Acid Rock Drainage Remediation with Bear River Clinoptilolite in a Slurry Bubble Column

by

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Abstract

Clinoptilolite, a natural zeolite, is capable of removing heavy metals from acid rock drainage (ARD). However, previous studies have predominantly been on artificial solutions, with no previous work on sorbent regeneration. This study investigated a novel process for capturing ARD and regenerating clinoptilolite based on a slurry bubble column (SBC) for enhanced mass transfer.

Uptake tests were performed with natural ARD and various sorbent particle sizes from 300 to 1400 μm in average diameter, superficial gas velocity from 0.08 to 0.23 m/s, initial aqueous pH from 2 to 6, Zn concentrations from 15 to 215 ppm and sorbent/solution ratio from 25 to 400 g/kg to test zinc uptake.

To obtain favorable regeneration, zinc in loaded clinoptilolite was displaced by NaCl as regenerant. Regenerant concentrations from 10 to 40 g/kg, regenerant/sorbent ratios from 100 to 400 g/kg, particle sizes from 300 to 1400 μm, and initial regenerant pH from 2 to 6 were tested to find suitable regeneration conditions.

To test the long-term viability of clinoptilolite sorbent, repeated capture-regeneration cycles were tested. It was shown that NaCl regenerant could be reused to minimize waste volume. Three removal-only cycles after 10 full cycles continuously decreased the accumulated zinc in the clinoptilolite, allowing the uptake capacity to be almost fully recovered. When 10 full cycles were tested after three removal stages, results were similar to those for the first 10 cycles. Only one-quarter of the regenerant was required to achieve a similar total zinc uptake when reused NaCl solution was utilized.

During the remediation, dealumination of clinoptilolite was observed, under certain circumstances. Increased Al in the aqueous phase led to co-precipitation of Zn-Al colloid, enhanced by abundant sulfate in solution. The unit zinc uptake of the Al colloid was much higher than that of the raw clinoptilolite.

Adsorption isotherms were fitted to the Langmuir model, and the overall aqueous
species and surface uptake were explored by the PHREEQC model. The cyclic capture/regeneration process is promising that further development work is warranted.
Preface

A slightly modified version of Chapter 2 was published as Xu, W., Li, L. Y. and Grace, J. R., Zinc removal from acid rock drainage by clinoptilolite in a slurry bubble column. Applied Clay Science, 50(1), 158-163 (2010).

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<th>Description</th>
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<tbody>
<tr>
<td>AAS</td>
<td>atomic adsorption spectroscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>anoxic limestone drains</td>
</tr>
<tr>
<td>ARD</td>
<td>acid rock drainage</td>
</tr>
<tr>
<td>AMD</td>
<td>acid mine drainage</td>
</tr>
<tr>
<td>BCMEM</td>
<td>British Columbia (Canada) Ministry of Energy and Mines</td>
</tr>
<tr>
<td>BCMELP</td>
<td>British Columbia (Canada) Ministry of Environment Lands and Parks</td>
</tr>
<tr>
<td>CCME</td>
<td>Canadian Environmental Quality Guidelines and Summary by Canadian Council of Ministers of the Environment</td>
</tr>
<tr>
<td>BET</td>
<td>BET method for surface area determination (Brunauer, Emmett and Teller, 1938)</td>
</tr>
<tr>
<td>EGME</td>
<td>EGME (Ethylene Glycol Monomethyl Ether or 2-Methoxyethanol) method for surface area determination</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>MMER</td>
<td>metal mining effluent regulations (Canada)</td>
</tr>
<tr>
<td>SBC</td>
<td>slurry bubble column</td>
</tr>
<tr>
<td>USEPA</td>
<td>US Environmental Protection Agency</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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# List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$C_0$</td>
<td>initial contaminant concentration (mg/kg)</td>
</tr>
<tr>
<td>$C_t$</td>
<td>contaminant concentration at time $t$ (mg/kg)</td>
</tr>
<tr>
<td>$c$</td>
<td>solid content in bubble column (vol%)</td>
</tr>
<tr>
<td>$c_e$</td>
<td>voidage, gas holdup (dimensionless)</td>
</tr>
<tr>
<td>IAP</td>
<td>ion activity product</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>equilibrium constant, SI = log(IAP/$K_{eq}$)</td>
</tr>
<tr>
<td>$K_{sp}$</td>
<td>solubility product</td>
</tr>
<tr>
<td>$m_{ARD}$</td>
<td>the mass of metal solution (g or kg)</td>
</tr>
<tr>
<td>$m_{clinoptilolite}$</td>
<td>the dry weight of clinoptilolite (g)</td>
</tr>
<tr>
<td>$q$</td>
<td>gas flow rate (m/s)</td>
</tr>
<tr>
<td>SI</td>
<td>saturation index</td>
</tr>
<tr>
<td>$u$</td>
<td>mean bubble speed (m/s)</td>
</tr>
<tr>
<td>uptake</td>
<td>the quantity of metal ion per gram onto clinoptilolite from ARD (mg/g)</td>
</tr>
</tbody>
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Chapter 1 Introduction

1.1 Background

1.1.1 General Acid Rock/Mine Drainage

One of the most serious environmental problems faced by the mining industry, Acid Mine Drainage (AMD) is predominantly caused by the weathering of pyrite, a mineral composed of iron and sulfur (FeS$_2$). Mineral deposits containing pyrite are usually present as sulfides, deposited beneath the earth's surface, where there is little or no oxygen. When mining/excavation occurs, these minerals are exposed and brought to the surface where a combination of weathering and mining activities results in acidic waters (Filion et al. 1990; Environmental Mining Council 1997; Eba Engineering Consultants Ltd. 2004; Akcil and Koldas 2006).

Pyrite oxidizes to produce very acidic waters (pH<3), which can dissolve heavy metals and other toxic elements and cause them to be transported into downstream waters. As a result, concentrations of heavy metals in natural surface waters are significantly enhanced after excavation and weathering of sulfide-rich minerals in mining site and construction areas. These acidic waters mobilize elements contained in the mineral deposits, such as iron, copper, zinc, cadmium and manganese, elements which are not biodegradable and thus tend to accumulate in living organisms, causing various diseases, disorders and even death. To diminish their toxic effects, these heavy metals contained in acidic wastewaters must be treated before being discharged into the receiving environment (Environmental Mining Council 1997; McGinness 1999; Johnson and Hallberg 2005; Valente and Leal Gomes 2009).

Although current mining activities result in the formation of AMD, the greatest AMD pollution originates from abandoned deep mines. Similar drainage resulting from construction sites is usually referred to as Acid Rock Drainage (ARD).
1.1.2 Highway 97C ARD Issues

Highway 97C, also known as the Okanagan Connector, links Merritt to Peachland, British Columbia (Figure 1.2). A road through local altered and pyrite-bearing sedimentary rock was exposed in the late 1980s. As the ARD potential was not recognized during construction, no means of mitigation was applied. After construction, ARD formed when surface water passing over the exposed rock, dissolved calcite and dolomite, leaving behind pyrite, which then be oxidized to sulfate making the aqueous phase acidic. Drainage then flowed into an unnamed creek (Figure 1.2) and onward to Pennask Creek, located south of Pennask Lake in British Columbia, Canada (see Figure 1.2). Pennask Creek is the main drainage course in the watershed, originating radially around Pennask Mountain to the south and draining generally northward into the southwest corner of the lake. The lake is also fed by other surrounding watersheds. Pennask Creek and Lake include a fish hatchery and fish habitat, protected under Canada’s Fisheries Act.

1.1.3 ARD Remediation

Water remediation systems are required worldwide for ARD. Relatively simple yet effective technologies utilizing low-cost abundant resources would be advantageous for the establishment of more sustainable treatment strategies.

ARD Treatment technologies mainly fall into two broad categories: Passive and Active treatment. Active treatment involves adding a neutralizing agent to the source or stream of the ARD. Active treatment can be very efficient, but requires long-term and continuous commitment to treatment. Equipment failure, weather conditions and budget restrictions commonly inhibit the remediation performance (Johnson and Hallberg 2005; Valente and Leal Gomes 2009).

Numerous chemicals are used in active remediation of ARD (for neutralization and precipitation), including ammonia (NH₃), calcium carbonate (CaCO₃), calcium oxide (CaO), calcium hydroxide (Ca(OH)₂), sodium hydroxide (NaOH) and sodium
Adding limestone as a neutralization and precipitation agent is currently the most common treatment method. However, this is expensive due to the low efficiency caused by reddish ferric hydroxide/salts coating on limestone, which results in rapid loss of effectiveness, as well as generating additional solid waste.

Activated carbon adsorption is considered to be a particularly competitive and effective process for removal of trace quantities of heavy metals (Rios et al. 2008; Depci et al. 2012). However, commercial activated carbon is not suitable due to the high costs associated with production and regeneration of spent carbon.

Prevailing passive treatment methods for ARD remediation are aerobic wetlands, anoxic limestone drains (ALD), limestone sand dosing, open limestone channels and channel bars, limestone diversion wells and settling ponds (Gazea et al. 1996).

Other treatment methods in use for ARD treatment include electrodialysis, electrolysis, reverse osmosis, adsorption (e.g. by natural zeolites, activated carbon, fly ash, Al or Fe flocculants and dead biomass) (Valente and Leal Gomes 2009).

1.1.4 Clinoptilolite and Its Application in ARD Remediation

Simple yet effective technologies utilizing low-cost abundant materials would be advantageous for the establishment of improved treatment strategies. When low-cost and suitable ion exchange materials are available, ion exchange is among the most promising treatment technologies for ARD or AMD. In this context natural silicate minerals, such as zeolites, are of a significant interest, mainly due to their valuable sorption characteristics provided by a combination of ion-exchange and molecular-sieve properties which can be modified relatively easily.

Zeolites are naturally-occurring hydrated aluminosilicate minerals. Their structures consist of three-dimensional frameworks of SiO₄ and AlO₄ tetrahedra containing voids which can be occupied by ions and water molecules, with considerable freedom of movement, facilitating ion-exchange and reversible dehydration. The aluminum ion is small enough to occupy the position at the center of
the tetrahedron of four oxygen atoms. The substitution of $\text{Si}^{4+}$ by $\text{Al}^{3+}$ defines the negative charge of the framework, which is compensated by monovalent (sodium, potassium) or divalent (calcium) cations in the channel (Jacobs et al. 2001). These cations are exchangeable with dissolved cations such as lead, cadmium, zinc and manganese. The fact that the zeolite exchangeable ions (sodium, calcium and potassium) are relatively innocuous makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters.

The application of zeolites as ion exchangers for environmental protection and other applications has been stimulated by promising results, the nontoxic nature of these materials, their availability in the many parts of the world, and their low cost (Rios et al. 2008; Li et al. 2011). Removal and recuperation of heavy metals from aqueous solutions by natural zeolites are commonly carried out cyclically, with uptake alternating with regeneration of the zeolite for reuse. The mineral stability of zeolites and their structural changes during treatment in various media play important roles in determining their potential as ion exchangers (Araya and Dyer 1981; Semmens and Martin 1988; Rivera et al. 2000; Rios et al. 2008; Ruiz-Serrano et al. 2010).

Clinoptilolite, probably the most abundant among more than 40 natural zeolite species, belongs to the heulandite family a structural variation of the zeolite mineral group and has the chemical formula $(K,Na,\frac{1}{2}Ca)_{2}O \cdot Al_{2}O_{3} \cdot 10SiO_{2} \cdot 8H_{2}O$. Large industrial deposits are connected with volcanic sedimentary high-silica rocks. Clinoptilolite differs from heulandite mineral by having a higher $\text{Si}/\text{Al}$ molar ratio (4.0-5.2), as well as greater thermal stability. $\text{Na}^{+}$ and $\text{K}^{+}$ dominate among exchangeable cations of clinoptilolite. With its high void volume and favorable cation-exchange capacity, clinoptilolite has received extensive attention due to its selectivity for heavy metal cations such as lead, cadmium and nickel (Semmens and Martin 1988).

Clinoptilolite has been effectively used in ion exchange processes as a sorbent material for removal of heavy metals, owing to its satisfactory ion exchange capacities and low cost (Rios et al. 2008; Motsi et al. 2009; Misaelides 2011).
Several aspects of metal removal via clinoptilolite, such as determination of removal capacity and the effects of particle size, temperature, other cations or pretreatment, have been investigated over the years for various metals, including zinc (Blanchard et al. 1984; Zamzow et al. 1990; Ouki and Kavannagh 1997; Cincotti et al. 2001; Inglezakis et al. 2002; Petrus and Warchol 2003; Inglezakis and Grigoropoulou 2004; Athanasiadis and Helmreich 2005; Petrus and Warchol 2005; Oren and Kaya 2006; Motsi et al. 2009). When utilizing natural materials for ARD remediation, it is important to characterize the materials well and to carry out studies on a specific target basis, since there are wide variations in capacity and other clinoptilolite properties. The nature and extent of ARD also tend to vary seasonally. Most previous studies have focused on specific clinoptilolite reserves and on synthetic ARD or specific contaminants. There has been very little focus on natural ARDs, which generally show far less satisfactory treatment performance due to their complex compositions compared with surrogate acidic solutions with similar concentrations of selected metals (Kesraoui-Ouki et al. 1993; Chmieleska-Horvathova and Lesny 1995; Faghihian et al. 1999; Petruzzelli et al. 1999; Langella et al. 2000; Abusafa and Yucel 2002; Doula et al. 2002; Inglezakis et al. 2002; Vasylechko et al. 2003; Athanasiadis and Helmreich 2005; Turan et al. 2005; Doula 2006; Trgo et al. 2006; Dimirkou 2007; Stylianou et al. 2007; Gedik and Imamoglu 2008; Rios et al. 2008; Lihareva et al. 2010; Li et al. 2011).

Even fewer studies have been performed on the regeneration of clinoptilolite after Zn removal. Since clinoptilolite is a low-cost and abundant mineral, regeneration and recycle may not seem profitable and worthwhile at first glance. However, improved treatment technologies require that waste production be reduced. Regeneration of clinoptilolite would enable sorbent to be recovered and the concentrated regenerant solution to have reduced volume relative to the original drainage. Regeneration studies are therefore important for future practical utilization of clinoptilolite in ARD treatment.
1.1.5 Slurry Bubble Column

The application of Slurry bubble columns (SBC) to industrial processes, such as in bioreactors for treatment of liquid effluents, has attracted much attention. A number of studies on both kinetic and fluid dynamic aspects of these systems have been published (Inglezakis and Grigoropoulou 2004; Jovanovic et al. 2012). Due to the complex mechanisms associated with the relative motion of the gas, liquid and solid phases, slurry bubble columns are not as well understood as conventional fixed beds. Nevertheless, SBC reactors have been applied successfully for a number of chemical, biochemical and physical processes involving liquids, solid particles and gases (three phases) due to their excellent heat and mass transfer characteristics.

