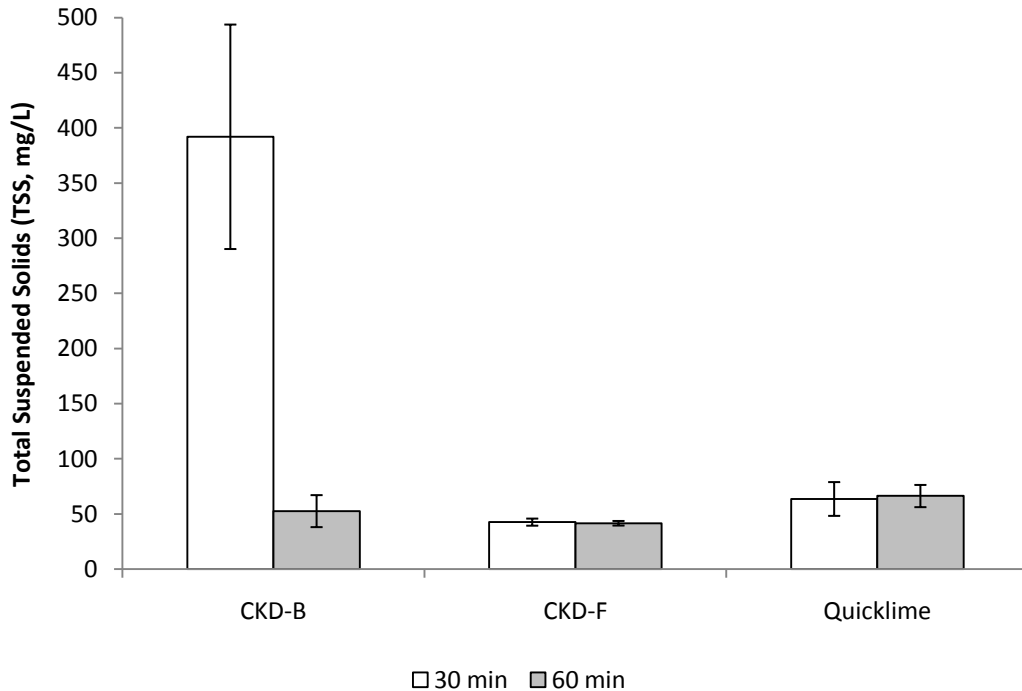
**Figure 6.22: Comparison between total iron of treated mine water samples settled for 30 and 60 minutes (n=3).**

The results presented here confirm that increased settling time does allow for increased removal of target metals. The increase was much more significant for samples treated with the CKD-B slurry than CKD-F or quicklime, which removed the majority of metals from the mine water samples within the initial 30 minute settling period.

### 6.7.3 Total Suspended Solids

The TSS concentrations remaining in the treated mine water samples after 30 and 60 minutes of settling are presented in Figure 6.23. The mine water samples treated with

slurries made from CKD-F and quicklime showed no change in TSS with additional settling time, while CKD-B showed a significant reduction in TSS.

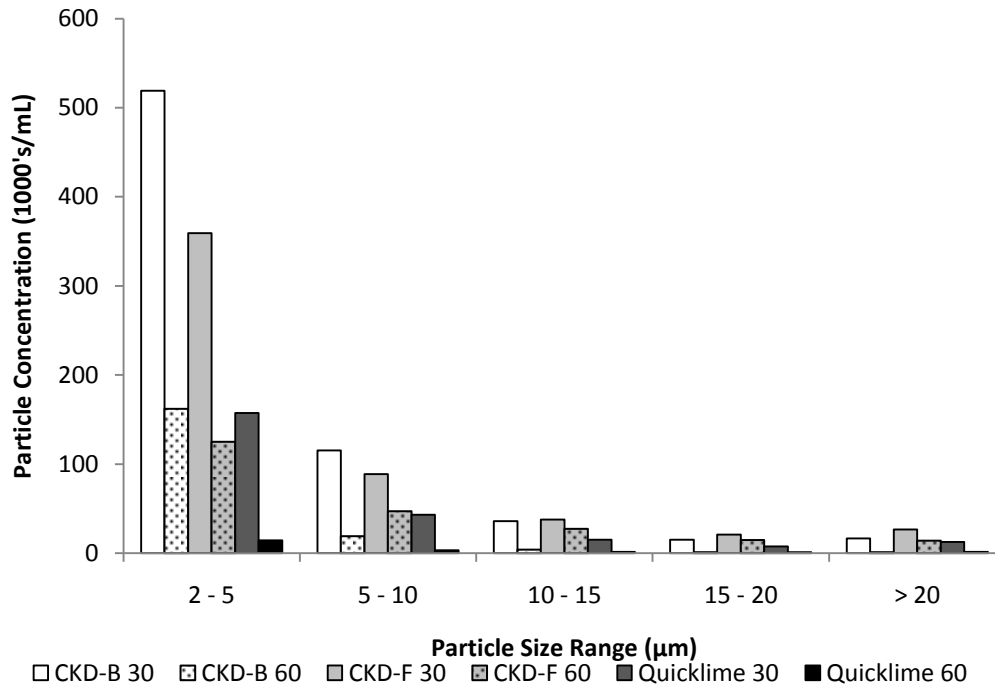


**Figure 6.23: Comparison between TSS of treated mine water samples settled for 30 and 60 minutes (n=3).**

The metals and TSS data taken together indicates that for CKD-F and quicklime, the hydroxides formed were larger and settled out more quickly than those in CKD-B. For CKD-B, with low free lime content, particles required longer settling times to be removed.

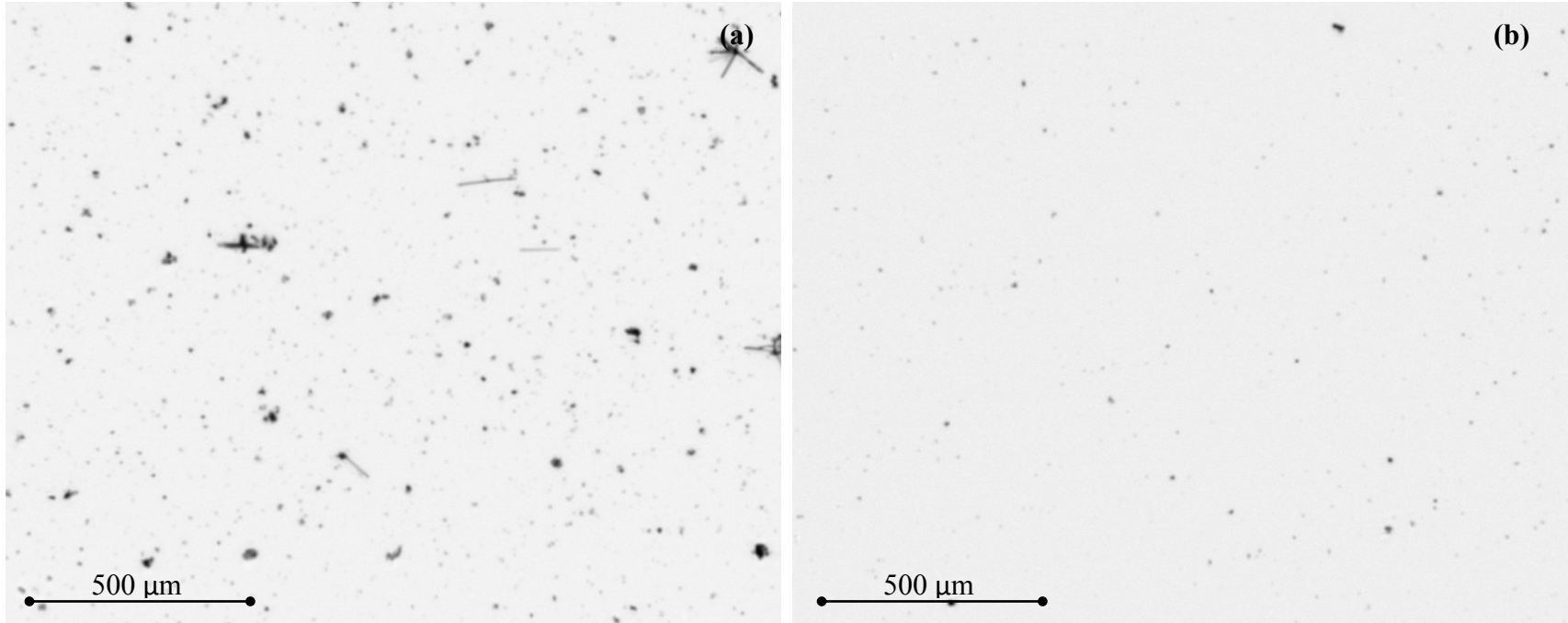
#### 6.7.4 Particle Size

The change in particle concentration by size range from 30 to 60 minutes of settling can be seen in Figure 6.24. This graph shows that high concentrations of small particles that were still present after 30 minutes of settling had been reduced significantly after 60 minutes of settling time.