In slurry bubble columns, gas is sparged into the bottom of the column through a distributor, and the resulting buoyancy-driven flow causes strong liquid recirculation. As long as the liquid superficial velocity is at least an order of magnitude less than that of the gas, it is the superficial gas velocity that is the dominant variable driving the fluid dynamics of the whole system. Solid particles, as long as they are small (typically less than 60 μm in diameter) follow the liquid motion closely, except perhaps at very high slurry loadings exceeding 20~30%. While in some applications bubbly flow is practiced (superficial gas velocities typically <2~3 cm/s), of current industrial interest is the churn-turbulent flow regime (with superficial gas velocities >10 cm/s and up to 30~50 cm/s), where vigorously interacting gas bubbles result in vigorous mixing of the slurry (Smith and Ruether 1985; Ohkawa et al. 1997; Lemoine et al. 2008).

Although mixing could also be achieved by mechanical stirring, as in stirred tank reactors, this would lead to additional capital and operating costs. The vigorous relative motion and relatively small particle sizes in slurry bubble columns result in higher rates of external and internal mass and heat transfer compared with fixed bed reactors or shaken vessels. Hence the SBC is ideal for many processes requiring high mass or heat exchange. Slurry bubble columns also facilitate loading and unloading of sorbent particles during continuous processes, including during regeneration of the
1.2 Motivation and Aims of Thesis

Conventional ARD treatment methods have a number of shortcomings, such as high land utilization, production of large secondary solid waste, and high capital and operating costs, especially for relatively dilute solutions, so that alternative technologies are needed (Coulton et al. 2003; Swash and Monhemius 2005).

An ideal method for treating ARD should include the following:

- Low cost capital and operating costs,
- Simple operation and maintenance,
- Minimization of solid waste volume,
- Minimization of liquid waste volume.

The treatment method should also be efficient compared to conventional methods.

The aim of this thesis is to investigate a low-cost and more sustainable alternative method for the ARD treatment. The efficiency of natural zeolite (clinoptilolite) for the removal of four heavy metal ions - Fe$^{3+}$, Cu$^{2+}$, Mn$^{2+}$ and Zn$^{2+}$ - from solution is determined. Zn and Mn are the heavy metal ions of greatest concern contained in Highway 97C ARD. The effectiveness of natural zeolite as an adsorbent was studied for the treatment of real AMD from Highway 97C, as a case study in this research.

The relative simplicity and high efficiency of a slurry bubble column reactor in preliminary work (Cui et al. 2006) suggested the need for a systematic analysis of a slurry bubble column system for ARD remediation. This analysis can provide underlying information and understanding needed for ultimate design and operation of real remediation process based on uptake/regeneration cycling.

The main goals of this research are then:

- to provide the detailed study of the operating conditions of a slurry bubble column system through batch studies;
- to test the regeneration of loaded clinoptilolite and subsequent reuse of
regenerated sorbent;

- to develop a more environmentally-friendly ARD remediation system by reusing regenerated clinoptilolite and minimizing the regenerant solution volume.

1.3 Thesis Structure

This thesis is divided into a number of chapters, each presenting different aspects of the overall investigation.

In Chapter 2, equilibrium and kinetic experiments are planned for the removal of iron, copper, zinc and manganese from ARD background solutions under different operating conditions, followed by the regeneration of loaded clinoptilolite. Then the lifespan of clinoptilolite with uptake/regeneration is investigated under various conditions. The experimental methods are also summarized in this chapter.

In Chapter 3, equilibrium experiments are described for removal of iron, copper, zinc and manganese from ARD background solutions under different operating conditions. The experimental data are also analyzed using adsorption isotherms, in particular the Freundlich and Langmuir adsorption isotherms. From these studies, appropriate conditions are found for uptake of heavy metals from ARD by natural clinoptilolite.

Chapter 4 describes studies performed to determine the efficiency of NaCl solution in removing heavy metals from loaded clinoptilolite. Loaded clinoptilolite is contacted with NaCl solutions under different conditions, for example at different initial pH and initial concentrations.

Studies involving multiple cycles are described in detail in Chapter 5. This includes determination of the effect of multi-cycle regenerations of used clinoptilolite and uptake on the regenerated clinoptilolite. The feasibility of multiple cycles and the deterioration of the clinoptilolite sorbent over repeated cycles are also explored.

Al colloids with zinc co-precipitates were observed during the remediation processes under certain conditions. In Chapter 5 the formation of the Al colloid is
studied, and the dealumination of clinoptilolite is described. The impacts of dealumination and colloid formation on zinc uptake are also discussed.

Major aqueous species in the ARD are incorporated in the commercial PHREEQC model in Chapter 6 to simulate and estimate hydrolysis, precipitation and adsorption. The predictions are then compared with experimental results.

Chapter 7 summarizes the major findings and conclusions of this project, as well as providing recommendations for further study.

Several appendices are also provided with supplemental details. Appendix A gives supplemental information of the clinoptilolite and compares its properties with those of clinoptilolites from other sources. Appendix B summarizes the SBC relevant parameters and comparisons. Appendix C lists supplements to aqueous species. Appendix D summarizes cation uptake performance reported in the literature. Appendix E summarizes the experimental equipment, instruments and methodology utilized in this thesis. Appendix F provides some information on what would be needed to extend the results of this thesis work to a continuous operation process, which would then require scale-up.

Figure 1.1 Highway 97C ARD, leachate along the road
Figure 1.2 Highway 97C ARD, BC map and site location
Chapter 2 Zinc Removal from Acid Rock Drainage

2.1 Introduction

Acid rock drainage or acid mine drainage (ARD/AMD) is generated when sulphide minerals are exposed to air and water. This can occur naturally or due to human activities such as mining and highway construction (Akci1 and Koldas 2006). Serious environmental problems result due to the oxidation of sulfide minerals, such as pyrite (FeS₂) and its polymorph marcasite (α-FeS) (Levings et al. 2005). These lead to release of hydrogen ions and mineral acidity, with quantities depending on the specific geologic setting and metal sulphide. Zinc is of concern due to its toxicity and non-biodegradability, with a negative impact on fish when released to streams (Besser and Rabeni 1987; Gerhardt et al. 2004).

A number of methods have been explored to treat ARD, including precipitation, electrochemical remediation, oxidation and hydrolysis, neutralization, ion exchange, solvent extraction, biosorption, adsorption, and reverse osmosis (Johnson and Hallberg 2005; Kalin et al. 2006). Many of these approaches are marginally cost-effective or very difficult to implement in remote areas (Whitehead and Prior 2005; Sheoran and Sheoran 2006). Treatment by adsorbents, including regeneration to reduce solid waste generation, has been explored as a relatively sustainable technique (Mohan and Chander 2006). Unfortunately, most sorbents, such as activated carbon, silica, clays and ion-exchange resins, suffer from low removal capacity, low selectivity, long times to reach equilibrium, or mechanical and thermal instability.

The inexpensive soil mineral clinoptilolite, a zeolite species abundant in nature, has a high adsorption capacity for zinc and copper (Doula et al. 2002; Lai 2005; Petrus and Warchol 2005; Dimirkou 2007) due to its large specific surface area, high cation exchange capacity and structural stability at low pH (Filippidis et al. 1996; Rivera et al. 2000; Li et al. 2008). Clinoptilolite has therefore been studied for removal of zinc and other metals from contaminated aqueous media (Inglezakis et al. 2002; Rios et al. 2008). Several aspects have been investigated such as removal capacity, effect of particle size, influence of temperature, impact of cations and benefits of pretreatment (Inglezakis et al. 2001; Dimirkou 2007; Doula 2007; Davila-Jimenez et al. 2008). Most previous studies have been carried out at either neutral pH or using simple artificial solutes (Rios et al. 2008). ARD is complex, containing various cations and anions due to leaching of metal from mineral rocks (Diz and Novak 1998; Peric et al. 2004; Akcil and Koldas 2006). Surrogate simple solutes tend to overestimate the sorption capacity of sorbents. In addition, sorption of zinc onto clinoptilolite is complex due to its porous structure, providing inner and outer charged surfaces (Inglezakis et al. 2002; Motsi et al. 2009).

Few previous studies have been performed on adsorption of clinoptilolite in complex natural ARD (Lai 2005; Li et al. 2008). Diz and Novak (1998) stated that the application of natural clinoptilolite is limited by its slow interaction with metal ions. However, a preliminary study by Cui et al. (2006) demonstrated that a slurry bubble column (SBC) was superior to traditional fixed beds and rotating columns for zinc removal onto clinoptilolite, indicating that enhanced external mass transfer can significantly accelerate sorption. Encouraged by these preliminary findings, a further more thorough SBC study, presented in this chapter, was initiated to develop a slurry bubble column based on low-cost clinoptilolite with high metal-removal efficiency. A key step is to identify the controlling factors in removing metals from ARD by clinoptilolite in a slurry bubble column, including reaction time, particle size, adsorption capacity (initial concentrations), sorbent dosage and pH.

One part of the study involved the determination of adsorption and fitting the
results by various adsorption isotherms. A test run with multiple cycles of adsorption was also conducted to determine whether clinoptilolite treatment could reduce the metals of concern to meet the ARD discharge concentration criteria of Metal Mining Effluent Regulations, MMER (SOR/2002-222), Environment Canada (2002).

This work is novel in using real ARD as the solute to truly reflect the field situation. The study comprehensively identifies the factors that affect the efficiency of ARD removal, as well as the sorption mechanism. To the author’s knowledge, this is the first study of multi-cycle adsorption of zinc by clinoptilolite in a slurry bubble column.
2.2 Materials and Methods

The clinoptilolite tested in the experiments was obtained from Bear River Zeolite, USA. Key properties are listed in Table 2.1. No attempt was made to activate or pre-treat the materials, except by oven-drying to equalize the moisture content of the various size fractions.

Table 2.1 Chemical composition and physical properties of clinoptilolite composite

<table>
<thead>
<tr>
<th><strong>Mineral components</strong></th>
<th><strong>85% Clinoptilolite; balance opaline silica</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Area</strong> (EGME*)</td>
<td>52.3 m²/g</td>
</tr>
<tr>
<td><strong>Surface Area</strong> (BET)</td>
<td>24.8 m²/g</td>
</tr>
<tr>
<td><strong>Bulk density</strong></td>
<td>0.92 g/cm³</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>2.19 g/cm³</td>
</tr>
<tr>
<td><strong>Chemical composition</strong></td>
<td><strong>Cations</strong></td>
</tr>
<tr>
<td></td>
<td>K 3.47%</td>
</tr>
<tr>
<td></td>
<td>Ca 1.60%</td>
</tr>
<tr>
<td></td>
<td>Na 0.44%</td>
</tr>
<tr>
<td></td>
<td><strong>Other elements</strong></td>
</tr>
<tr>
<td></td>
<td>Al 6.1%</td>
</tr>
<tr>
<td></td>
<td>Fe 1.3%</td>
</tr>
<tr>
<td></td>
<td>Ba 1200 ppm</td>
</tr>
<tr>
<td></td>
<td>Sr 560 ppm</td>
</tr>
<tr>
<td></td>
<td>Zr 480 ppm</td>
</tr>
<tr>
<td></td>
<td>Ce 130 ppm</td>
</tr>
<tr>
<td></td>
<td>Rb 120 ppm</td>
</tr>
<tr>
<td></td>
<td>La 55 ppm</td>
</tr>
<tr>
<td></td>
<td>Y 55 ppm</td>
</tr>
<tr>
<td></td>
<td>Nd 45 ppm</td>
</tr>
<tr>
<td></td>
<td>Nb 40 ppm</td>
</tr>
<tr>
<td></td>
<td>Zn 35 ppm</td>
</tr>
<tr>
<td></td>
<td>Cu 25 ppm</td>
</tr>
<tr>
<td></td>
<td>Pb 20 ppm</td>
</tr>
</tbody>
</table>

* EGME surface area determination method of Bower and Gschwend (1952)
**provided by the supplier. All percentage values are by mass

ARD from Highway 97C in British Columbia (Coquihalla Merritt-to-Peachland connector) with a pH of 3.2 was used in the experiments.
Major background metal concentrations are given in Table 2.2. Detailed metal concentration are listed in Appendix E, Table E4. Since zinc is the key contaminant of concern in this ARD, it was our major focus. Note that the Fe concentration is very low (<1 ppm), as most Fe precipitated in the field. This means that the iron and copper oxidation and the associated microbial activities were insignificant, and they are therefore not considered in this thesis.

<table>
<thead>
<tr>
<th>Units</th>
<th>Metal concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Mn</td>
</tr>
<tr>
<td>mg/kg</td>
<td>14.4</td>
</tr>
<tr>
<td>mmol/kg</td>
<td>0.220</td>
</tr>
<tr>
<td>Mn</td>
<td>10.6</td>
</tr>
<tr>
<td>Al</td>
<td>21.9</td>
</tr>
<tr>
<td>Ca</td>
<td>198</td>
</tr>
<tr>
<td>K</td>
<td>4.5</td>
</tr>
<tr>
<td>Na</td>
<td>179</td>
</tr>
<tr>
<td>Si</td>
<td>40.4</td>
</tr>
<tr>
<td>Ca</td>
<td>0.193</td>
</tr>
<tr>
<td>K</td>
<td>0.812</td>
</tr>
<tr>
<td>Na</td>
<td>4.94</td>
</tr>
<tr>
<td>Si</td>
<td>0.115</td>
</tr>
<tr>
<td>K</td>
<td>7.79</td>
</tr>
<tr>
<td>Si</td>
<td>1.44</td>
</tr>
</tbody>
</table>

A slurry bubble column (Appendix E, Figure E1) of inside diameter 0.090 m and overall height 1.4 m was employed for the experiments. Air was introduced into the bottom of the column through a ‘wind box’ before passing through a distributor plate containing 57 uniformly-distributed orifices of diameter 6.3 mm, with a screen underneath to prevent loss of particles. The bubble formation and coalescence caused by the air flow created strong liquid circulation, often called “Gulf-Streaming” (up in the core and down at the walls).

Slurries were prepared to provide concentrations of 100 g clinoptilolite per kilogram liquid. 2.0 kg ARD were used for each batch adsorption test. One-hour agitation time was adopted based on preliminary contacting time test results. Operational parameters examined were particle size 300-500, 500-600, 600-850 and 850-1400 µm, sorbent dosage 25-400 g/kg ARD, and initial aqueous pH 2-5. The zinc ion concentration in the ARD could vary due to seasonal changes. The Zn adsorption capacity onto clinoptilolite in ARD was determined. The ARD was spiked with zinc ions in the adsorption batch experiments by adding zinc chloride (ZnCl₂) solution to give final Zn concentrations of 15 to 215 mg/kg to match possible seasonal high and low zinc concentrations at the contaminated site. The experiments are summarized in Table 2.3.
Table 2.3 Experimental testing program to determine effects of various parameters on the removal of Zn using clinoptilolite in slurry bubble column

<table>
<thead>
<tr>
<th>Tests Parameters</th>
<th>Batch Test 1</th>
<th>Batch Test 2</th>
<th>Batch Test 3</th>
<th>Batch Test 4</th>
<th>Batch Test 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial clinoptilolite particle size (μm)</td>
<td>600-850</td>
<td>300-500</td>
<td>300-500</td>
<td>600-850</td>
<td>600-850</td>
</tr>
<tr>
<td>Sorbent dose (g/kg ARD)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>25,100,200,300,400</td>
<td>100</td>
</tr>
<tr>
<td>Initial aqueous Zn (mg/kg)</td>
<td>100</td>
<td>100</td>
<td>15,25,35,65,115,215</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Initial aqueous pH</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2,3,4,5</td>
</tr>
<tr>
<td>Contact time (min)</td>
<td>5,10,15,20,25,30,40,60,120</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

Note:
(1) All tests were performed at 16±1°C; the slurry bubble column operated at an air superficial velocity of 0.08 m/s.
(2) Test 6, the multi-cycle adsorption in slurry bubble, with initial 100 mg/kg Zn concentration in ARD at pH 3, through batches of sorbent in series. Contacting time for each cycle was 60 minutes. Particle size of clinoptilolite was 600-850 μm. Sorbent dose was 100 g/kg of clinoptilolite.

For quality control and quality assurance, there were ten replicates for the 600-850 μm clinoptilolite. Multiple cycle tests were performed in duplicate, and stand-alone tests were in triplicate. Replication absolute error ranged from 0.1 to 0.8%, except for the 5-minute contacting time results where it was 1.1%.

After contacting for the designated reaction time, the supernatant liquid was separated from the clinoptilolite samples by filtration. The metal ion concentrations of the supernatant were determined by an Atomic Adsorption Spectrophotometer (AAS) (Varian SpectrAA 220FS). Aqueous zinc ion concentrations were determined before and after each adsorption test. The clinoptilolite uptake efficiency was then calculated by:

$$Uptake_t (mg/g) = m_{ARD} (C_0 - C_t) / m_{	ext{clinoptilolite}}$$

(Eq. 2.1)

where $C_0$ is the initial contaminant concentration (mg/kg), and $C_t$ is the contaminant
concentration at time $t$ (mg/kg). $m_{ARD}$ is the mass of metal solution (kg), and $m_{clinoptilolite}$ is the dry weight of clinoptilolite (g) (USEPA 1987). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 7300DV) was used for the determination of multiple metal concentrations in solution.

The overall feasibility of adsorption using clinoptilolite was next tested in multi-cycle operation. These tests were performed in the same manner as for the batch adsorption tests, but after each adsorption test, the clinoptilolite was replaced by a fresh batch to simulate exposure to batches of sorbent in series.

### 2.3 Results and Discussion

#### 2.3.1 Effect of Contact Time and Adsorbent Particle-size

The effects of contact time for different particle sizes are shown in Figure 2.1a. Zn adsorbed rapidly onto clinoptilolite during the first 25 min in the slurry bubble column for all particle sizes studied, while the pH increased over time and amorphous co-precipitates were observed. The adsorption approached equilibrium in ~60 min, with very little (~2-3% more) adsorption during an additional hour of contact. Peric et al. (2004) showed that surface sorption properties change during the binding of Zn ions onto the inner and outer surfaces of clinoptilolite, resulting in fewer sites being available for ion exchange after initial rapid sorption. Hence, the observed adsorption behaviour is likely due to changes in the available clinoptilolite exchange sites. Based on these results, a contact time of 60 min is considered practical for sorption of Zn onto clinoptilolite, and this time was used for all remaining batch adsorption experiments reported in this chapter.

Figure 2.1b shows that the sorption of zinc increased with decreasing sorbent particle size. This was likely due to the increased external surface area per unit mass and reduced internal diffusion resistance for smaller particles. As seen in Figure 2.1c, the aqueous pH did not differ significantly for various particle sizes. While finer particles are found to have higher sorption capacities, they require more energy to
prepare and may present more difficulties in terms of filtration and entrainment. Hence the optimum particle size would need to be determined on a case-by-case basis.
Figure 2.1 Adsorption test results for initial aqueous pH 3, temperature 16°C, at a sorbent dose of 100 g oven-dried and sieved clinoptilolite per kg of ARD with an initial Zn concentration of 100 mg/kg for various particle sizes: a) Time variation of Zn concentration in aqueous solution after contacting. b) Zn adsorbed onto clinoptilolite. c) pH vs. time.
2.3.2 Zinc Adsorption on Clinoptilolite at Different Initial Spiked Concentrations

The adsorption of different spiked Zn in ARD onto clinoptilolite and the corresponding pH during the tests are presented in Figure 2.2. The maximum sorption capacity ranged from ~0.36 to 0.5 mg/g clinoptilolite for the four different particle sizes ranges investigated, and was somewhat higher for finer particles.

![Graph](image)

Figure 2.2 Adsorption test results for initial pH 3, temperature 16°C, with 100 g oven-dried and sieved clinoptilolite per kg ARD and various initial Zn concentrations for four particle size ranges: a) Zinc uptake vs. final Zn concentration; b) Aqueous pH after isotherm tests.
Adsorption on clinoptilolite is a complex process because of the porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds and other surface imperfections. To characterize the adsorption capacity of the solid surfaces, Langmuir and Freundlich isotherms are compared with the data. The fitted constants and correlation coefficients for the zinc adsorption isotherms are summarized in Table 2.4. The processes are seen to be better described by the Langmuir model than by the Freundlich equation. Due to the significant deviation in the lowest initial concentration (15 ppm) and the previous finding (Schulthess and Dey, 1996) that low concentrations should be excluded over a significant concentration range, this value was excluded in the fitting. The Langmuir model fits the experimental data well, with correlation coefficients exceeding 0.96. Q\textsubscript{m} in the Langmuir equation is related to the adsorption capacity, with higher Q\textsubscript{m} indicating higher adsorption capacity. As expected, finer particles show more effective exchange sites.

<table>
<thead>
<tr>
<th>Sorbent Particle Size (µm)</th>
<th>Langmuir equation ([1])</th>
<th>Freundlich equation ([2])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(r^2)</td>
<td>(Q_m) mg/g</td>
</tr>
<tr>
<td>300-500 µm</td>
<td>0.980</td>
<td>0.615</td>
</tr>
<tr>
<td>500-600 µm</td>
<td>0.967</td>
<td>0.588</td>
</tr>
<tr>
<td>600-850 µm</td>
<td>0.985</td>
<td>0.551</td>
</tr>
<tr>
<td>850-1400 µm</td>
<td>0.960</td>
<td>0.518</td>
</tr>
</tbody>
</table>

\([1]\) \(1/(q_e)=1/Q_m+1/(KQ_mC_e)\) where \(q_e\) is the zinc uptake at equilibrium (mg adsorbed/g sorbent), \(Q_m\) is the maximum adsorption capacity at saturation (mg/g), \(C_e\) is the equilibrium concentration (mg/kg) and K is the adsorption coefficient.

\([2]\) \(\log(q_e)=\log(K_f+1/n)\log(C_e)\) where \(q_e\) is the metal ion uptake at equilibrium (mg adsorbed/g sorbent), \(C_e\) is the equilibrium concentration (mg/kg), \(K_f\) is the Freundlich constant, sometimes referred to as the adsorption capacity, and n is the adsorption intensity.

### 2.3.3 Effect of Adsorbent Dose

Figure 2.3a shows the percentage of zinc removed from the solution during the adsorption tests for different sorbent dosages. Higher dosages resulted in more Zn
ions removed in the final solution. However, the Zn uptake per unit mass of sorbent (Figure 2.3b) decreased as the mass of sorbent increased.

Athanasiadis and Helmreich (2005) reported that less solid sorbent resulted in more adsorption per unit mass. In our study, as shown in Figure 2.4b, the highest zinc uptake per unit solid corresponded to a sorbent dosage of 25 g clinoptilolite per kg ARD, the lowest sorbent dosage tested. This total aqueous zinc removal may be affected by both the available surface area and neutralization. The latter the solution pH to rise slowly during contacting with the clinoptilolite particles, with the increment in pH greater as the clinoptilolite dosage increased (Figure 2.3c). These results indicate that the equilibrium sorption capacity and percentage removal are sensitive to sorbent dosage, pH, number of surface sites (Athanasiadis and Helmreich 2005), and neutralization (Li et al. 2008).
Figure 2.3 Clinoptilolite dosage effect on adsorption: a) Zn remaining in aqueous phase after treatment, b) Adsorption on clinoptilolite at various clinoptilolite dosages, c) Aqueous pH vs. time. These tests were conducted at initial aqueous pH of 3, temperature 16°C, with 25 – 400 g of sieved 600 – 850 μm clinoptilolite per kg ARD and initial Zn concentration 100 mg/kg.
2.3.4 Effect of Initial Solution pH

The results in Figure 2.4 indicate that the pH of the initial test solution significantly affected Zn uptake over the pH range (2-5) investigated. An initial pH of 6 was also tested, but is excluded here due to significant precipitation during sample preparation. The extremely weak sorption found at pH 1 is also excluded as it likely resulted from a high concentration of metals, due to dissolution of clinoptilolite (Li et al. 2008; Rios et al. 2008).

Adsorption increased significantly from a retention of ~0.2 mg of Zn per g of clinoptilolite at an initial pH of 2 to ~0.5 mg of Zn per g of clinoptilolite at an initial pH of 5. At pH 2, more H⁺ occupied the surface of the sorbent, reducing the access of zinc ions to surface sites, resulting in a decrease in Zn uptake onto clinoptilolite. Repulsive forces also likely contributed to this trend. Other mechanisms may also have been important. For instance, neutralization enhances the hydrolysis of metal species, such as Al and Fe, to form hydroxide precipitates with increasing pH (David and Driscoll 1984; Oelkers et al. 1994). Miyazaki et al. (2003) also reported a solid-liquid interfacial reaction of Zn on aluminum hydroxide. For an initial pH of 4 and 5, white precipitates were observed after completing the test and sitting for 1 h. Both zinc and aluminum were detected in these precipitates, i.e. they were Al/Zn co-precipitates. These co-precipitates are further considered in Chapter 5.
Figure 2.4 Adsorption results for initial aqueous pH of 2 – 5, temperature 16°C, sorbent dose of 100 g oven-dried and sieved 600 – 850 μm clinoptilolite particles per kg of ARD after 1 h of contact with an initial Zn concentration of 100 mg/kg: a) Zn concentration in aqueous phase after treatment, b) Zn adsorption vs. initial aqueous pH, and c) Aqueous pH vs. initial pH.
2.3.5 Multi-Cycle Adsorption

The overall efficiency of adsorption on clinoptilolite was next tested in multiple cycles to provide information on multi-stage operation. For practical on-site ARD treatment, shorter contacting time is preferable. Therefore, 20 and 60 min multiple-cycle adsorptions were performed. The Zn adsorption and corresponding pH results are shown in Figure 2.5. Comparison of the test results for 20 min cycles (Figure 2.5a, b) and 60 min cycles (Figure 2.5c, d) shows that the latter had higher pH after each cycle, and, beyond four cycles, significantly lower zinc concentration after each cycle. The better performance for 60 min cycles in the later stages was probably caused by the overall increase in pH and likely Al co-precipitation. As shown in Figure 2.5c, repeated adsorption lowered the concentration of metal ions in ARD. The zinc concentration after 8 adsorption cycles was as low as 0.8 ppm, below the 1 ppm limit listed in metal mining effluent regulations (MMER) for the maximum authorized concentration in a grab sample. Loss of adsorption activity in multi-cycle adsorption may be caused by the gradual decrease in the concentrations of zinc, manganese, aluminum etc., despite the increase in pH (Figure 2.5d).
Figure 2.5 Multiple-cycle adsorption in slurry bubble column at 16°C with initial 100 mg/kg Zn concentration in ARD at pH 3, contacting time for 20 and 60 minutes cycles; particle size: 600–850 μm; sorbent dose: 100 g/kg of clinoptilolite: (a) and (c) Aqueous metal concentrations at end of each adsorption cycle; (b) and (d) Corresponding pH at end of each cycle.

2.4 Conclusions

- Zinc adsorption on clinoptilolite increased with increasing initial Zn concentration. There was also a slight increase with decreasing particle size.
- Initial pH significantly affected the adsorption performance. Higher pH resulted in higher zinc adsorption.
- Clinoptilolite is an effective sorbent for removing Zn from ARD. After 8 adsorption stages in series, Zn concentration could be decreased from 100 ppm to as low as 0.8 ppm.
Chapter 3 Zinc Removal from Used Clinoptilolite (Clinoptilolite Regeneration)

3.1 Introduction

Concentrations of heavy metals in natural surface waters often increase significantly after excavation and weathering of sulfide-rich minerals in mining and construction areas. The resulting aqueous stream is then called acid mine drainage (AMD) or acid rock drainage (ARD). Due to the toxic effects to the aquatic environment, these heavy-metal-containing acidic wastewaters must be treated before being discharged into the receiving environment (USEPA 1995; Environmental Mining Council 1997; BCMEM and BCMELP 1998; Environment-Canada 2002).

Remediation systems are needed for ARD throughout the world (Clarke, 1995; Evangelou 1998; Brown et al., 2002). Relatively simple yet effective technologies utilizing low-cost abundant resources would be advantageous for establishing sustainable treatment strategies.

Clinoptilolite, a naturally occurring zeolite, can be effectively used in ion exchange processes as a sorbent materials for heavy metal removal, owing to its satisfactory ion exchange capacities and relatively low cost (Inglezakis et al., 2004; Petrus and Warchol, 2005; Cui et al., 2006; Dimirkou, 2007; Li et al., 2008).