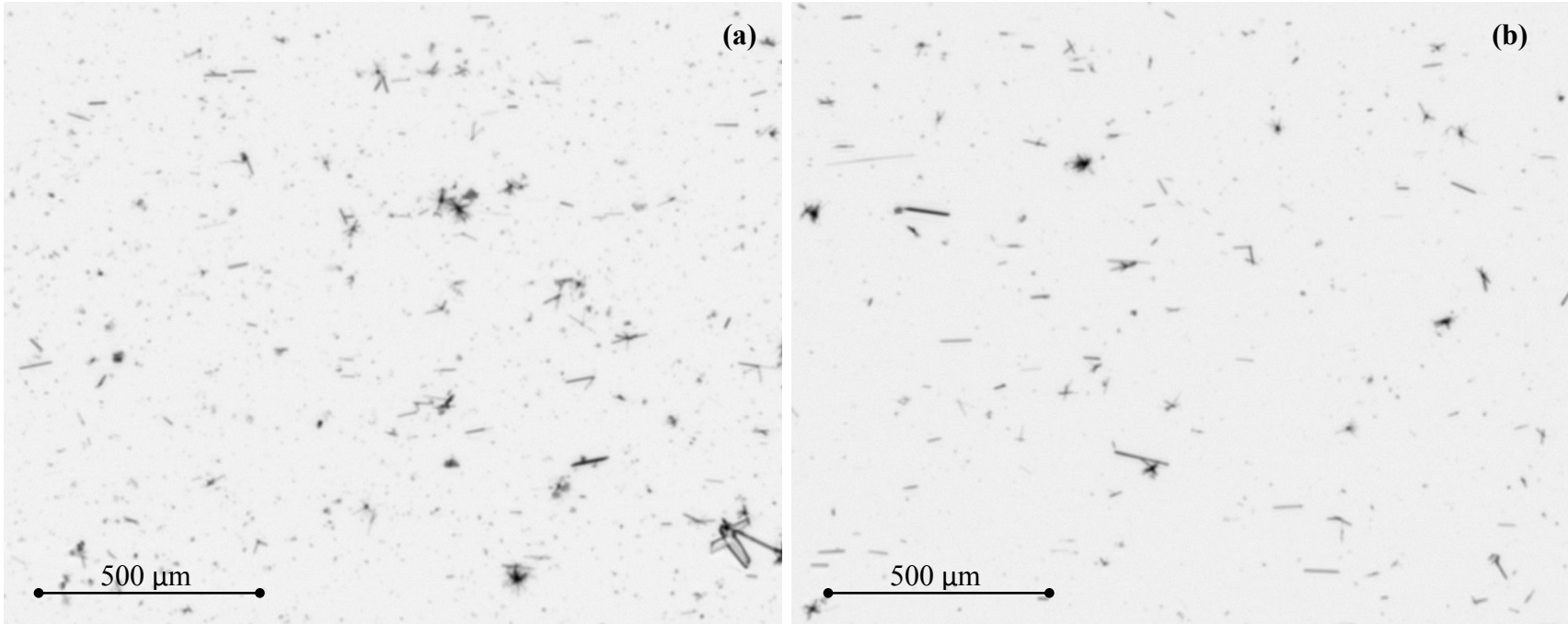


**Figure 6.24: Comparison between particle concentrations of treated mine water samples settled for 30 and 60 minutes (n=1).**

Figure 6.25 through Figure 6.27 present images of treated mine water samples taken after 30 (left image) and 60 minutes (right image) of settling. These images illustrate the increased removal of small particles that resulted from increased settling time. The smallest particles that can be seen in the images are approximately 2 µm in diameter. These images also illustrate the continued precipitation of iron hydroxides in the treated samples, which are the short bars seen in the images. The precipitation of iron hydroxides has been shown to be slow compared to that of other metal hydroxides (El-Awady & Sami, 1997).

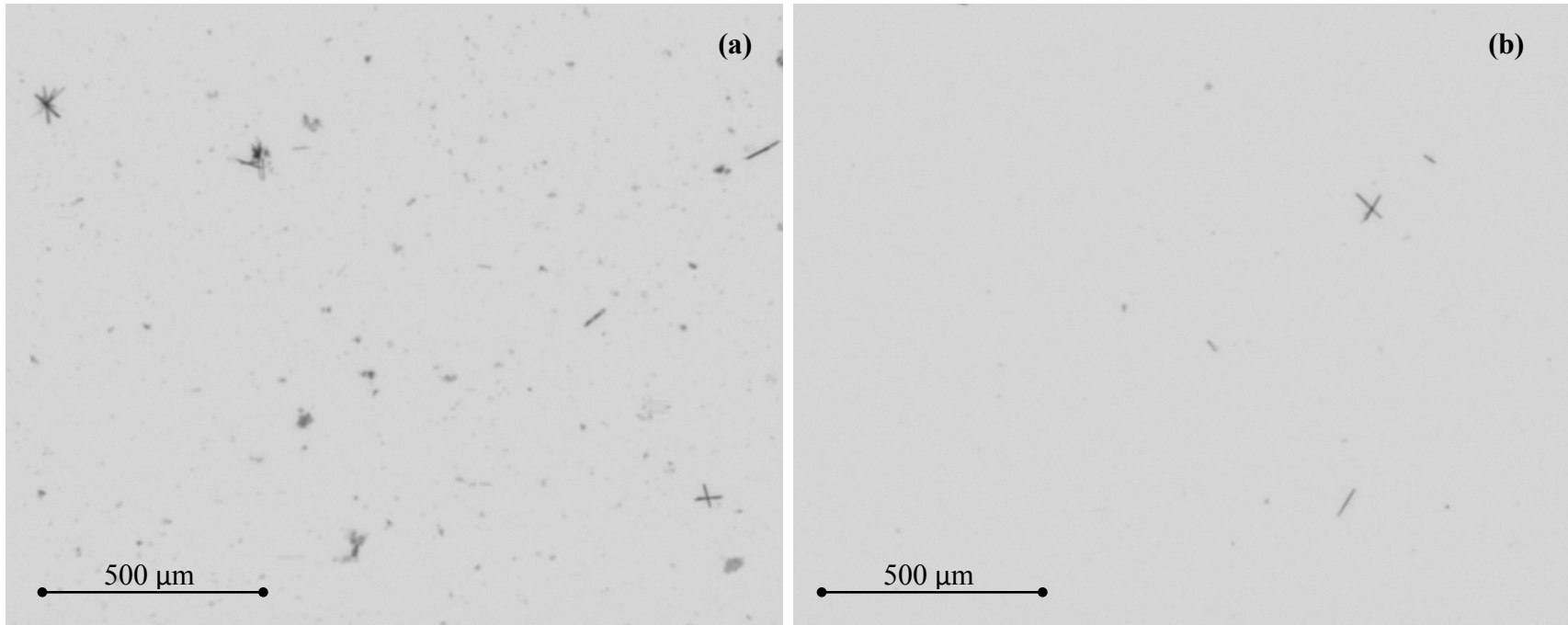


**Figure 6.25: Images of settled mine water after treatment with CKD-B with (a) 30 min settling and (b) 60 min settling.**



**Figure 6.26: Images of settled mine water after treatment with CKD-F with (a) 30 min settling and (b) 60 min settling.**

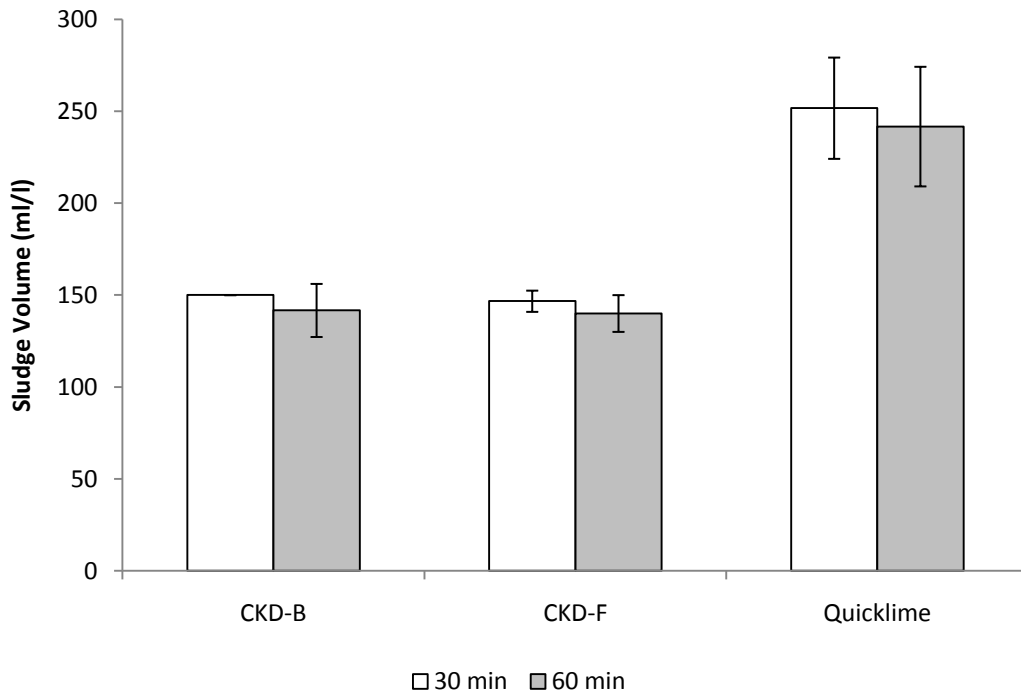




**Figure 6.27: Images of settled mine water after treatment with quicklime with (a) 30 min settling and (b) 60 min settling.**

### 6.7.5 Sludge Generation

Figure 6.28 shows that an additional 30 minutes of settling time did not significantly increase or decrease the volume of sludge generated in mine water treated with slurries made from either CKD samples tested or quicklime. Since most of the larger, heavier particles were removed within the first 30 minutes of settling, the settling of additional particles, indicated by the further reduction in TSS and metals concentrations, for the samples treated with CKD-B would not affect the sludge volume significantly. The main conclusion to be drawn from this data is that increasing the settling time from 30 to 60 minutes does not decrease the sludge volume significantly.



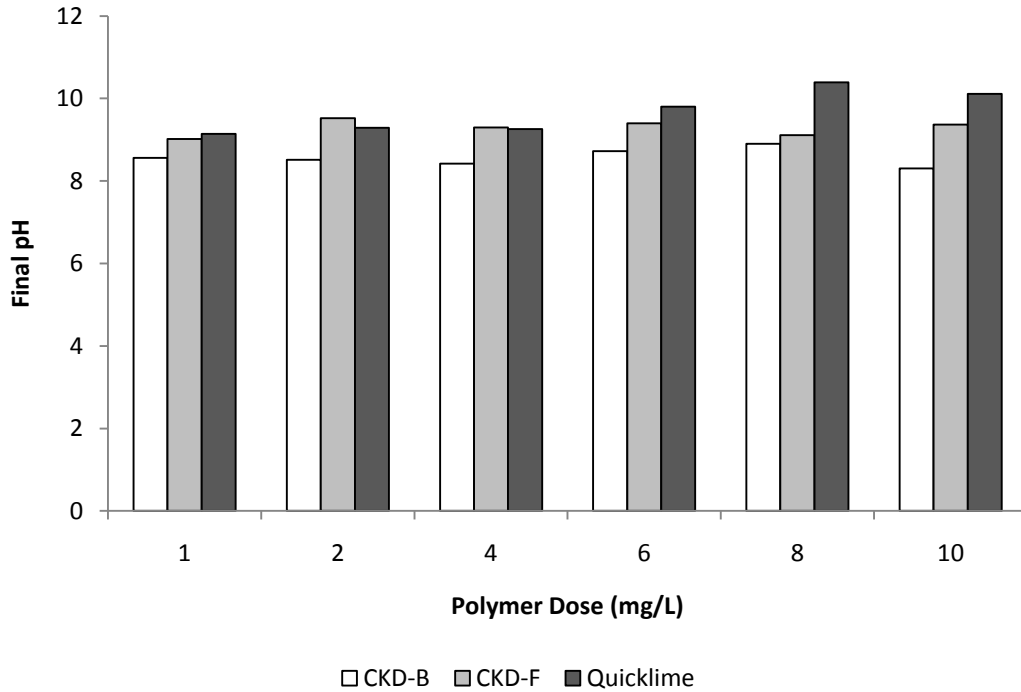
**Figure 6.28: Comparison between sludge volumes generated in treated mine water samples settled for 30 and 60 minutes (n=3).**

### 6.8 Effect of Polymer Dose on Settled Water Quality

Polymer doses were increased from the 1 mg/L used in the original experiments to 2 mg/L up to 10 mg/L for mine water samples treated with slurries made from CKD-B, CKD-F, and quicklime. Repeated trials at each polymer dose were not conducted.

### 6.8.1 pH

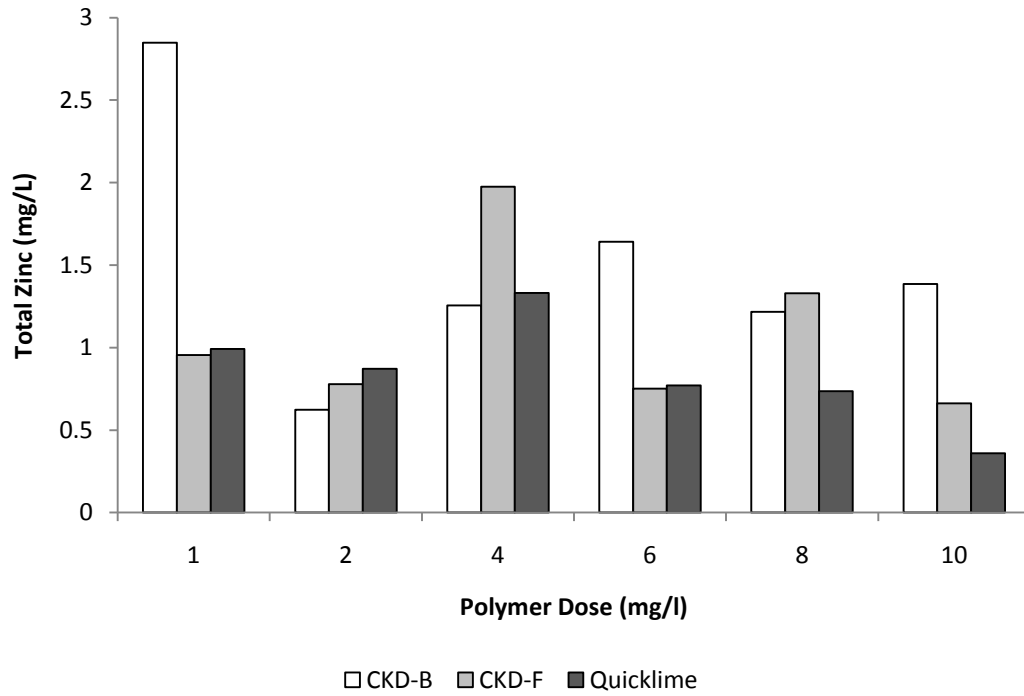
Increasing the polymer dose did not have an effect on the final pH of the treated mine water samples, seen in Figure 6.29. The increase in polymer dose was not expected to have any effect on pH.