Several aspects of metal removal via clinoptilolite, such as determination of removal capacity, effect of particle size, temperature, other cations or pretreatment have been investigated (Doula, 2007; Petrus and Warchol, 2003; Rivera et al., 2000;

2 A slightly modified version of this chapter was published in Applied Clay Science, Xu, W., Li, L.Y. and Grace, J.R. Regeneration of natural Bear River clinoptilolite sorbents used to remove Zn from acid mine drainage in a slurry bubble column. Applied Clay Science 55(0), 83-87, (2011).
While a number of studies have been carried out on adsorption by clinoptilolite, little has been done on the regeneration of clinoptilolite after removal of Zn or other heavy metals (Chen, 2005; Cui et al., 2006). As a low cost and abundant mineral, regeneration and re-use of clinoptilolite may not seem profitable and worthwhile at first glance. However, development of sustainable treatment technologies requires minimal waste production. Regeneration of clinoptilolite would enable the recovery of the sorbent and potentially concentrated regenerant solution with lower volume than for the original drainage. Regeneration studies are therefore important for future practical application of this natural material for ARD treatment.

Since few works investigated the regeneration of loaded clinoptilolite, the process performance has previously been judged solely on the basis of the adsorption process, which is the reverse process and therefore comparable. Diz and Novak (1998) reported that the application of natural clinoptilolite is limited by its slow interaction with metal ions. However, Cui et al. (2006) and the results in Chapter 2 demonstrated that a slurry bubble column (SBC) was superior to traditional fixed beds and rotating columns for zinc removal onto clinoptilolite, indicating that enhanced external mass transfer can significantly accelerate sorption.

This chapter investigates the feasibility of regeneration of Bear River clinoptilolite loaded with Zn. NaCl solutions with different concentrations and pHs were tested with different sorbent-regenerant ratio. The combination of conditions that performed best was then used in further ARD remediation tests with the regenerated clinoptilolite in a slurry bubble column. The effect of regeneration was then tested with cyclical Zn loading and removal.

### 3.2 Materials and methods

The clinoptilolite tested in the experiments was obtained from Bear River Zeolite, USA. Key properties are listed in Table 2.1. No attempt was made to activate or pre-treat the materials, except for oven-drying to equalize the moisture content of the
various size fractions.

ARD from Highway 97C in British Columbia (Coquihalla Merritt-to-Peachland connector) with a pH of 3.2 was used in the experiments. Heavy metal concentrations are given in Table 2.2.

As in the Chapter 2, a slurry bubble column (Appendix E, Figure E1) of inside diameter 0.090 m and overall height 1.4 m was employed for the experiments, the same column as in previous work (Cui et al., 2006; Xu et al., 2010). Air was introduced into the bottom of the column through a ‘wind box’ before passing through a distributor plate containing 57 uniformly-distributed orifices of diameter 6.3 mm, with a screen underneath to prevent loss of particles. Bubble formation and coalescence caused by the air flow created strong liquid circulation, often called “Gulf-Streaming” (up in the core and down at the walls).

Based on previous work (Lai, 2005; Chen, 2005; Cui et al., 2006; Xu et al., 2010), slurries were prepared to provide concentrations of 100 g clinoptilolite per kilogram liquid. 2.0 kg ARD were used in each adsorption test, with 1 h of agitation time in each test. Operating conditions adopted for sorption were particle size 600-850 µm, sorbent dosage 100 g/kg ARD, room temperature ~16°C and initial aqueous pH 3. The ARD was spiked with zinc ions in the absorption batch experiments by adding zinc chloride (ZnCl₂) solution to give final Zn concentrations of 100 mg/kg. After contacting for 1 h, the supernatant liquid was separated from the clinoptilolite samples by filtration. The Zn-loaded clinoptilolite was then drained in the column and stored for later regeneration.

The metal ion concentrations of the supernatant were determined by an Atomic Adsorption Spectrophotometer (AAS) (Thermo Jarrell Ash Video 22, TJA Solutions, US). Aqueous zinc ion concentrations were measured before and after each adsorption test. The clinoptilolite uptake efficiency was then calculated by:

\[
Uptake_{mg / g} = \frac{m_{ARD} (C_0 - C_t)}{m_{clinoptilolite}}
\]

(Eq. 3.1)

where \(C_0\) is the initial contaminant concentration (mg/kg), and \(C_t\) is the contaminant concentration at time t (mg/kg). \(m_{ARD}\) is the mass of metal solution (kg), and
m_{clinoptilolite} is the dry weight of clinoptilolite (g) (USEPA 1987).

NaCl was selected as the regenerant based on previous studies (Semmens and Martin, 1988; Chen, 2005; Li et al., 2007), which indicated that potassium and calcium ions were strongly held by clinoptilolite, in preference to sodium. It is apparent from these tests that the sites occupied by potassium and calcium are not readily able to participate in ion exchange. The pH of NaCl solutions were adjusted by the addition of HCl or NaOH.

Desorption/regeneration was then undertaken by re-suspending the 200 g of loaded clinoptilolite particles with aqueous NaCl solution in the column by means of an upward flow of air at the same temperature and superficial velocities as in the absorption tests for pre-specified time periods to determine the rate of desorption of zinc as a function of time. NaCl solutions of different concentrations (5, 10, 20 and 30 g/kg) and pHs (2, 3, 5, 7 and 10) were tested. Various sorbent/regenerant ratios (5, 10, 20 and 30 g/g) were also tested. These studies were carried out in batch mode using the slurry bubble column The removal of Zn from the regenerated clinoptilolite is calculated based on the Zn concentrations in the initial regenerant and final regenerant, in a similar manner to the adsorption tests. After the desorption period, regenerated particles were drained (filtered and air dried) before the next adsorption test. The operating conditions for the regeneration experiments are summarized in Table 3.1.
Table 3.1 Experimental testing program to determine effects of various parameters on the removal of Zn using clinoptilolite in SBC

<table>
<thead>
<tr>
<th></th>
<th>Batch Test 1</th>
<th>Batch Test 2</th>
<th>Batch Test 3</th>
<th>Batch Test 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time (min)</td>
<td>5, 15, 30,45,60,120</td>
<td>60</td>
<td>5, 15, 30, 45, 60, 120</td>
<td>5, 15, 30, 45, 60, 120</td>
</tr>
<tr>
<td>Regenerant (NaCl) concentration (g/kg)</td>
<td>20</td>
<td>5, 10, 20, 30</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>pH</td>
<td>3</td>
<td>3</td>
<td>2,3,5,7,10</td>
<td>3</td>
</tr>
<tr>
<td>Regenerant/Sorbent ratio (g/g)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>5, 10, 20</td>
</tr>
</tbody>
</table>

Note:
(1) All tests were performed at 16±1 ℃, particle size 600-850 μm; the slurry bubble column was at an air superficial velocity of 0.08 m/s.
(2) Test 5, the comparison of different water quality: distilled water vs. tap water; adjusted to same pH 3; NaCl concentration 20 g/kg, regenerant/sorbent ratio at 10 g/g. (For results, see Figure 3.5)
(3) Test 6, the feasibility adsorption test of regenerated clinoptilolite was carried in slurry bubble column, with initial 100 mg/kg Zn concentration in ARD at pH 3, through batches of sorbent in series. Contacting time was 60 minutes. Particle size of clinoptilolite was 600-850 μm. Sorbent dose was 100 g/kg of clinoptilolite/ARD. (For results, see Figure 3.6)

For quality control and quality assurance, all regeneration tests were repeated three times. Sorption tests on the regenerated clinoptilolite were performed in duplicate, whereas stand-alone regeneration tests were in triplicate. Replication errors ranged from 1.3 to 4.4%, except for the 5-minute operation time results where it was 6.1%. The increased error might have been caused by the extended reaction time during filtration.

The effectiveness of the regenerated clinoptilolite was tested in an adsorption batch test with fresh ARD. This test was performed in the same manner as for the initial batch adsorption tests, to determine the adsorption capacity of the regenerated clinoptilolite.

3.3 Results and discussion

3.3.1 Selection of Batch Regeneration Time

The performance of regenerants for different regeneration time (during which Zn
was removed from contaminated clinoptilolite) are presented in Figure 3.1

It is evident from Figure 3.1 that Zn removal efficiency increased with longer contact time. These results also indicate that NaCl was successful in significantly removing Zn from contaminated clinoptilolite, in agreement with most relevant literature on metal removal (Cincotti et al., 2001; Faghihian et al., 1999). It is clear from Figure 3.1 that the improvement after 1h was small compared to the first hour, so 1 h was considered practical for the remaining batch tests.

![Graph showing desorption as a function of contact time.](image)

Figure 3.1 Desorption as a function of contact time.
For operating conditions, see Table 3.1, batch test 1.

### 3.3.2 Effect of Concentration

Removal of Zn from loaded clinoptilolite is plotted vs. the NaCl concentration of the regenerant solution in Figure 3.2. The results indicate that raising the concentration above 20 g/kg had little effect on the effective Zn desorption. The reduction in Zn desorption for lower NaCl concentrations of 5 and 10 g/kg is probably due to decreased mass transfer due to reduced amplitude of the driving force, i.e. concentration difference between the solution and solid during the ion exchange process. With increasing solution concentration, the clinoptilolite is saturated with Na$^+$ ions, so that further increase has little or no effect (Inglezakis et al., 2001; Inglezakis et al., 2004).
3.3.3 Effect of pH

Figure 3.3 shows that desorption was more effective at low pH, with the greatest desorption observed at pH 2 (the lowest practical value tested). Desorption is based on ion-exchange. Heavy metal ions are more soluble at lower pH, thus promoting ion-exchange and favoring desorption (Ouki and Kavannagh, 1997). The different behavior for pH 5 (desorbed less than pH 7), may be caused by the buffering of Zn around pH 5. Jennings et al. (1999) reported that samples with high levels of Zn can be buffered at ~5 by the formation of zinc hydroxide complexes given complicated anion background. The working pH selection depends on the adsorption performance of the regenerated clinoptilolite, which is explored below.
3.3.4 Effect of Regenerant Solution/Sorbent Ratio

Zn desorption time vs. mass ratio is plotted in Figure 3.4, for three different regenerant/sorbent mass ratios. Only a small improvement in desorption occurred when the regenerant/sorbent mass ratio was raised from 10 g/g to 20 g/g. Hence a ratio of 10 g/g is likely to be sufficient for sorbent regeneration.
3.3.5 Tests of Water Quality Influence

Tap water contains several ions which can influence the ion exchange process (Curkovic et al., 1997). However, as shown in Figure 3.5, extents of desorption obtained with tap water (from the UBC McMillan building) and distilled water were very similar. It can be concluded that tap water can be used for regeneration, giving essentially the same product quality as distilled water. However, for study purposes, all other tests in this work were carried out with distilled water.

![Figure 3.5](image)

Figure 3.5 Comparison of desorption with distilled water and tap water.

For operating conditions, see Table 3.1, test 5.

3.3.6 Adsorption Capacity/Feasibility Test on Regenerated Clinoptilolite

The adsorption capacity of the regenerated clinoptilolite for 1 h of operation is plotted vs. the pH of the regenerant solution in Figure 3.6. The best working pH is 3. Curkovic et al. (1997) reported that low pH, i.e. a high concentration of H ions, leads to simultaneous uptake of hydrogen ions by clinoptilolite. This could explain the lower adsorption capacity for pH 2. The lower adsorption for pH 10, can be explained if OH ions are entrapped by the structure of clinoptilolite during pretreatment. During the adsorption process, internal precipitation of metal hydroxide or the formation of complexes could then clog the pores (Kesraoui-Ouki et al., 1993).
Another explanation is the partial destruction of the clinoptilolite structure, expected for high pH (see Section 5.3.1 for further discussion).

![Graph showing adsorption capacity as a function of regenerant pH.](image)

Figure 3.6 Adsorption capacity as a function of regenerant pH. For operating conditions, see Table 3.1, batch test 3.

Considering the desorption behavior as a function of regenerant pH (Figure 3.3), discussed above, a pH of 3 was selected for further study due to its combined relatively high Zn removal during desorption and the subsequent satisfactory adsorption capacity of the regenerated clinoptilolite. The comparable zinc adsorption of raw clinoptilolite was 383-394 mg/kg, which is lower than for the regenerated clinoptilolite, likely due to the improved sorption capacity of the homoionized clinoptilolite. The NaCl-pretreated (pH at 3, same condition as regeneration test) clinoptilolite shows ~15% higher adsorption capacity than the raw sorbent, and slightly higher than for the regenerated clinoptilolite (Figure 3.6).

### 3.4 Conclusion

The effects of the time of contacting, regenerant pH, regenerant/sorbent mass ratio, and water purity on clinoptilolite regeneration were investigated. Regenerated clinoptilolite was also subject to further adsorption tests. The full set of experimental results indicates that satisfactory regeneration results could be achieved.

Based on the test results, the following conditions were selected as promising for further tests: One hour contacting in the slurry bubble column, 20 g/kg NaCl
concentration, initial regenerant pH of 3, temperature 16°C, 10 g/g regenerant/sorbent mass ratio. The regenerated clinoptilolite with the above test conditions was able to achieve 440 mg/kg zinc adsorption capacity.

It was also found that tap water can be used instead of distilled water to lower the cost, without significantly changing the extent of regeneration.

Further work is required to explore repeated Zn removal/clinoptilolite regeneration cycles, focusing on alternative cycle arrangements to reduce heavy metal (zinc) concentration in the product stream at a reasonable cost in a continuous remediation system. This is taken up in the next chapter.
Chapter 4 Multi-Cycle Studies

4.1 Introduction

Concentrations of heavy metals in natural surface waters increase significantly after excavation and subsequent weathering of sulfide-rich minerals in certain mining sites and construction areas (Gray 1998; Valente and Leal Gomes 2009). The resulting aqueous solution is known as acid mine drainage (AMD) or acid rock drainage (ARD). Due to the toxic effects of heavy metals (Jacobs et al. 2001), it is necessary to treat ARD before it is discharged to the receiving environment. ARD remediation is therefore in demand around the world (Gazea et al. 1996; Johnson and Hallberg 2005; Akcil and Koldas 2006). Use of relatively simple, yet effective, technologies utilizing low cost abundant natural resources would be advantageous to help establish more sustainable treatment strategies.

Clinoptilolite particles can be effectively used in ion exchange processes as sorbent materials for heavy metal removal applications in wastewater, owing to their favorable ion exchange capacities and low cost (Breck 1974; Barrer et al. 1978; Inglezakis et al. 2004; Roic et al. 2005). Several aspects of metal removal via clinoptilolite, such as determination of removal capacity, effect of particle size, temperature, other cations and pretreatment, have been investigated over the years (Semmens and Martin 1988; Ouki and Kavannagh 1997; Inglezakis et al. 2001; Petrus and Warchol 2003; Inglezakis et al. 2004; Petrus and Warchol 2005; Doula 2006; Oren and Kaya 2006). However, very few studies have been carried out using natural ARD (Cui et al., 2006; Rios et al. 2008; Xu et al. 2010, 2011). The results of these studies show less satisfactory treatment performance of clinoptilolite, due to the complex composition of ARD, than for surrogate acidic solutions with similar metal concentrations of only one or two metals (Motsi et al. 2009).