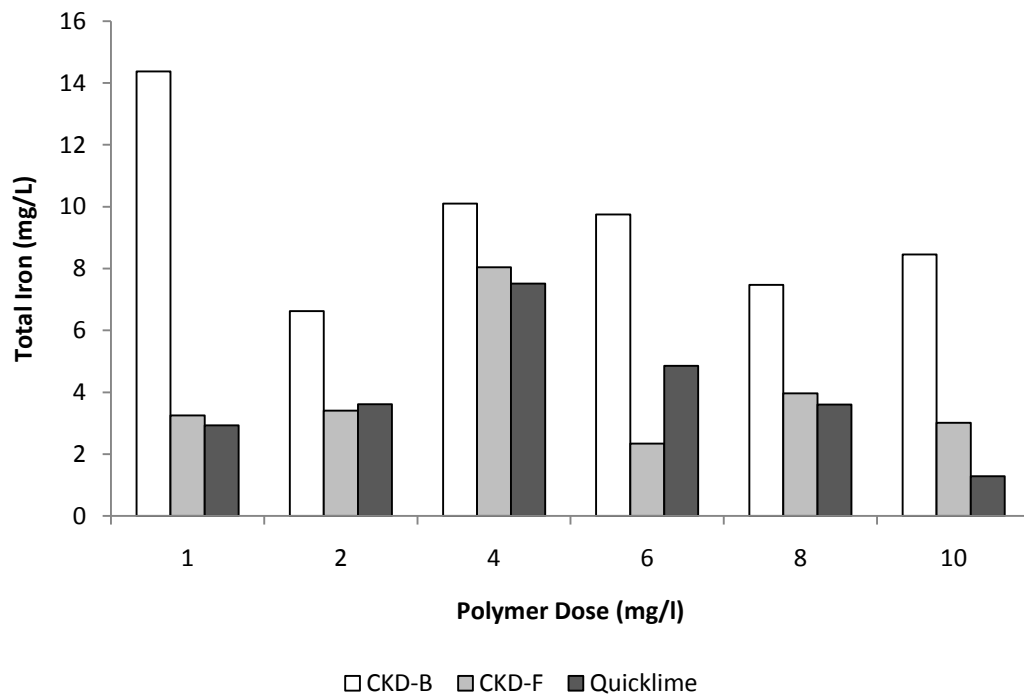
**Figure 6.29: Effect of increasing polymer dose on final pH of treated mine water (n=1).**

### 6.8.2 Target Metals

No definite trend was discernable with regards to removal of zinc and iron, as can be seen in Figure 6.30 and Figure 6.31. Increasing the polymer dose from 1.0 to 2.0 mg/L did reduce both zinc and iron concentrations significantly in samples treated with the CKD-B slurry, after which further polymer increases appear to be detrimental. The effect of increasing the polymer dose from 1.0 to 2.0 mg/L on the samples treated with CKD-F and quicklime was negligible.



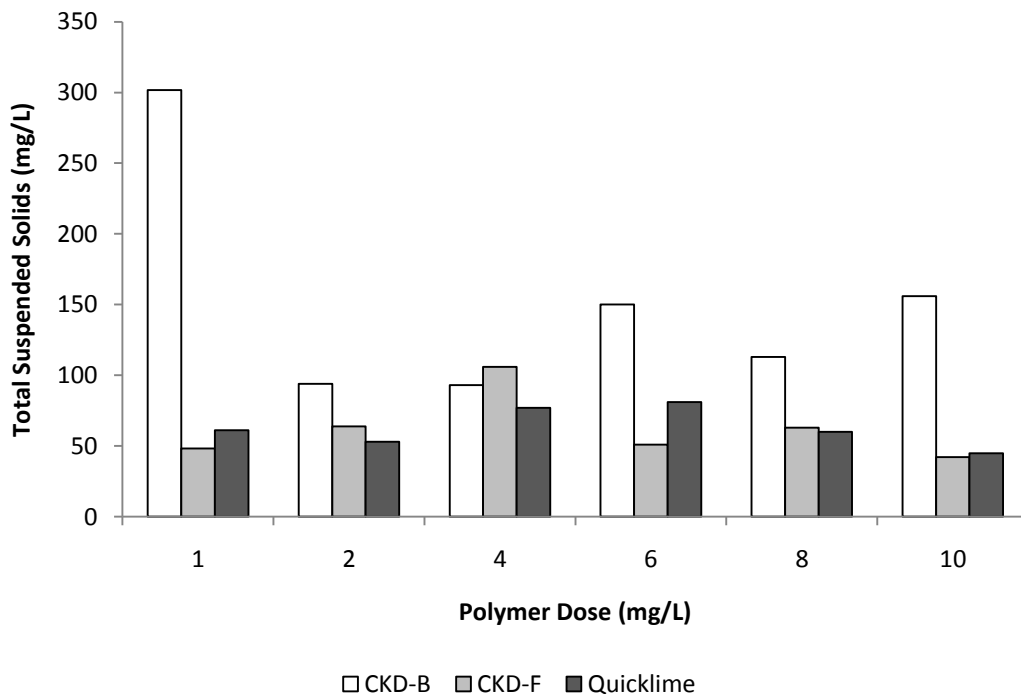
**Figure 6.30: Effect of increasing polymer dose on final total zinc concentrations (n=1).**



**Figure 6.31: Effect of increasing polymer dose on final total iron concentrations (n=1).**

### 6.8.3 Total Suspended Solids

The final TSS concentrations in settled mine water samples treated with CKD-B, CKD-F, and quicklime slurries and with polymer doses from 1.0 to 10.0 mg/L are presented in Figure 6.32. As with total metals, increasing the polymer dose from 1.0 to 2.0 mg/L reduced the TSS concentration of the mine water sample treated with CKD-B considerably. Increasing the polymer dosage beyond this had little effect. The TSS concentrations of the mine water samples treated with the CKD-F and quicklime slurries were unaffected by increases in polymer dose.

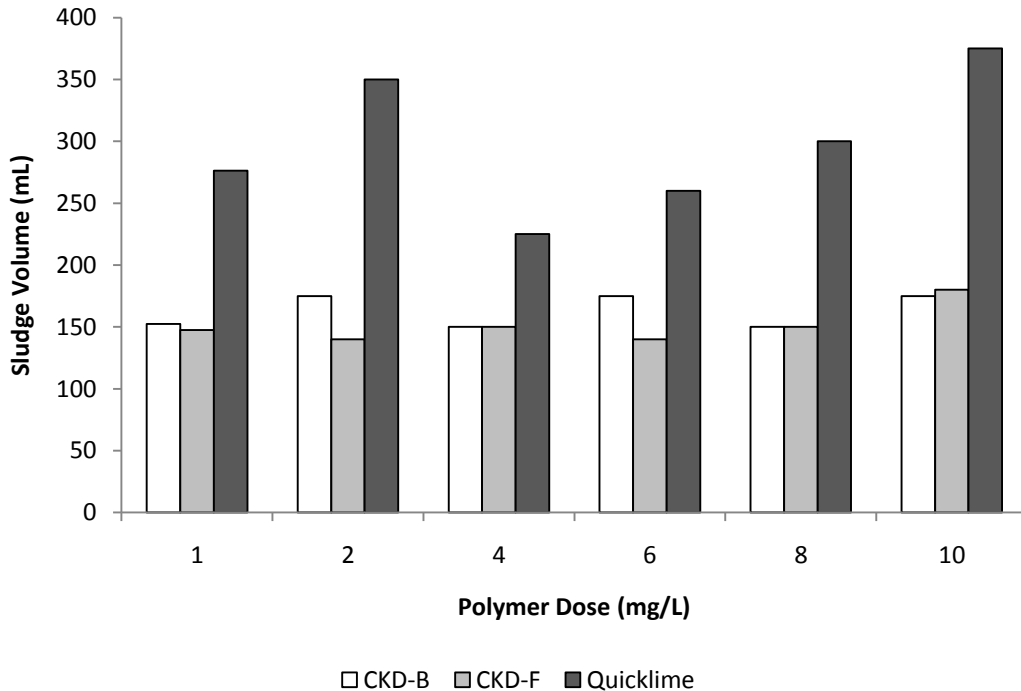


**Figure 6.32: Effect of increasing polymer dose on final TSS concentrations (n=1).**

### 6.8.4 Sludge Generation

The effect of increasing polymer dose on the volume of sludge generated after the sedimentation stage of treatment with the CKD-B, CKD-F, and quicklime slurries is presented in Figure 6.33. Increasing the polymer dose was not found to have an effect on the sludge volume generated in experiments using slurries made from CKD-B and CKD-F. The data also indicates that an increase in polymer dose up to 4 mg/L may potentially

reduce sludge volumes when treating with quicklime, but volumes were found to increase with increasing polymer dose above this.



**Figure 6.33: Effect of increasing polymer dose on sludge volumes generated (n=1).**

## 6.9 Conclusions

Overall, the data presented here from the analyses of the settled water quality of mine water samples confirm that slurries generated using CKD can effectively treat mine water to remove soluble metals. All CKD slurries evaluated, CKD-A, CKD-B, CKD-C, and CKD-F, were able to treat mine water comparably to the quicklime slurry. Treatment with CKD slurries required that more material be added in order to reach the target pH of 9.5, corresponding to the lower free lime and reactive oxides content of the CKD samples evaluated.

Particle analysis of the flocculated mine water samples indicates that although their size distributions were similar, CKD samples generated more particles and flocs overall than quicklime. Particle concentrations were 5 times higher in the flocculated samples that had been treated with CKD-B or CKD-F than in quicklime-treated samples.

Simulated active chemical treatment of mine water with CKD-generated slurries removed over 98 % of zinc and 97 % of iron, the two metals found in the highest concentrations in the untreated mine water. Further, all CKD slurries, generated from CKD-A, CKD-B, CKD-C, and CKD-F, were as effective at removing zinc and iron as the quicklime slurry at the 99 % confidence level. The total metal concentrations remaining in treated mine water samples were higher for the lower free lime content CKD-treated samples (i.e. CKD-A, CKD-B, and CKD-C) than for CKD-F- or quicklime-treated samples, though this was not statistically significant. Soluble zinc and iron concentrations remained low for all treatments, indicating that metals remain mostly in their insoluble, precipitated form during flocculation and sedimentation. The CKD slurries were also effective at removing or reducing concentrations of other metals.

The TSS concentrations remaining in settled mine water samples treated with CKD-A, CKD-B, CKD-C slurries were higher than those remaining in samples treated with CKD-F or quicklime. Particle analysis of settled mine water samples also showed that treatment with the lower free lime content CKD-B resulted in higher concentrations of particles than were found in samples treated with CKD-F or quicklime.

An analysis of the sludge generated during the settling experiments showed that all mine water samples treated with CKD slurries generated significantly less sludge by volume than samples treated with quicklime. Overall sludge volumes generated in quicklime-treated samples were 1.66 to 1.86 times higher than volumes generated with CKD slurries. This could be attributed to the smaller, denser particles generated from treatment with CKD.

Reducing the slurry solids concentration from 25 % to 5 % resulted in significantly lower removals of zinc and iron for all sample treatments. The percent removal of zinc was reduced from over 98 % to between 79 and 87 %, and iron from over 97 % to between 66 and 84 %. Lowering the slurry solids concentration had little to no effect on the pH, TSS, or sludge volume of the settled mine water samples.

Increasing the settling time from 30 minutes to 60 minutes resulted in lower final total iron and zinc concentrations in the treated mine water samples. This was most

significant for samples treated with the low free lime CKD-B slurry. Only CKD-B, CKD-F, and quicklime slurries were evaluated. The increased settling time also significantly reduced TSS concentrations in the mine water treated with CKD-B. TSS concentrations were not significantly reduced with increased settling time for those samples treated with CKD-F or quicklime. However, settled water TSS concentrations were found to be comparably low within the 30 minute settling time experiments for both CKD-F and quicklime.

Increasing the polymer dose from 1 mg/L to 2 mg/L reduced concentrations of zinc and iron as well as TSS for the mine water sample treated with CKD-B. Again, only CKD-B, CKD-F, and quicklime slurries were evaluated. Increasing the polymer dose beyond this had little to no effect.



## Chapter 7: Conclusion

### 7.1 Conclusions

CKD is a fine-grained material with a high lime content that signifies its potential to be used to replace or augment quicklime in acidic wastewater neutralization applications. The CKD samples used in this study were characterized as having total lime contents between 35 and 57 % by weight and free lime from 3.5 to 37 % by weight. The commercial quicklime sample used as a comparison had total and free lime of 90 and 87 % by weight, respectively. The CKD samples also had smaller particle size distributions and larger specific surface areas than the quicklime sample. Free lime content was found to be the strongest predictor of the reactivity of a CKD sample, determined by pH achieved in solution. The modified total reactive oxides ( $TRO = [(CaO + MgO) - LOI] + (Na_2O + K_2O)$ ) value,  $TRO - SO_3$ , was found to correlate most directly to the free lime content of a CKD sample, and could potentially be used to indicate the reactivity of CKD samples if a free lime analysis is not available.

Neutralization experiments showed that all CKD samples tested, even those with low free lime contents, were capable of increasing the pH of both a synthetic acid solution and acidic mine water from a lead/zinc mine. The amount of CKD required for neutralization of samples to a specific pH was found to vary linearly with the sample's free lime content. The CKD samples required from 1.6, for the highest free lime CKD-F, to 14.3, for the lowest free lime CKD-C, times more product addition than quicklime to reach the target pH of 9.5 in bench-scale mine water treatment experiments. Blends of 25 % CKD and 75 % quicklime neutralized samples using doses similar to those required when using 100 % quicklime, while blends of 75 % CKD and 25 % quicklime performed more closely to samples using 100 % CKD.

It was determined that all CKD slurries tested, made from CKD-A, CKD-B, CKD-C, and CKD-F, precipitated more than 99 % of the soluble zinc and iron in the mine water samples. All samples were also comparable to quicklime in this respect. The bench-scale settling experiments showed that all CKD slurries tested were effective at removing over 98 % of total zinc and 97 % of total iron from mine water. The CKD

slurries were also just as effective as quicklime in this respect. CKD slurries generated more particles than the quicklime slurry during precipitation and flocculation, though their size distributions were similar. Treatment of mine water with the CKD-F slurry was comparable to quicklime in terms of TSS and final total metals in settled water, but treatment with the lower free lime content CKDs (CKD-A, CKD-B, and CKD-C) resulted in higher residual TSS and total metals. Increasing the settling time from 30 to 60 minutes reduced these parameters in treatment with CKD-B slurry to be comparable to quicklime. Increasing the polymer dose from 1 to 2 mg/L also reduced TSS and final total metals for the mine water sample treated with CKD-B slurry, however higher polymer doses showed no further reductions. Reducing the solids concentration of the CKD and quicklime slurries used for neutralization of the mine water samples from 25 % to 5 % decreased the precipitation and removal performance of all treatments.