3 A slightly different version of this chapter was submitted to Applied Clay Science in May, 2012, and is still under review.
Limited studies have been performed on the regeneration of clinoptilolite after Zn removal. Blanchard et al. (1984) sought optimum regeneration conditions for removing NH$_4$ and mixed metals (including Zn) from solution in clinoptilolite-packed beds. Zamzow et al. (1990) demonstrated effective removal and complete elution of Zn for 27–37 removal/regeneration cycles from a clinoptilolite-packed column for water treatment, attempting to meet US EPA drinking water standards, with NaCl as the regenerant. Vasylechko et al. (2003) tested HCl-modified clinoptilolite for Zn removal with potassium salts for successful regeneration. However, regenerant recycling over repeated uptake/removal cycles has not been previously investigated. Successful regeneration of clinoptilolite would enable the recovery of the sorbent and concentration of regenerant solution to a volume significantly less than for the original solution. Studies of this possibility are essential for future practical application of this natural material in ARD treatment.

Most previous research on adsorption capacity has investigated artificial solutions. Batch desorption tests have been based on spiked surrogate feed, with single (Vasylechko et al. 2003; Turan et al. 2005) or multiple (Blanchard et al. 1984; Zamzow et al. 1990) metals in distilled water, where the performance tends to be much better than for ARD. In our previous studies, freshly prepared regenerant was introduced in each cycle (Rios et al. 2008; Xu et al. 2011). No study has been reported on recycling the regenerant. Cyclic regeneration was limited to only 1-3 cycles in surrogate solution (Blanchard et al. 1984). Only a single study (Rios et al. 2008) has been reported for ARD treatment. In that case, a small batch rotating column provided multiple regenerations.

The present study aims to minimize the solid waste (used-clinoptilolite) and liquid waste (loaded-regenerant) resulting from ARD treatment. To achieve this, tests were performed in a slurry bubble column on Zn uptake by clinoptilolite, followed by removal of zinc from the resulting partially-loaded clinoptilolite by contacting with regenerant. In this chapter, we use the terms “uptake” and “removal”, rather than “sorption” and “regeneration”. (Chapters 2 and 3).

In the first set of tests, denoted as FRESH, fresh NaCl was used for each removal
to extract Zn from the partially loaded-clinoptilolite. In the second set, fresh NaCl regenerant was used only for the initial cycle, after which the same regenerant was used repeatedly for nine further cycles. To examine the recovery of the uptake capacity of the loaded-clinoptilolite, three removals with fresh NaCl solution were carried out next, followed by 10 cycles of uptake/removal following the same procedures as for the previous 10-cycle sequence. The work is novel as this is the first time that natural ARD has been tested with multiple uptake/removal cycles up to 10 cycles. No previous study has been conducted on reused regenerant to determine the recovery of Zn uptake capacity and the service life of the clinoptilolite. The results are helpful in developing a more sustainable treatment system to minimize liquid and solid wastes associated with ARD treatment.

4.2 Materials and Methods

A slurry bubble column (Cui et al. 2006; Xu et al. 2010; Xu et al. 2011) of inside diameter 0.090 m and overall height 1.4 m was employed for the experiments. Air was introduced into the bottom of the column through a ‘wind box’ before passing through a distributor plate containing 57 uniformly-distributed orifices of diameter 6.3 mm, with a screen underneath to prevent loss of particles. The bubble formation and coalescence caused by the air flow created strong liquid circulation, often called “Gulf-Streaming” (up in the core and down at the walls).

The clinoptilolite tested in the experiments was from Bear River Zeolite, USA, with key properties listed in Table 2.1. This material was first oven-dried to equalize the moisture content of the various size fractions. Based on Chapter 2, the Zn uptake by raw clinoptilolite is ~12-15% lower than that of the NaCl pre-treated clinoptilolite. For consistency, the batches of clinopilolite for all regeneration tests in this chapter were pre-treated with NaCl (as in Chapter 2) to homogenize the ions onto the adsorption sites.

ARD from Highway 97C in British Columbia (Coquihalla Merritt-to-Peachland connector) with a pH of 3.2 was used in the experiments. Background concentrations
are given in Table 2.1. Our major focus was zinc, as it is the contaminant of major concern in this ARD.

Based on Chapter 2 and 3, slurries were prepared to provide concentrations of 100 g clinoptilolite per kg liquid. 2.0 kg ARD were added for each test. One-hour agitation time was adopted for each uptake test and also for each removal test. Operational parameters examined were particle size 600-850 µm, sorbent dosage 100 g/kg ARD, and initial aqueous pH 3. The zinc ion concentration in the ARD could vary due to seasonal changes. The ARD was spiked with zinc ions in the absorption batch experiments by adding zinc chloride (ZnCl₂) solution to give Zn concentrations of 100 mg/kg, to match the highest seasonal zinc concentrations at the contaminated site. After being in contact for 60 min in the slurry bubble column, the supernatant liquid was separated from the clinoptilolite samples by filtration using Whatman No. 2 filter paper. The Zn-loaded clinoptilolite was then drained in the column prior to the removal test.

The metal ion concentrations of the supernatant were determined by an Atomic Adsorption Spectrophotometer (AAS) (Thermo Jarrell Ash Video 22, TJA Solutions, US) after acidification with 0.5% HNO₃ and passage through a 0.45 µm filter (Eaton et al. 1992). Aqueous zinc removal was determined by comparing concentrations before and after each adsorption test (USEPA 1987).

Based on chapter 3, 20 g/kg NaCl solution at pH 3 was adopted for removal of the Zn from the loaded clinoptilolite. Studies were carried out in batch mode in the slurry bubble column at room temperature (~16°C) with 100 g of loaded clinoptilolite per kg regenerant. 2.0 kg regenerant were used for each test. The removal of Zn is calculated from the Zn concentrations in the initial regenerant and final regenerant, based on the same principle as for adsorption tests (USEPA 1987).

For quality control and quality assurance, all uptake/removal tests were at least in triplicate. The second set of cycles was replicated for the 10-cycle tests. When uptake/removal tests were conducted, liquid samples could be analyzed after each cycle, but the quantity of solid sample needed for each analysis was large enough that no subsequent cycles could be carried out with that batch. As a result, runs were
carried out with one complete cycle, then two, three, etc. to a total of ten, in each case going back to the beginning with a fresh batch of clinoptilolite. Next, we conducted three removal stages, each with fresh NaCl solution, without any intervening uptake, followed by ten further uptake/removal cycles (in each case starting from the very beginning). This complete series was then repeated twice. The overall result was three solid samples to be analyzed for each of the 23 cycle numbers, and a decreasing number of liquid samples, 69 for one cycle, 66 for two, etc. until there were 3 for 10+3+10 uptake/removal and desorption + uptake/removal cycles. Replication error between highest and lowest for cycle tests ranged from 3.7% for the first cycle to 11.3% for the 23rd cycle, higher when there were more cycles.

Used clinoptilolite was washed with deionized water to remove soluble phases which may interfere with the measurement of the Cationic Exchange Capacity (CEC). Samples were dried and transferred to a centrifuge tube into which 1N NH₄OAc buffered to pH 7 had been added (Rhodes 1982). The suspension was next shaken overnight and then centrifuged. Na⁺, K⁺, Ca²⁺, and Mg²⁺ were finally analyzed by the Inductively Coupled Plasma (ICP) instrument. Alternatively, unbuffered ammonium nitrate solution (1N NH₄NO₃) (Rhodes 1982) was used in a parallel test to determine the CEC.

4.3 Results and Discussion

4.3.1 Cycles of Zinc Uptake and Removal

The two series of 10 cycles of Zn uptake onto clinoptilolite and Zn removal from loaded-clinoptilolite are presented in Figure 4.1a, for fresh NaCl solution (FRESH) and in Figure 4.1b for recycled NaCl solution (REUSED). The net changes of Zn concentration in clinoptilolite between uptake and removal for each cycle, as well as the cumulative Zn in clinoptilolite over 10 full cycles, the desorption stage and 10 additional fill cycles, are presented in Figure 4.1a/b. The NaCl-pretreated clinoptilolite shows higher Zn removal than the raw clinoptilolite tested previously.
(Xu et al., 2010); in agreement with previous finding (Araya and Dyer 1981; Semmens and Martin 1988; Zamzow et al. 1990; Abusafa and Yucel 2002; Roic et al. 2005), likely due to the improved exchangeable cation amount and locations.

The general trends for the first four cycles of the uptake/removal tests for FRESH (Figure 4.1a) and REUSED were similar in terms of Zn-uptake by clinoptilolite and Zn removal from clinoptilolite. The 5th-10th FRESH cycles showed almost constant uptake, whereas the REUSED experienced a substantial decrease in Zn uptake due to its accumulation onto the clinoptilolite. The three successive Zn removal stages were able to recover the uptake capacity for both cases. The second 10-uptake/removal sequence was similar to the first 10-uptake/removal cycles in both cases.
Figure 4.1 Zinc changes during batch tests over 10 regeneration cycles, subsequent three desorption tests and the following 10 regeneration cycles; the dark bar shows the zinc uptake on clinoptilolite during each adsorption batch test, the white bar shows the zinc removal from used clinoptilolite during regeneration (a) with fresh NaCl solution for each batch (discussed as FRESH), (b) reusing NaCl solution from last batch for next batch (discussed as REUSED). The striped bars show the accumulated zinc in the clinoptilolite after regeneration.

4.3.1.1 Uptake Decrease versus Cycling

Note that for both the FRESH and REUSE tests, the Zn uptake by clinoptilolite was much higher than the Zn removal from the clinoptilolite over the first 1-4 uptake/removal cycles, resulting in Zn accumulation in the solids. This reduces the uptake capacity for the remaining cycles.

The Zn uptake is almost equal to, or slightly less than, the removal capacity for FRESH throughout the 5th-10th cycles (Figure 4.1a), therefore resulting in only a slight decrease in Zn accumulation. On the other hand, the REUSED Zn uptake capacity decreased until the last cycle (Figure 4.1b). This is due to the high Zn
concentration in the regenerant accumulated from previous uptake/removal cycles.

4.3.1.2 Removal Variation versus Number of Cycles

Figure 4.2 shows the Zn removal from clinoptilolite versus Zn accumulation in clinoptilolite for the entire test (i.e. first 10 cycles of uptake/removal, 3 of removal only and a second set of 10 uptake/removal cycles, for a total of 23 cycles) to demonstrate the effect of Zn accumulation in the clinoptilolite on the removal performance. For the FRESH test (Figure 4.2a), the first 10 cycles performed only slightly better than the second 10 cycles. However, for the REUSED (Figure 4.2b), only the first five cycles of the first and second 10-cycle sets showed the same trend as for the FRESH. The increase of Zn removal over the first five cycles was likely due to an increase in Zn accumulation in clinoptilolite and a relatively low Zn concentration in the NaCl regenerant, while there was a significant drop in Zn removal from clinoptilolite during the last five cycles, resulting from Zn accumulation in the regenerant.
Figure 4.2 a) Zn accumulation in used clinoptilolite before regeneration vs. Zn removal during regeneration; b) Zn in aqueous regenerant before regeneration vs. Zn removal during regeneration. The tests were carried out with fresh NaCl solution in each cycle.

The Zn removal performance versus the Zn concentration in the regenerant is shown in Figure 4.2. The first and second sets of 10 cycles exhibited similar trends. When FRESH NaCl solution was used as regenerant each time (Figure 4.2a), the final aqueous Zn concentration, which was very low (35 mg/kg), reflects the Zn removal
from loaded clinoptilolite. It appears that for REUSED, after the Zn accumulation in the regenerant reached 100 mg/kg (4\textsuperscript{th} and 5\textsuperscript{th} cycles), the removal then decreased (Figure 4.3b). This result concurs with Figure 4.2b where removal is plotted versus Zn accumulation in clinoptilolite. The 100 mg/kg Zn concentration corresponds to the original Zn concentration of the spiked ARD. This indicates that the removal was affected by both Zn concentration and ion affinity in the regenerant (Abusafa and Yucel 2002; Inglezakis et al. 2002)
Figure 4.3 a) Zn accumulation in used clinoptilolite before regeneration vs. Zn removal during regeneration; b) Zn in aqueous regenerant before regeneration vs. Zn removal during regeneration. The tests were carried out reusing the same NaCl solution for each cycle during cycles 2-10.

4.3.2 Variation of Cation Exchange Capacity

Two Cation Exchange Capacity (CEC) determination methods, based on ammonium acetate and nitrate, were applied to clinoptilolite after each cycle to
To determine whether there was any effect due to the process, Figure 4.4 shows that the CEC varied only slightly over the uptake/removal cycles (~15% reduction in CEC). However, after the three successive Zn removal stages, ~90% CEC was recovered, and then it slightly decreased over the second set of 10 uptake/removal cycles. The overall CEC decrease was ~11-15% after 20 complete cycles.

The CEC results for both the FRESH and REUSED regenerants showed similar trends, consistent with the uptake and removal performance in Figs. 4.1a and b, where the clinoptilolite showed significant uptake capacity, despite the high accumulation.

The differences in the two CEC test results are detailed in Figure 4.4. The CEC remained almost constant from the first to the fifth cycle (155 meq/100g vs. 151 meq/100g), followed by a decrease over cycles 6-10 (to 137 meq/100g), then recovery over the three Zn removal stages (to 145 meq/100g). These CEC levels correspond to significant uptake capacity (Athanasiadis and Helmreich 2005). The analysis errors are listed in Table 4.1 and are small enough that the trend of CEC fluctuation is not obscured.