In summary, slurries made from all CKD samples tested were able to treat mine water to reduce acidity and metals concentrations comparably to treatment with quicklime slurries. The amount of solid alkaline material required for treatment with CKD slurries is higher, varying linearly with free lime and reactive oxide content. This increase in material is minimal for a CKD with high free lime. The approximate dose of CKD required for treatment of an acidic effluent stream can be estimated by the modified acid neutralization procedure outlined in Chapter 5. The CKD slurry treatments resulted in significantly lower settled sludge volumes than treatment with quicklime, due to differences in particle size, shape, and density.

## **7.2 Recommendations**

The bench-scale mine water treatment experiments showed that CKD can be used to neutralize acidic wastewater and precipitate and remove soluble metals just as effectively as quicklime. Further testing at pilot- and full-scale should be undertaken to determine the practicality of replacing or augmenting quicklime in mine water treatment plants. The effect of recycling the sludge produced from treatment of mine water with CKD to the lime reactor, as in the HDS process, should be investigated at the bench-scale as well.

Further testing of the sludge generated from treatment with CKD slurries should also be performed to determine if the lower sludge volumes observed compared to treatment with quicklime slurry are an indication of lower overall sludge generation by weight and increased dewaterability of the sludge (i.e. capillary suction time or time to filter). The effect of replacing or augmenting quicklime for mine water treatment with CKD on sludge stability and leaching characteristics (i.e. TCLP) should also be determined.

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## **Appendix: Bench-Scale Mine Water Treatment Data**

**CKD-A**

Tests Performed:

June 19 2009

Slurry Concentration: **50 g/L**

		<b>Polymer = 1 mg/l</b>						
		N/A	1	2	3	average	st dev	
<b>COAGULATION</b>	Replicate Number	N/A	1	2	3	average	st dev	
	Slurry Amount	ml	200	200	200	200	0	
	CKD Concentration	g/l	10	10	10	10	0	
	pH	N/A	9.65	9.58	9.46	9.6	0.1	
	Conductivity	mS/cm	4.92	5.062	5.161	5.0	0.1	
	Total Suspended Solids	mg/l	6386	6356	6126	6289.3	142.2	
	Total Zinc	mg/l	121.8	126	123.1	123.6	2.2	
	Dissolved Zinc	mg/l	28.4	26.9	28.9	28.1	1.0	
	Zinc Precipitation	%	81.02	82.02	80.68	81.2	0.7	
	Total Iron	mg/l	465.5	497.2	452.5	471.7	23.0	
	Dissolved Iron	mg/l	121.6	130.1	118.5	123.4	6.0	
	Iron Precipitation	%	74.20	72.40	74.86	73.8	1.3	
<b>FINAL</b>	Settled Sludge Volume	ml	200	200	200	200	0	
	pH	N/A	9.4	8.41	5.76	7.9	1.9	
	Conductivity	mS/cm	5.028	5.001	5.118	5.0	0.1	
	Total Suspended Solids	mg/l	192	46	70	102.7	78.3	
	Total Zinc	mg/l	35.7	27.4	33.2	32.1	4.3	
	Dissolved Zinc	mg/l	31.9	35.2	29.4	32.2	2.9	
	Zinc Removal	%	76.57	82.02	78.22	78.9	2.8	
	Total Iron	mg/l	151.9	152.6	134.9	146.5	10.0	
	Dissolved Iron	mg/l	108.2	117.9	119.4	115.2	6.1	
	Iron Removal	%	69.96	69.82	73.32	71.0	2.0	

**CKD-B**

Tests Performed:

June 12 2009

Slurry Concentration: **50 g/L**

		Polymer = 1 mg/l						
		Replicate Number	N/A	1	2	3	average	st dev
		Slurry Amount	ml	200	230	230	220	17.32051
<b>COAGULATION</b>	CKD Concentration	g/l	10.0	11.5	11.5	11.0	0.9	
	pH	N/A	9.1	9.9	9.5	9.5	0.4	
	Conductivity	mS/cm	4.681	4.442	4.583	4.569	0.120	
	Total Suspended Solids	mg/l	5208	6110	5248	5522	510	
	Total Zinc	mg/l	66.8	85.2	73.6	75.2	9.3	
	Dissolved Zinc	mg/l	15.0	12.3	12.3	13.2	1.6	
	Zinc Precipitation	%	86.0	88.5	88.5	87.7	1.5	
	Total Iron	mg/l	248.8	359.1	303.4	303.8	55.2	
	Dissolved Iron	mg/l	107.8	76.5	91.5	91.9	15.7	
	Iron Precipitation	%	71.6	79.9	75.9	75.8	4.1	
	<b>FINAL</b>	Settled Sludge Volume	ml	150.0	150.0	150.0	150.0	0.0
pH		N/A	6.4	6.9	5.7	6.3	0.6	
Conductivity		mS/cm	4.569	4.657	4.864	4.697	0.151	
Total Suspended Solids		mg/l	10	276	300	195	161	
Total Zinc		mg/l	17.3	13.0	14.2	14.8	2.2	
Dissolved Zinc		mg/l	13.1	11.2	6.5	10.3	3.4	
Zinc Removal		%	83.5	87.6	86.5	85.8	2.1	
Total Iron		mg/l	137.3	129.4	122.5	129.7	7.4	
Dissolved Iron		mg/l	104.1	80.2	71.3	85.2	17.0	
Iron Removal		%	64.1	66.2	68.0	66.1	1.9	

**CKD-C**

Tests Performed: June 18 2009

Slurry Concentration: 50 g/L

		<b>Polymer = 1 mg/l</b>						
		Replicate Number	N/A	1	2	3	average	st dev
<b>COAGULATION</b>	Slurry Amount	ml		350	350	350	350	0
	CKD Concentration	g/l		17.5	17.5	17.5	17.5	0
	pH	N/A		9.36	9.3	9.16	9.3	0.1
	Conductivity	mS/cm		5.881	5.734	5.704	5.8	0.1
	Total Suspended Solids	mg/l		9360	8178	6546	8028.0	1413.0
	Total Zinc	mg/l		132.3	127.6	133.1	131.0	3.0
	Dissolved Zinc	mg/l		18.7	20	17.7	18.8	1.2
	Zinc Precipitation	%		87.95	87.11	88.60	87.9	0.7
	Total Iron	mg/l		287.7	214.4	268.4	256.8	38.0
	Dissolved Iron	mg/l		65.5	73.2	68.8	69.2	3.9
	Iron Precipitation	%		86.80	85.25	86.13	86.1	0.8
	<b>FINAL</b>	Settled Sludge Volume	ml		200	200	200	200
pH		N/A		7.29	7.52	7.35	7.4	0.1
Conductivity		mS/cm		5.795	5.69	5.637	5.7	0.1
Total Suspended Solids		mg/l		160	128	150	146.0	16.4
Total Zinc		mg/l		22	25.1	18.7	21.9	3.2
Dissolved Zinc		mg/l		18.4	18.2	19	18.5	0.4
Zinc Removal		%		84.59	82.42	86.90	84.6	2.2
Total Iron		mg/l		64.4	80.6	90.7	78.6	13.3
Dissolved Iron		mg/l		67	63.9	62.8	64.6	2.2
Iron Removal		%		87.19	83.96	81.95	84.4	2.6

**CKD-F**

Tests Performed:

June 16 2009

Slurry Concentration: **50 g/L**

		<b>Polymer = 1 mg/l</b>						
		N/A	1	2	3	average	st dev	
<b>COAGULATION</b>	Replicate Number	N/A	1	2	3	average	st dev	
	Slurry Amount	ml	55	55	55	55	0	
	CKD Concentration	g/l	2.75	2.75	2.75	2.75	0	
	pH	N/A	9.59	9.66	9.75	9.7	0.1	
	Conductivity	mS/cm	4.75	4.80	4.80	4.78	0.03	
	Total Suspended Solids	mg/l	2158	2462	2272	2297	154	
	Total Zinc	mg/l	89.5	94.6	100.8	95.0	5.7	
	Dissolved Zinc	mg/l	10.7	4.3	8.7	7.9	3.3	
	Zinc Precipitation	%	85.80	94.29	88.46	89.52	4.34	
	Total Iron	mg/l	348.3	361.8	373.8	361.3	12.8	
	Dissolved Iron	mg/l	100.7	96.1	96.3	97.7	2.6	
	Iron Precipitation	%	70.32	71.68	71.62	71.21	0.77	
<b>FINAL</b>	Settled Sludge Volume	ml	200	200	200	200	0	
	pH	N/A	8.76	8.6	9.25	8.9	0.3	
	Conductivity	mS/cm	5.05	4.97	4.79	4.93	0.13	
	Total Suspended Solids	mg/l	306	46	12	121	161	
	Total Zinc	mg/l	14.5	16.2	17.9	16.2	1.7	
	Dissolved Zinc	mg/l	7.1	4.8	8.7	6.9	2.0	
	Zinc Removal	%	88.49	87.14	85.79	87.1	1.3	
	Total Iron	mg/l	105.4	107.3	101.4	104.7	3.0	
	Dissolved Iron	mg/l	96.1	93	93.9	94.3	1.6	
	Iron Removal	%	75.21	74.76	76.15	75.37	0.71	

# Quicklime

Tests Performed:

June 12 2009

Slurry Concentration: 50 g/L

		Polymer = 1 mg/l						
		Replicate Number	N/A	1	2	3	average	st dev
COAGULATION	Slurry Amount	ml		45	45	45	45	0
	CKD Concentration	g/l		2.25	2.25	2.25	2.25	0
	pH	N/A		9.85	10.21	10.71	10.3	0.4
	Conductivity	mS/cm		4.785	4.6	5.022	4.8	0.2
	Total Suspended Solids	mg/l		1758	1620	1688	1688.7	69.0
	Total Zinc	mg/l		90.3	89.5	96.3	92.0	3.7
	Dissolved Zinc	mg/l		12.1	11.8	11.4	11.8	0.4
	Zinc Precipitation	%		88.69	88.97	89.35	89.0	0.3
	Total Iron	mg/l		326.9	322.6	350.4	333.3	15.0
	Dissolved Iron	mg/l		88.2	91.2	77	85.5	7.5
	Iron Precipitation	%		76.78	75.99	79.73	77.5	2.0
	FINAL	Settled Sludge Volume	ml		240	300	300	280
pH		N/A		9.65	9.81	10.79	10.1	0.6
Conductivity		mS/cm		5.022	4.665	4.635	4.8	0.2
Total Suspended Solids		mg/l		26	30	20	25.3	5.0
Total Zinc		mg/l		12.7	14.3	13.5	13.5	0.8
Dissolved Zinc		mg/l		9.6	10.9	12.7	11.1	1.6
Zinc Removal		%		87.88	86.35	87.12	87.1	0.8
Total Iron		mg/l		91.6	100.7	98.4	96.9	4.7
Dissolved Iron		mg/l		88.9	78.5	80.4	82.6	5.5
Iron Removal		%		76.06	73.68	74.28	74.7	1.2

**CKD-A**

Tests Performed: Jan 20 & 26, 2010

Slurry Concentration: **250 g/L**

		<b>Polymer = 1 mg/l</b>							
		Replicate Number	N/A	1	2	3	4	average	st dev
		Slurry Amount	ml	50	55	55	55	53.75	2.5
<b>COAGULATION</b>	CKD Concentration	g/l	12.5	13.75	13.75	13.75	13.75	13.44	0.63
	pH	N/A	9.49	9.51	9.44	9.56	9.5	0.0	
	Dissolved Zinc	mg/l	0.193	0.139	0.134	0.205	0.2	0.0	
	Zinc Precipitation	%	99.81	99.88	99.88	99.82	99.8	0.0	
	Dissolved Iron	mg/l	0.016	0.226	0.119	0.392	0.2	0.2	
	Iron Precipitation	%	99.99	99.94	99.97	99.89	99.9	0.0	
	<b>FINAL</b>	Settled Sludge Volume	ml	160	160	160	180	165.0	10.0
		pH	N/A	8.75	9.3	8.96	9.59	9.2	0.4
Total Suspended Solids		mg/l	149	371	327	203	262.5	103.9	
Total Zinc		mg/l	0.96	3.47	2.76	1.296	2.1	1.2	
Dissolved Zinc		mg/l	0.092	0.144	0.141	0.109	0.1	0.0	
Zinc Removal		%	99.14	97.11	97.70	98.92	98.2	1.0	
Total Iron		mg/l	4.371	20.15	14.21	8.39	11.8	6.9	
Dissolved Iron		mg/l	<mdl	0.469	0.242	0.243	0.3	0.1	
Iron Removal		%	98.56	94.69	96.26	97.79	96.8	1.7	

<mdl less than method detection limit



**CKD-B**

Tests Performed: Jan 25 2010

Slurry Concentration: **250 g/L**

		Polymer = 1 mg/l						
		N/A	1	2	3	4	average	st dev
Replicate Number		N/A	1	2	3	4	average	st dev
Slurry Amount		ml	70	70	70	70	70	0
<b>COAGULATION</b>	CKD Concentration	g/l	17.5	17.5	17.5	17.5	17.5	0.0
	pH	N/A	9.48	9.45	9.6	9.53	9.5	0.1
	Dissolved Zinc	mg/l	0.197	0.858	0.709	0.151	0.5	0.4
	Zinc Precipitation	%	99.82	99.22	99.35	99.86	99.6	0.3
	Dissolved Iron	mg/l	0.669	3.882	4.323	0.428	2.3	2.1
	Iron Precipitation	%	99.83	99.00	98.89	99.89	99.4	0.5
	<b>FINAL (30 minute settling)</b>	Settled Sludge Volume	ml	150	150	160	150	152.5
pH		N/A	8.63	8.67	8.66	8.27	8.6	0.2
Total Suspended Solids		mg/l	449	252	334	172	302	118
Total Zinc		mg/l	4.86	1.96	2.83	1.738	2.8	1.4
Dissolved Zinc		mg/l	0.133	0.087	0.078	0.135	0.1	0.0
Zinc Removal		%	95.88	98.34	97.60	98.53	97.6	1.2
Total Iron		mg/l	25.13	10.08	14.36	7.902	14.4	7.7
Dissolved Iron		mg/l	0.153	0.033	0.016	0.175	0.1	0.1
Iron Removal		%	94.30	97.71	96.74	98.21	96.7	1.7

## CKD-B

Tests Performed:

Jan 25 2010

Slurry Concentration: **250 g/L**

		Polymer = 1 mg/l						
		Replicate Number	N/A	1	2	3	average	st dev
<b>COAGULATION</b>	Slurry Amount	ml		70	70	70	70	0
	CKD Concentration	g/l		17.5	17.5	17.5	17.5	0.0
	pH	N/A		9.46	9.48	9.53	9.5	0.1
	Dissolved Zinc	mg/l		0.299	0.286	0.168	0.5	0.4
	Zinc Precipitation	%		99.76	99.77	99.87	99.6	0.3
	Dissolved Iron	mg/l		1.215	1.124	0.573	2.3	2.1
	Iron Precipitation	%		99.69	99.71	99.85	99.4	0.5
<b>FINAL (30 minute settling)</b>	Settled Sludge Volume	ml		150	150	150	152.5	5.0
	pH	N/A		9.3	8.8	9.13	8.6	0.2
	Total Suspended Solids	mg/l		486	406	284	302	118
	Total Zinc	mg/l		5.77	5.33	3.11	2.8	1.4
	Dissolved Zinc	mg/l		0.073	0.085	0.075	0.1	0.0
	Zinc Removal	%		95.70	96.03	97.68	97.6	1.2
	Total Iron	mg/l		24.1	20.22	12.58	14.4	7.7
	Dissolved Iron	mg/l		<mdl	0.223	0.24	0.1	0.1
	Iron Removal	%		94.31	95.22	97.03	96.7	1.7
<b>FINAL (60 minute settling)</b>	Settled Sludge Volume	ml		125	150	150	141.7	14.4
	pH	N/A		9.22	8.55	9.04	8.9	0.3
	Total Suspended Solids	mg/l		67	53	38	52.7	14.5
	Total Zinc	mg/l		0.161	0.202	0.166	0.2	0.0
	Dissolved Zinc	mg/l		0.091	0.093	0.081	0.1	0.0
	Zinc Removal	%		99.88	99.85	99.88	99.9	0.0
	Total Iron	mg/l		1.14	1.404	1.247	1.3	0.1
	Dissolved Iron	mg/l		<mdl	<mdl	<mdl	<mdl	<mdl
	Iron Removal	%		99.73	99.67	99.71	99.7	0.0