Figure 4.4 Clinoptilolite Cation Exchange Capacity (meq/100g) variation. The solid lines are for tests with fresh NaCl in each cycle; dotted lines are for tests with reused NaCl during cycles 2-10. Annotation 1 refers to results from the ammonium acetate method, and 2 to the results from the ammonium nitrate method.
Table 4.1 Discrepancies in the experimental tests and sample analysis

<table>
<thead>
<tr>
<th>Test type</th>
<th>Error sources</th>
<th>Relative Range %&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Range&lt;sup&gt;1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-analysis of same STD (ICP - Zn)</td>
<td>Instrument</td>
<td>-</td>
<td>Up to 0.2 ppm</td>
</tr>
<tr>
<td>Re-analysis of same STD (AAS - Zn)</td>
<td>Instrument</td>
<td>-</td>
<td>Up to 0.5 ppm</td>
</tr>
<tr>
<td>Re-analysis of test samples (ICP - Zn)</td>
<td>Instrument (with sample impact)</td>
<td>-</td>
<td>Up to 0.4 ppm</td>
</tr>
<tr>
<td>Re-analysis of test samples (AAS - Zn)</td>
<td>Instrument (with sample impact)</td>
<td>-</td>
<td>Up to 1.1 ppm</td>
</tr>
<tr>
<td>Reanalysis of same solid samples (acid digestion - ICP - Zn)&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Method + instrument + test</td>
<td>4.2-5.1</td>
<td>-</td>
</tr>
<tr>
<td>Analysis of duplicate test solid samples (acid digestion - ICP - Zn)&lt;sup&gt;5&lt;/sup&gt;</td>
<td>Method + instrument + test</td>
<td>5.3-7.9</td>
<td>-</td>
</tr>
<tr>
<td>Duplicate run for single adsorption batch test (ICP - Zn)&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Instrument + test</td>
<td>0.8-2.3</td>
<td>-</td>
</tr>
<tr>
<td>Duplicate run for 1 cycle test (ICP - Zn)</td>
<td>Instrument + test</td>
<td>1.1-3.7</td>
<td>-</td>
</tr>
<tr>
<td>Duplicate run for 10 cycle tests (ICP - Zn)</td>
<td>Instrument + test</td>
<td>6.4-11.3</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>1</sup> Due to the lack of the true value, the relative fluctuation is presented by the percentage relative range (range over average value) or range (difference between the maximum and minimum measured values).

As seen from the CEC results, the clinoptilolite sample from Bear River contained a significant complement of exchangeable potassium and calcium ions in the as-received form. However, by exposing the raw clinoptilolite to large volumes of concentrated sodium chloride, much of the potassium could be displaced. Since the potassium ions are very selectively held by the clinoptilolite, the removal of these ions results in an effective increase in clinoptilolite capacity, and in the apparent selectivity for heavy metals such as zinc (Semmens and Martin 1988; Kesraoui-Ouki et al. 1993; Chmielewska-Horvathova and Lesny 1995).

The reused regenerant solution resulted in a further decrease in CEC over the cycles, also shown in Figure 4.4. This decrease may correspond to additional zinc.

<sup>4</sup> The same sample was separated to two portions, each was acid digested and analyzed by ICP for Zn concentration.

<sup>5</sup> Two sample obtained from two tests of same conditions, each sample was acid digested and analyzed by ICP for Zn concentration.

<sup>6</sup> Two samples obtained from two adsorption test of same conditions, each sample was analyzed by ICP for Zn concentration.
accumulation for the REUSED relative to the FRESH. The retained zinc may have occupied internal pores and formed complexes, thereby resulting in lower measured exchangeable cation charges (Chmielewska-Horvathova and Lesny 1995; Ouki and Kavannagh 1997).

Since the sorbent in the column did not change, the variation in metal removal efficiency may be interpreted as a change in the relative importance of different Zn removal mechanisms. The increase in Zn removal in further cycles may be attributed to two mechanisms:

1. Ion exchange of Zn with Na and other exchangeable cations on the clinoptilolite structure is expected to be the dominant removal mechanism (Inglezakis et al. 2002; Athanasiadis and Helmreich 2005). As ion exchange is a dynamic process, the binding forces between the cations and clinoptilolite can be considered to be relatively weak (Langella et al. 2000; Trgo et al. 2006; Stylianou et al. 2007). This allows clinoptilolite to approach its homoionic Na-form more closely with each successive uptake/removal cycle as it is further exposed to concentrated NaCl solution. Zn replacement, especially with low mobility and strongly bonded cations (K, Ca) in exhaustion cycles, may make replacement of Na by Zn easier than for other cations. Examination of exchangeable cations (Na, K, Ca and Mg) in the effluent of Zn removal runs reveals this progressive conversion of clinoptilolite into its homoionic form.

2. As the metal concentration increases, metal ions which can no longer form outer-sphere complexes (e.g. ion exchange) are forced into internal sites and start to form inner-sphere complexes (Doula et al. 2002; Doula and Ioannou 2003; Dimirkou 2007). During removal with NaCl, it may be possible that Cl\(^-\) ions become entrapped in the channels or pores of clinoptilolite, remaining even after washing. These may in turn form inner-sphere complexes with Zn ions during removal stages, accounting for the increasing Zn capacity. The results of Doula and Ioannou (2003) reveal inner-sphere complex formation of Cu in the presence of KCl. This type of complexation is stated to affect the reversibility of sorption reactions when inner-sphere complexation appears to be irreversible, due to the formation of covalent
bonds (Doula et al. 2002; Doula and Ioannou 2003). The results of the present study are in line with these discussions, with lower desorption efficiencies for the sixth and later removal runs, accompanied by relatively stable metal removal compared to the initial runs. Furthermore, an inner-sphere complex with Cl\(^-\) is expected to facilitate dissolution of clinoptilolite (Doula et al. 2002; Doula 2006; Doula 2007). In order to investigate this, framework cations (Si and Al) of clinoptilolite were measured in the aqueous phase, and dealumination was observed over the tests.

Other researchers have noted either unchanging or decreasing metal removal capacity of clinoptilolite in successive cycles, with almost complete elution of the sorbed metal. The CEC of our initial clinoptilolite was 152 meq/100 g as ammonium, whereas that of the NaCl-pretreated clinoptilolite was 165 meq/100 g by the same method. Ammonium acetate and NH\(_4\)NO\(_3\) extracted different amounts of exchangeable divalent base cations in our tests, indicating that NH\(_4\)OAc at pH 7.0 extracted slightly less exchangeable cations than unbuffered NH\(_4\)NO\(_3\). The difference is probably due to different pH in the extracting solutions, resulting in an increased negative charge on the soil solid phase in the NH\(_4\)OAc extract, and therefore stronger adsorption of divalent cations.

Matsue and Wada (1985) reported that the specific adsorption of sulfate anions on the sesqui-oxides results in higher measured CEC. The fluctuation of CEC over uptake/removal cycles may also be attributed to the aluminum hydroxide caused by Al hydrolysis and the resulting sulfate impact on new surfaces (Matsue and Wada 1985).

### 4.3.3 Overall Assessment of Uptake/Removal Process

Figure 4.5 compares the total Zn uptake from ARD and the mass of NaCl added over cycles. Figure 4.5a shows that FRESH and REUSED gave similar total Zn uptake from ARD over the first eight cycles, with FRESH then outperforming REUSED in subsequent cycles.

The total Zn uptake from ARD is plotted against total NaCl in Figure 4.5b. The REUSED only utilized one-quarter of the FRESH mass required for the same net Zn
uptake.

Based on the final points in Figure 4.2b and the deviation between USED and REUSED in Figure 4.5a, the ninth and tenth cycles performed relatively poorly. This suggests that the number of uptake/removal cycles should be reduced from 10 to 8 for this ARD. The 8-cycle performance is shown in Figure 4.6a and b. Note that the optimum number of cycles is likely to depend on the composition of the ARD.
Figure 4.5 a) Total Zn removed from ARD vs. numbered cycles. b) Total Zn removed from ARD vs. Volume of NaCl solution used.
Solid Line: tests carried out with fresh NaCl solution each cycle; Dotted line with hollow symbols: tests carried out reusing same NaCl solution each cycle during cycles 2-10.
Figure 4.6 a) Total Zn removed from ARD vs. reduced total number of cycles (from 10 to 8). b) Total Zn removed from ARD vs. Volume of NaCl solution with number of sorption/regeneration cycles reduced from 10 to 8 to enhance efficiency. Solid Line: tests with fresh NaCl solution for each cycle; Dashed line with open symbols: tests carried out with reused NaCl solution for cycles 2-8. The zinc uptake/regeneration amounts for Cycles 9-19 (after cycle 8) were simulated by interpolating the results in Figure 4.4 a and b, that is, correlate the zinc removal during regeneration cycle to the solid phase accumulation and the aqueous phase concentration.

The mass balance results for single adsorption batch test, single cycle and multiple cycles are listed in the Table 4.2. The error ranges from 5.6% to 16.4%, most likely due to the instrumental fluctuations and multiple test variations.
Table 4.2 Mass balance errors

<table>
<thead>
<tr>
<th>Test type</th>
<th>Error Sources</th>
<th>Relative range$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass balance for single adsorption batch test (acid digestion - ICP - Zn)</td>
<td>Method + instrument + test</td>
<td>5.6-7.1%</td>
</tr>
<tr>
<td>Mass balance for 1 cycle test (acid digestion - ICP - Zn)</td>
<td>Method + instrument + test</td>
<td>6.4-10.2%</td>
</tr>
<tr>
<td>Mass balance for 10 cycle test (acid digestion - ICP - Zn)</td>
<td>Method + instrument + test</td>
<td>16.4%</td>
</tr>
</tbody>
</table>

$^1$ Due to the lack of the true value, the relative fluctuations are represented by the percentage relative range (range over average value), where the range shows difference between the maximum and minimum measured values.

### 4.4 Conclusions

- Clinoptilolite used to capture zinc from ARD can be reused repeatedly after removing the loaded zinc. Uptake/removal cycles could be repeated multiple times while maintaining significant uptake and removal.
- Zinc uptake from ARD decreased with cycling, with the decrease being slower when fresh NaCl solution was fed, rather than reused NaCl solution.
- Zinc removal from loaded clinoptilolite increased over the first four cycles for both fresh and reused NaCl solution tests, then stayed nearly stable for the former, while decreasing for the latter over the following six cycles.
- The difference between uptake and removal during each cycle decreased over the first four cycles, then became zero or slightly negative for fresh NaCl solution, while staying positive for reused regenerant solution over the next six cycles.
- Three removal-only stages after the initial 10 uptake/removal cycles greatly decreased the zinc accumulated in clinoptilolite, leading to almost total recovery of the removal capacity for subsequent uptake/removal cycles.
- Only one-quarter of regenerant was required to achieve the same total zinc uptake from ARD for reused NaCl regenerant compared with fresh NaCl solution for 20 cycles.
- It is recommended that there be 8 rather than 10 uptake/removal cycles before continuous removal stages for the ARD tested in this study.
Chapter 5 Dealumination of Clinoptilolite during ARD Treatment and Its Impact

5.1 Introduction

Acid rock drainage (ARD) treatment using clinoptilolite has been studied extensively (Inglezakis et al. 2002; Rios et al. 2008; Calvo et al. 2009; Motsi et al. 2009) due to its low cost, effective adsorption capacity and feasibility of regeneration. A slurry bubble column has been proven to have higher efficiency and better performance than a fixed bed or rotating column (Xu et al.; Cui et al. 2006).

Previous work (Inglezakis et al. 2002; Oztas et al. 2008) has demonstrated that some zeolites (those with a high siliceous module SiO$_2$/Al$_2$O$_3$) exhibit higher capacity and lower diffusion resistance than others. The high acid stability of natural clinoptilolite allows modification by HCl without destroying the mineral skeleton (Inglezakis et al. 2003). The extent of the changes depends on the cation content, the amount and type of impurities, as well as the process conditions.

Decationization (exchange of zeolite cations with H$^+$ ions) and zeolite dealumination take place under acid conditions (de las Pozas et al. 1996; Rivera et al. 2000; Inglezakis et al. 2003; Hernandez-Beltran and Olguin 2007). Partial dealumination could enlarge the pore volume, thereby improving the zeolite thermal stability, increasing the hydrophobicity and making the minerals better sorbents (de las Pozas et al. 1996; Cakicioglu-Ozkan and Ulku 2005; Rozie et al. 2005).

According to Brønsted and Lewis theory, dealumination of clinoptilolite results from acidic/basic behaviour of the aluminosilicate structure in the presence of H$^+$ or OH$^-$ in solution (Rozie et al. 2005). Al can be progressively displaced from the aluminosilicate framework in acidic solutions because of proton binding on Lewis basic sites according to:
\[-\text{Al} - \text{OH} + \text{H}^+ \rightarrow \text{AlOH}^+\quad \text{(Eq. 5.1)}\]

This reaction is favored at low pH and high Al total concentrations. Because of their high degree of surface protonation, \(\text{AlOH}^+\) species tend to detach from the surface (Rozic et al. 2005).

The hydrolysis of Al(III) ions involves several steps and is promoted by increased pH over time due to clinoptilolite neutralization, with the most relevant species being a mixture of weak conjugate acids and bases in weakly acidic dilute solution. Polymeric ions form in more concentrated solution by sharing \(\text{–OH}\) groups (Allen 2009).

Aluminum hydrolysis and colloids were inferred in our previous study in Chapter 2. In view of the potential metal adsorption capacity of Al colloid, we investigated zinc associated with Al colloids in this study, and compare this with zinc adsorption on clinoptilolite to study the colloid impact on ARD treatment. The aims of the present work were:

(1) To investigate the dealumination of clinoptilolite and consequent Al hydrolysis with increasing pH;
(2) To study hydrolysis of aluminum and colloid formation;
(3) To access the impact of Al colloid formation on Zn removal from ARD.

### 5.2 Methodology

The clinoptilolite tested in the experiments was obtained from Bear River Zeolite, USA. Its chemical composition is shown in Table 2.1. The cation exchange capacity was 2.16 mol/kg. No attempt was made to activate or pre-treat the materials except by oven-drying to equalize the moisture contents of the various size fractions.

ARD from Highway 97C in British Columbia (Coquihalla Merritt-to-Peachland connector) with a pH of 3.4 was used in the experiments. Background ions are listed in Table 2.2. Slurries were prepared with concentrations of 25-400 g clinoptilolite (particle size 300-1400 \(\mu\)m) per kilogram liquid and 2 kg ARD for each batch adsorption test. This ARD was spiked with zinc ions for the adsorption batch
experiments by adding zinc chloride (ZnCl\textsubscript{2}) solution to give a final Zn\textsuperscript{2+} concentration of 15-215 mg kg\textsuperscript{-1} to match possible seasonal high and low zinc concentrations in the field. For all tests, before adding clinoptilolite particles to the solutions, the pH was adjusted to predetermined values (2-5) by adding 1M HCl or NaOH.

A slurry bubble column (Figure E1) of inside diameter 0.090 m and overall height 1.4 m was employed for the experiments. Air was introduced into its bottom through a ‘wind box’, before passing through a distributor plate containing 57 uniformly-distributed orifices of diameter 6.3 mm, with a screen underneath to prevent loss of particles during idle periods. Bubble formation and coalescence created a strong internal liquid circulation pattern, often called “Gulf-Streaming” (up the core, and down at the walls).