<mdl      less than method detection limit

**CKD-C**

Tests Performed: Jan 19 & 25, 2010

Slurry Concentration: 250 g/L

		<b>Polymer = 1 mg/l</b>						
		N/A	1	2	3	4	average	st dev
<b>COAGULATION</b>	Replicate Number	N/A	1	2	3	4	average	st dev
	Slurry Amount	ml	100	120	120	120	115	10
	CKD Concentration	g/l	25	30	30	30	28.75	2.5
	pH	N/A	9.53	9.51	9.56	9.58	9.5	0.0
	Dissolved Zinc	mg/l	0.198	0.364	0.192	0.19	0.2	0.1
	Zinc Precipitation	%	99.82	99.67	99.83	99.83	99.8	0.1
	Dissolved Iron	mg/l	0.076	1.202	0.534	0.282	0.5	0.5
	Iron Precipitation	%	99.97	99.66	99.85	99.92	99.9	0.1
<b>FINAL</b>	Settled Sludge Volume	ml	175	150	160	180	166.25	13.77
	pH	N/A	8.29	8.24	8.75	9.08	8.6	0.4
	Total Suspended Solids	mg/l	256.8	362	379	242	310.0	70.5
	Total Zinc	mg/l	4.14	2.015	1.948	1.464	2.4	1.2
	Dissolved Zinc	mg/l	0.13	0.14	0.164	0.194	0.2	0.0
	Zinc Removal	%	96.29	98.30	98.36	98.77	97.9	1.1
	Total Iron	mg/l	8.058	9.254	9.364	6.451	8.3	1.4
	Dissolved Iron	mg/l	<mdl	<mdl	0.031	0.759	0.4	0.5
	Iron Removal	%	97.42	97.57	97.54	98.31	97.7	0.4

<mdl      less than method detection limit

## CKD-F

Tests Performed: Jan 22 & 29, 2010

Slurry Concentration: 250 g/L

		Polymer = 1 mg/l						
		N/A	1	2	3	4	average	st dev
<b>COAGULATION</b>	Replicate Number	N/A	1	2	3	4	average	st dev
	Slurry Amount	ml	13	13	13	13	13	0
	CKD Concentration	g/l	3.25	3.25	3.25	3.25	3.25	0
	pH	N/A	9.45	9.52	9.51	9.47	9.5	0.0
	Dissolved Zinc	mg/l	0.222	0.773	0.522	0.268	0.4	0.3
	Zinc Precipitation	%	99.80	99.22	99.47	99.73	99.6	0.3
	Dissolved Iron	mg/l	2.032	2.626	1.505	0.578	1.7	0.9
Iron Precipitation	%	99.52	99.27	99.58	99.84	99.6	0.2	
<b>FINAL (30 minute settling)</b>	Settled Sludge Volume	ml	150	150	140	150	147.5	5
	pH	N/A	9.16	9.27	8.79	8.84	9.0	0.2
	Total Suspended Solids	mg/l	65	44	45	39	48.3	11.5
	Total Zinc	mg/l	0.984	---	1.039	0.84	1.0	0.1
	Dissolved Zinc	mg/l	<mdl	0.126	0.181	0.153	0.2	0.0
	Zinc Removal	%	99.21	---	99.02	99.21	99.1	0.1
	Total Iron	mg/l	4.576	---	2.836	2.343	3.3	1.2
	Dissolved Iron	mg/l	0.388	0.022	0.016	0.009	0.1	0.2
	Iron Removal	%	98.98	---	99.25	99.38	99.2	0.2
<b>FINAL (60 minute settling)</b>	Settled Sludge Volume	ml	N/A	140	130	150	140	10
	pH	N/A	N/A	8.74	8.64	8.74	8.71	0.06
	Total Suspended Solids	mg/l	N/A	44	40	41	41.67	2.08
	Total Zinc	mg/l	N/A	0.679	0.509	0.381	0.52	0.15
	Dissolved Zinc	mg/l	N/A	0.11	0.16	0.089	0.12	0.04
	Zinc Removal	%	N/A	99.36	99.52	99.64	99.51	0.14
	Total Iron	mg/l	N/A	1.69	1.219	1.224	1.38	0.27
	Dissolved Iron	mg/l	N/A	0.136	0.142	0.154	0.14	0.01
	Iron Removal	%	N/A	99.56	99.68	99.68	99.64	0.07

--- sample was contaminated  
 <mdl less than method detection limit

## Quicklime

Tests Performed: Jan 21 & 27, 2010

Slurry Concentration: 250 g/L

		Polymer = 1 mg/l							
		Replicate Number	N/A	1	2	3	4	average	st dev
		Slurry Amount	ml	8	8	8	8	8	0
<b>COAGULATION</b>	CKD Concentration	g/l	2	2	2	2	2	2	0
	pH	N/A	9.51	9.5	9.49	9.47	9.5	0.0	
	Dissolved Zinc	mg/l	0.256	0.648	0.539	0.762	0.6	0.2	
	Zinc Precipitation	%	99.75	99.38	99.49	99.28	99.5	0.2	
	Dissolved Iron	mg/l	0.093	2.058	1.589	3.11	1.7	1.3	
	Iron Precipitation	%	99.97	99.38	99.52	99.06	99.5	0.4	
	<b>FINAL (30 minute settling)</b>	Settled Sludge Volume	ml	350	225	280	250	276.3	54.1
pH		N/A	9.61	9.1	9	8.85	9.1	0.3	
Total Suspended Solids		mg/l	54	46	72	73	61.3	13.4	
Total Zinc		mg/l	0.801	0.881	1.023	1.261	1.0	0.2	
Dissolved Zinc		mg/l	0.115	0.102	0.359	1.328	0.5	0.6	
Zinc Removal		%	99.28	99.25	99.13	98.93	99.1	0.2	
Total Iron		mg/l	3.638	2.555	2.886	2.64	2.9	0.5	
Dissolved Iron		mg/l	<mdl	<mdl	0.869	4.94	2.9	2.9	
Iron Removal		%	99.05	99.33	99.24	99.30	99.2	0.1	
<b>FINAL (60 minute settling)</b>	Settled Sludge Volume	ml	N/A	210	275	240	241.67	32.53	
	pH	N/A	N/A	8.99	9.18	8.74	8.97	0.22	
	Total Suspended Solids	mg/l	N/A	65	77	57	66.33	10.07	
	Total Zinc	mg/l	N/A	0.46	0.678	0.984	0.71	0.26	
	Dissolved Zinc	mg/l	N/A	0.139	0.1	0.101	0.11	0.02	
	Zinc Removal	%	N/A	99.61	99.42	99.17	99.40	0.22	
	Total Iron	mg/l	N/A	0.443	1.024	0.54	0.67	0.31	
	Dissolved Iron	mg/l	N/A	0.033	<mdl	<mdl	0.03	0.01	
	Iron Removal	%	N/A	99.88	99.73	99.86	99.82	0.08	

<mdl less than method detection limit