After operating for the designated reaction time, the supernatant was separated from the clinoptilolite samples by filtration, and colloids were obtained by ultra-filtration (5kDa) with centrifugation. After separating the supernatant liquid from the samples, the metal ion concentrations of the supernatant and the solid phase after digestion (Method 3050b) with concentrated acid (USEPA 1996) were determined by an Atomic Adsorption Spectrophotometer (AAS) (Thermo Jarrell Ash Video 22, TJA Solutions, US).

Zinc is the key contaminant of concern in this ARD. Hence its removal during the process was the major focus in this study. Aluminum concentrations in the various phases were also monitored to track the dealumination and hydrolysis/precipitation processes.

From speciation and saturation index calculation using the PHREEQC computer program with the phreeqc.dat database, hydrolysis of aluminum ions is predicted for the given system (in this study, mainly sulfate, carbonate and chloride) with the cationic and anionic aluminum complexes vs. pore pH considered. Further discussion of the anion impact and the aqueous species is provided in Section 6.4.3.
5.3 Results and Discussion

5.3.1 Dealumination of Clinoptilolite in Acid Rock Drainage

The ARD uptake results by clinoptilolite and for sorbent regeneration are discussed in Chapters 2, 3 and 4. During these studies, it was noticed that the proportions of interchangeable cations in clinoptilolite and hydrolyzable constituents in ARD have an impact on the final mineral species when ARD contacts clinoptilolite. The concentration of Fe and Al species are controlled by (complex) species solubility. Fe was negligible in this study due its very low initial concentration (precipitated at pH 2.5, see 6.4.3 discussion and the brown iron precipitates observed in field when sampling). However, leaching of aluminum was found to occur during the initial stages where the system was acidic. Table 5.1 shows more aluminum in colloid form than retained in solution after agitation and in the initial aqueous portion, indicating clinoptilolite dealumination.

<table>
<thead>
<tr>
<th>Ini. pH</th>
<th>colloid Zn in ARD</th>
<th>Zn in clinop.</th>
<th>Zn in colloid</th>
<th>Al in ini. ARD</th>
<th>Al in final ARD</th>
<th>Al in clinop.</th>
<th>Al in colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4.10 g/g</td>
<td>6.30E-05 g/g</td>
<td>2.90E-04 g/g</td>
<td>3.90E-03 g/g</td>
<td>2.03E-5 g/g</td>
<td>1.44E-05 g/g</td>
<td>6.10E-02 g/g</td>
</tr>
<tr>
<td>4</td>
<td>10.4 g/g</td>
<td>5.30E-05 g/g</td>
<td>3.10E-04 g/g</td>
<td>3.30E-03 g/g</td>
<td>1.70E-5 g/g</td>
<td>7.90E-06 g/g</td>
<td>5.79E-02 g/g</td>
</tr>
<tr>
<td>5</td>
<td>13.4 g/g</td>
<td>4.80E-05 g/g</td>
<td>3.10E-04 g/g</td>
<td>2.80E-03 g/g</td>
<td>8.52E-6 g/g</td>
<td>6.10E-06 g/g</td>
<td>6.05E-02 g/g</td>
</tr>
</tbody>
</table>

Al can be progressively removed from the aluminosilicate framework in acidic solutions by proton binding on Lewis basic sites (Rozic et al. 2005). According to Brønsted and Lewis theory, dealumination results from the acidic/basic behaviour of the clinoptilolite aluminosilicate structure in the presence of H⁺ or OH⁻ in solution (de las Pozas et al. 1996; Cakicioglu-Ozkan and Ulku 2005; Rozic et al. 2005).

Among anionic ligands, sulfate is believed to form inner-sphere complexes with surface active sites and to increase the net negative surface charge, promoting metal adsorption (Stumm and Morgan 1996; Munk and Faure 2004; Ranville et al. 2004). The precipitation of aluminum (oxy)hydroxysulfate is further discussed in Section
6.4.3. On the other hand, Cl\(^-\) and NO\(_3^-\) form outer-sphere complexes, indirectly enhancing metal adsorption (Davis and Burgoa, 1995; Sposito, 1989).

The anion impacts of Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\) on the acidic behaviour of clinoptilolite were compared by Vasylechko et al. (2003). The degree of aluminum elimination from clinoptilolite was higher with SO\(_4^{2-}\) than with either Cl\(^-\) or NO\(_3^-\) for the same H\(^+\) concentration. Hence, in this study, the abundant SO\(_4^{2-}\) as a background anion in the ARD may have accelerated dealumination.

At the same time, SO\(_4^{2-}\) tends to inhibit Si dissolution, with sulfate ions adsorbing onto soils by ligand exchange, inhibiting Si dissolution (Davis and Burgoa, 1995; Doula and Ioannou, 2002).

The exchange of pore H\(^+\) ions with clinoptilolite cations is not well understood, judging from previous work. Solution acidity, temperature, original crystal structure, and composition all strongly influence zeolite decationization, dealumination and the resulting zeolite structure (Armbruster and Galarneau 2001; Omegna et al. 2001; Doula et al. 2002).

**5.3.2 Hydrolysis of Aluminum Species and Formation of Colloids**

Increase of pH in solution with contact time (due to the neutralization impact of clinoptilolite, Figure 2.4c) leads to the removal of metal ions, mostly by precipitation, co-precipitation and adsorption (Davis and Burgoa, 1995). Figure 5.3 shows the isolated zinc uptake by clinoptilolite and by colloid. As noted above, formation of surface complexes increases Al dissolution, consequently increasing Al\(^{3+}\) hydrolysis, which take place when Al\(^{3+}\) species dissolve (Doula and Ioannou, 2002).

The hydrolysis equilibrium for Al(III) ions involves several steps, with the most relevant species being weak conjugate acids and bases in weakly acidic dilute solution (Allen 2009):

\[
\text{Al(H}_2\text{O)}_6^{3+} = \text{Al(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}^+ \quad pK_1 = 4.9
\]

\[
\text{Al(H}_2\text{O)}_5(\text{OH})^{2+} = \text{Al(H}_2\text{O)}_4(\text{OH})^{+} + \text{H}^+ \quad pK_2 = 5.5
\]
\[
\text{Al(H}_2\text{O)}_4\text{(OH)}_2^+ = \text{Al(H}_2\text{O)}_3\text{(OH)}_3^+ + \text{H}^+ \quad \text{pK}_3 = 6.7
\]

Polymeric ions form in more concentrated solution by sharing –OH groups, e.g.:

\[
13 \text{Al(H}_2\text{O)}_6^{3+} = \text{Al}_{13}\text{O}_{4}(\text{OH})_{24}^{7+} + 32\text{H}_3\text{O}^+ + 18\text{H}_2\text{O} \quad \text{or}
\]

\[
13\text{Al}^{3+} + 32\text{H}_2\text{O} = \text{Al}_{13}(\text{OH})_{32}^{7+} + 32\text{H}^+
\]

These hydrolysis reactions are shown as Figure 5.1. The sulfate-affected Al hydrolysis/precipitates are shown in Chapter 6, Figure 6.1.

![Figure 5.1 Hydrolysis of Al in aqueous solution](image)

With final aqueous pH > 4, white flocs/precipitates were observed after the uptake test. Both zinc and aluminum were detected in those colloid precipitates (Table 5.1). It was found that the total Al in the colloid and supernatant exceeded that in the original ARD, as noted above. Hence, clinoptilolite leaching contributed to excess Al after agitation in SBC over time (depends on initial and final pH). With higher aqueous Al concentrations, colloid/amorphous Al was observed to form at a final pH of 4.0-6.0 in this study.

The formation of aluminum colloid/precipitates depends on the initial and final aqueous pH, and the related total soluble and precipitated Al concentration. Based on the tested pH, with an initial aqueous pH < 5 (~4.2), there is possibility of the clinoptilolite dealumination over time. Dealumination occurs faster with lower initial pH, given sufficient/adequate mass transfer.

Dealumination contributes to the increased total Al concentration in treated ARD. The reaction between clinoptilolite and ARD increases the pH, contributing to the Al
precipitates. For instance, one test with initial pH 2 and 100 g clinoptilolite per kg ARD, after 1 h and 2 h of contacting time, the aqueous pH was 3.3 with no Al precipitates formed. However, precipitation was observed with final pH 4.1 after 6 h contact time.

Hydrolysis of Si was excluded as a possible cause of the colloid since the pH required to initiate Si hydrolysis (>7) is much higher than the test pH with the experimental Si concentrations. In this particular ARD, Fe has already precipitated in field in form of Fe(III) hydroxide or hydroxysulfate (Chapter 1, Figure 1.1) and shows very low initial aqueous concentration (2-5 ppm).

The concentration of Al in the solution is plotted vs. the final pH in Figure 5.2. This indicates oversaturation of Al minerals at higher pH, consistent with the formation of precipitation/colloid mixtures.

![Figure 5.2 Al concentration vs. final pH in multi-cycle adsorption tests in SBC with initial 100 mg/kg Zn concentration in ARD at pH 3, contacting time for each cycle: 20 or 60 minutes; particle size: 600–850 μm; sorbent dose: 100 g/kg of clinoptilolite.](image)

According to the calculation of the software PHREEQC, several aluminum minerals, became supersaturated when pH<4.7, including jurbanite (AlSO₄OH), alunite (KAl₃(SO₄)₂(OH)₆) and a basic aluminum sulfate (AlOHSO₄) (Stollenwerk 1994). In near-neutral solutions, Al concentrations are generally low and can be
assumed to be controlled by gibbsite and kaolinite (Hem, 2005). However, in acidic sulfate waters, gibbsite and kaolinite are unstable, and it has been suggested (Nordstrom and Ball, 1986) that jurbanite, \( \text{Al} (\text{SO}_4) (\text{OH}) \cdot 5\text{H}_2\text{O} \), may control aluminum concentrations. At low pH, the water may also tend to equilibrate with alunite, \( \text{Al}_3 (\text{SO}_4) (\text{OH}) \) (Miyazaki et al. 2003). According to Nordstrom (1982) and Stollenwerk (1994), \( \text{Al} \text{OHSO}_4 \) controls the solubility of Al at \( \text{pH} < 4.7 \) (acidic and sulfate-abundant solution), whereas amorphous \( \text{Al} (\text{OH})_3 \) dominates at \( \text{pH} > 4.7 \). Gibbsite-like minerals also participate in this precipitation process, although gibbsite is rarely identified mineralogically (Hendershot et al. 1996), possibly due to an amorphous gibbsite-like phase, or to surface adsorption effects (Wang et al. 2006).

No tests were conducted at \( \text{pH} > 6 \) as this would not be relevant for remediation purpose (direct chemical neutralization approach instead).

PHREEQC simulation predicts precipitation of amorphous \( \text{Al} (\text{OH})_3 \) (amorphous) from the solution; colloidal Al formation would dominate the species for \( \text{pH} \) 4.4-5.6, forming sulfate complex over the \( \text{pH} \) range 3.8-5.2. Al is predicted to be mainly removed as basaluminite, boehmite and alunite at \( \text{pH} \) 5.28-6.95 and as gibbsite and diaspore at \( \text{pH} \) 5.53–9.12. Cu and Zn are predicted to be removed by adsorption onto the precipitating iron(oxy)-hydroxides and aluminum (oxy)-hydroxides, both of which are abundant. The Al species simulation matches the observed flocculates/precipitates over the designated \( \text{pH} \) ranges. White flocculation was observed and separable by ultra-filtration, acid digestion of the flocs shows higher unit zinc uptake and high Al concentration (Figure 5.4). While the XRD results (Appendix A) do not show basaluminite, boehmite or alunite peaks, the colloid/precipitates are considered to be amorphous. According to Bigham and Nordstrom (2000) and Sanchez-Espana et al. (2006), these Al precipitates probably consist of poorly ordered hydroxysulfates with composition intermediate between hydrobasaluminite and basaluminite, which hardly show diffraction patterns.
5.3.3 Adsorption/Co-precipitation of Zinc on Al-colloids

Adsorption of zinc on clinoptilolite is likely to be the main cause of its decreased aqueous phase concentration during laboratory adsorption studies (Cui, 2007 and Chapter 3), showing significant adsorption of heavy metals, even at low pH (<3).

For the effects of adsorption to be significantly higher in the new precipitates at higher pH (especially at pH>4, see Table 5.1), a higher adsorption capacity in the precipitates would be necessary.

The possibility of zinc hydrolysis/precipitates appears to be excluded by the solubility data for solubility of Zn compounds (Lindsay, 1979; McBride and Blasiak, 1979; Brummer et al., 1983). Zn$^{2+}$ dominates the species distribution with pH<6.3 as shown in Chapter 6, Figure 6.2. With the given initial test pH range(3, 4, 5), the only species couple which seems likely to precipitate is Zn-Fe, but this seems to be impossible given the low Fe concentration. However, Zn-Fe could co-precipitate with other ARD of higher initial Fe concentration.

Since the hydrolysis/precipitation of zinc requires neutral or alkaline pH, the most likely mechanism underlying most of the decrease in zinc and sulfate concentrations is co-precipitation and adsorption onto Al-dominated precipitates. Figure 5.3 shows a significant difference between total zinc removal and removal by clinoptilolite, supporting the hypothesis that the co-precipitation of zinc onto colloid was a significant contributor to the overall zinc removal.
Our test results indicate that zinc adsorption onto clinoptilolite is relatively stable for initial pH of 3, 4 and 5, while zinc uptake on a unit mass basis by the colloid decreases with increasing pH, likely due to the greater amount of colloid formed (see Table 5.1 and Figure 5.4). In other words, a higher dosage of colloid leads to lower unit uptake (Figure 5.5), but higher total zinc removal.

Figure 5.3 Total zinc uptake & zinc uptake on clinoptilolite during this study. For test conditions, see Chapter 4, Table 4.1, various dosage tests.
Figure 5.4 Total colloid collected, total Zn uptake on colloid and unit Zn uptake on colloid (mmol Zn per mg colloid) after 1 h of contact with initial pH of 3, 4 and 5;

Figure 5.5 Unit Zn uptake per mole of Al in colloid after 1 h of contact with initial pH of 2, 3, 4 and 5

The study also shows that final aqueous pH>4 does not result in co-precipitates with colloids, in agreement with the tests reported by Inglezakis et al. (2003), whose solutions were acidified with HNO₃ at pH 2 to avoid precipitation of hydroxides for all test solutions during removal of Cu²⁺, Fe³⁺ and Cr³⁺ by clinoptilolite; for 2<pH<3,
the aluminum minerals are still below saturation level.

Chapter 2 shows that higher clinoptilolite dosage results in higher pH, leading to colloid/precipitate formation. Figure 5.2 shows that for the same final aqueous pH, the Al concentration was at a similar level regardless of the test conditions investigated (various initial pH and various clinoptilolite dosages). However, unit leaching of Al from clinoptilolite varied; when more clinoptilolite was added, unit Al leaching was lower. At the same time, the final aqueous Al concentration remained lower than the initial concentration (Figure 5.5) due to colloid formation, despite the extra Al derived from dealumination of solid clinoptilolite.

![Figure 5.6 Al in ARD solution before and after contact with clinoptilolite](image)

As seen in Figure 5.6 and Table 5.1, the final Al concentration in the aqueous product is lower than the Al concentration in the untreated ARD; thus dealumination does not make the solution more hazardous with respect to Al, as long as the colloid is collected and retained. The high zinc uptake capacity of the Al colloid mixture (over 10 times higher than for clinoptilolite, as seen in Table 5.1) could be useful for the remediation process. However, additional separation may be necessary to take advantage of the capture by the colloids.
Due to the impact of cations (Fe or Ca, if abundant) and the anions (SO$_4^{2-}$ and Cl$^-$), the hydrolysis of Al would be greatly affected (Georgantas and Grigoropoulou, 2007). The treatment of ARD with clinoptilolite may therefore be site-specific, i.e., the effectiveness of the treatment process will depend on the quality of the clinoptilolite and the initial constituents of the ARD.

5.4 Conclusions

- Dealumination of clinoptilolite contacted with ARD occurs due to the acidic initial conditions.
- Leached Al hydrolyzed over time, and sulfate anions had an impact on this process. Al colloid formed at a pH of about 4. More colloid formed at higher final pH after zinc uptake.
- Unit zinc uptake was higher on Al colloid than on clinoptilolite particles; higher pH resulted in less Zn uptake per mass of Al.
- The final Al concentration in the product aqueous solution was less than the initial Al concentration of ARD; thus the dealumination was not hazardous, so long as the colloid can be collected and retained.
Chapter 6 Modeling of Aqueous Species in ARD and Surface Uptake during Remediation

6.1 Background

As stated in Chapter 5, clinoptilolite dealuminates during contact with ARD, and aluminum hydroxide formation has been observed.

Theoretically, specific metals precipitate at certain pH levels. For example, hydroxide of Fe$^{3+}$ precipitates at pH of 2.5~3.3, and Al$^{3+}$ at pH of 3.7~4.5. These pH limits vary with the total metal concentration, redox potential, carbon dioxide concentration and anions which could form complexes (Nordstrom and Ball 1986; Appelo and Postma 2005). In the ARD tested in this study, not only is sulfate present as a strong complex ion, which decreases the solubility of aluminum hydroxide species (Lindsay 1979; Palmer and Wesolowski 1992), but sorption on newly-formed amorphous precipitates and relative surface complexation/co-precipitation lead to divalent metal uptake (Parkhurst and Appelo 1999).

Before dealing with acid mine/rock drainage, it is useful to model the metal species of concern in solution to justify whether it is chemically feasible to form precipitates / flocs, and to predict the conditions needed for their formation.

To perform these tasks, zinc uptake from acid rock drainage by clinoptilolite was evaluated by the well-known PHREEQC computer program, which involves the calculation of aqueous species distribution, the saturation index of relevant minerals, surface sorption onto clinoptilolite and precipitates, if any. A potential strategy is proposed for the estimation of zinc uptake from acid drainage by clinoptilolite.
6.2 Introduction

Various minerals have been used to protect groundwater aquifers from contamination by adsorbing pollutants (e.g., heavy metals) onto solid soil structure. Materials with high cation exchange capacity are of particular interest in remediation (Mackenzie et al. 1999; Wissmeier and Barry 2009). This chapter focuses on uptake of zinc from acid drainage by the natural zeolite, clinoptilolite.

Neutralization has an impact on the accumulation of metals in clinoptilolite particles and on hydrolysis reactions because of the heterogeneous nature of the clinoptilolite sorbent. Owing to the variable composition of acid mine drainage and the complexity of clinoptilolite itself, it is difficult to predict the optimum conditions for overall remediation without understanding the dominant mechanisms (Morpurgo et al. 1996; Ruby et al. 2006).

White precipitates have been observed in solution during equilibration with clinoptilolite (see Chapter 5, sections 5.3.2 and 5.3.3). This suggests that reduced concentrations of metals at higher pH do not result from adsorption alone, but rather metal removal under these conditions can be explained through sorption combined with precipitation of new phases.

Our modeling work is motivated by the need to predict equilibrium metal uptake with various initial compositions and the frequently-observed sorbent deterioration. PHREEQC, an aqueous geochemical calculation computer program developed by the US Geology Survey (Parkhurst and Appelo 1999), was used in this study to calculate the saturation-index (SI) and to predict speciation by modeling precipitation–dissolution chemical equilibria.
6.3 Methodology and Model Structure

6.3.1 Relevant Experiments

The batch test conditions are the same as for the zinc uptake tests in Chapter 2. The elemental concentration vs. time trends for the operating conditions were used to discern which elements control the solubility in the neutralization process.

In the experiments, liquid samples were analyzed by AAS and ICP, whereas solid and solid residues (SR) were analyzed by X-ray diffraction (XRD) in an attempt to detect the minerals controlling the inorganic contaminant concentrations in solution. The colloid portion was separated by ultrafiltration as in Chapter 5. Surface areas were determined by the EGME and BET methods.

6.3.2 Model Structure

In the zinc uptake simulation in this study, the initial parameters were: zinc concentration, equilibrium pH, temperature, and acid rock drainage composition. The compiled programs were calculated based on the WATEQ4F database (Parkhurst and Appelo 1999). Potential minerals with solubility product (K_{sp}) in the PHREEQC database were adopted. The output data of the activities, the free ionic activities product and saturation-indexes of every species, as well as the solution ionic strength, were used to evaluate the potential precipitates in the zinc uptake process.

PHREEQC (Parkhurst and Appelo 1999) is designed to model geochemical reactions, based on an ion pairing aqueous model. This program can calculate pH, redox potential, and mass transfer (amounts of solid or gaseous phases entering or leaving the aqueous phase) as a function of reaction progress, and it can calculate the composition of solutions in equilibrium with multiple phases.

The main objective of calculations in PHREEQC is to estimate saturation indices (SI), \([= \log_{10} (IAP/K_{sp}(T))]\). SI is approximately zero when water is at equilibrium. According to Truesdell and Jones (1974), it is of interest to determine mineral phases
with which the water is saturated or nearly so, as the aqueous species may not be accessible to observation or determination. For SI >0, the water is supersaturated with that mineral, and the mineral tends to precipitate. When SI<0, the water is undersaturated with respect to the mineral, and the mineral tends to dissolve in the water. Because of thermodynamic and analytical errors, SI is subject to uncertainty, and this must be taken into account. This uncertainty varies according to both the complexity of the mineral stoichiometry and input data errors.

Two useful databases, phreeqc.dat and wateq4f.dat, distributed with the PHREEQC software are used for the SI calculations (Wigley, 1977, Ball and Nordstrom, 1991; Nordstrom et al., 1990). Another database from MINTEQA2 (Allison et al. 1990) is also used. The database files provided with the program should be considered to be preliminary (Parkhurst and Appelo 1999). The log K’s and enthalpies of reaction have been derived from various sources (listed below).

The calculated activities of the dissolved ions in water may be combined to produce the appropriate activity product which may be compared with the solubility equilibrium constant to determine the degree of saturation of the water for each mineral considered.

The Davies and Debye-Hueckel equations are used in WATEQ4F to calculate the activity coefficients of all charged species except Ca, Mg, Na, K, Cl, SO₄, HCO₃, CO₃, H₂CO₃ and Sr. The extended Debye-Hueckel equation is applied for these species because of the thermodynamic data used for the species (Plummer and Busenberg, 1982; Busenberg et al., 1984; Cloke, 1963).

\[ -\log f_\pm = 0.5z_1z_2\left(\sqrt{I} - 0.15I\right) \]

(Eq. 6.1)

where, \( f_\pm \) is the activity coefficient, \( I \) is ionic strength, \( z_1 \) and \( z_2 \) are the charges of ions dissociated from the electrolyte.

The Davies equation (Eq. 6.1) is used in most cases to calculate individual ion activity coefficients for the solute species (Davies, 1962), because the parameter required for the Debye-Hueckel equation is more difficult to find from references. The
calculations become less precise for electrolytes that dissociate into ions with higher charges. Further discrepancies arise if there is association between the ions, with the formation of ion-pairs, such as Mg\(^{2+}\)SO\(_4^{2-}\).

The high ionic strength of the regenerant requires the Pitzer database for ionic strength impact on activity calculations to be applied (typically necessary for solutions with high NaCl added during regeneration).

The Pitzer model is a formalism to deal with extremely concentrated salty water:

\[
\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j D_{ij} \log m_j + \sum_{jk} E_{ijk} m_j m_k \tag{Eq. 6.2}
\]

where, \(\gamma_i\) is activity coefficient, DH stands for Debye Hueckel, \(m\) is molality (mol/kg), \(D_{ij}\) are ion-ion interaction coefficients and \(E_{ijk}\) are ion-ion-ion interaction coefficients.

The temperature range over which WATEQ4F.dat can be used is 0 to 100°C. However, uncertainties increase considerably when there are large departures from 25°C. The effect of pressure is not calculated because, for the majority of natural waters, it is negligible (Truesdell and Jones, 1974; Nordstrom and Munoz, 1986).

The number assigned to the specific chemical reaction in the computer code, the reaction, selected reaction enthalpy (\(H_r\)), equilibrium reaction constant (\(\log K_{eq}\)), and the sources of the thermodynamic data are mainly from WATEQ4F.dat. Bisulfate ion association constants are given or estimated for Fe\(^{2+}\), Fe\(^{3+}\), Ca\(^{2+}\), and Al\(^{3+}\) because of their importance in acid waters, typically in this ARD case. The enthalpy and log K values for the AlSO\(_4^{2+}\) and Al(SO\(_4\))\(^{2-}\) aqueous species, were reported by Nordstrom et al. (1990).

Data from various sources may not be consistent because uncertainties in thermodynamic data are reaction-specific, as noted by Parkhurst and Appelo (1999). No attempt has been made to determine whether the aqueous models defined by these database files are consistent with the original experimental data where the individual log K’s cited were developed. So the aqueous model is limited due to uncertain data and poor internal consistency in the data of available databases.

The relevant redox areas which may be of concern in this study include: Fe
species distribution; Mn species with valence other than +2; Cu species having a valence of +1; As species distribution; Se species distribution; Ion activity product calculations; Calculation of the partial pressure of atmospheric O₂; Calculation of the activity of H₂S from input SO₄, pH and Eₖ. Overall, due to the low Fe, Cu, and As concentrations in this (Highway 97C) ARD, the redox impact is insignificant.

When the retention of zinc on clinoptilolite is investigated, the remaining solute concentration of the zinc (C) can be compared with the concentration of zinc, Q, retained on solid particles. The relationship \( Q = f(C) \) is named the "sorption isotherm". The uniqueness of this relationship requires that two conditions be met: (i) The various reaction equilibria of retention/release must have been reached, (ii) All other physico-chemical parameters must remain constant. (Bolan et al. 1999; Limousin et al. 2007)

The retention (or release) of zinc on solid surfaces is quantified in terms of the "sorption isotherm" in this work, without distinguishing the sorption mechanisms. When the concentration of the retained substance (zinc in this case) is low enough, the composition of the bulk solution remains constant and a single-species isotherm is often sufficient, although it remains strongly dependent on the background medium (Sposito 1989). However, at higher concentrations, sorption may be driven by the competition between several species that affect the composition of the bulk solution (Limousin et al. 2007).

Unlike the stable-equilibration of clinoptilolite with deionized water, the ARD contains high concentrations of H, Ca, Mg, Al, K and Fe species, all of which are also present in clinoptilolite, and may well leach on interaction with ARD. (Recall that the Al-leaching was observed/detected during the tests discussed in Chapter 5). In the reactions, direct ion concentration in pores/channels cannot be measured. Inverse modeling with DDL (double diffusive layer) is therefore adopted here to estimate the pore chemistry.

PHREEQC assumes equilibrium conditions. However, due to slow kinetics during some mineral phases, equilibrium may not have fully achieved during the 1 h reaction times employed. In particular, the dissolution/leaching of clinoptilolite
(treated as slowly leachable aluminosilicates by Rozic et al. (2005) is considered to not reach equilibrium in the following sections.

The pH-dependent dealumination is responsible for the increased total aqueous Al concentration, which is incorporated empirically (based solely on experimental data solely) due to lack of theoretical parameters.

Adsorption on aluminum hydroxide is modeled according to the Langmuir and Freundlich isotherms, whereas adsorption on clinoptilolite is modeled according to the Freundlich or the two-surface Langmuir equations. A similar approach can be followed for iron hydroxide, but in this study, the Fe level in the ARD collected was very low, so iron hydroxide is assumed to be negligible.

Values of the specific surface area (600 m$^2$/g), stoichiometry (Fe$_2$O$_3$.H$_2$O; 89 g Fe oxide/mole Fe), and surface site densities (strong sites 0.005 mole/mole Fe, weak sites 0.2 mole/mole Fe) for hydrous ferric oxide were reported by Dzombak and Morel (1990) related to acid mine water dilution tests. The adsorption of metals onto newly precipitated Al oxides could be carried out with hydrous Al oxide (1.3x10$^{-4}$ moles of sites/g of oxide) (Paulson 2001).

**6.4 Results and Discussion**

PHREEQC calculations indicate that dilution or acidity neutralization affect the concentrations of all dissolved elements. In addition, dissolved Al and Fe concentrations decrease due to mineral precipitation (gibbsite, schwertmannite and ferrirhydrite), whereas the dissolved concentrations of Cd, Co, Cu, Ni, Pb and Zn decrease due to adsorption onto newly formed Fe or Al precipitates. However, metal uptake is insignificant at low pH due to competition between H$^+$ and metal ions for binding sites.

**6.4.1 Solution Composition**

The ARD background information is listed in Table 2.2. The major concern in this ARD is zinc, whose concentration may fluctuate seasonally or due to sampling
locations. Cu and Mn have also been reported to be major concerns in other studies.

In order to obtain more detailed information about the geochemical Al control in the aqueous phase, the PHREEQC model, is complemented by the WATEQ4F mineral database, which predicts saturation index (SI) results.

Mineral equilibrium calculations for a water samples are useful to predict the presence of reactive minerals in aqueous systems and to estimate mineral reactivity (Deutsch, 1997). The equilibrium calculations based on this model show that four reactive minerals (minerals precipitated directly from the solution) need to be considered in the system: gibbsite (Al(OH)₃), allophane (hydroxi-aluminosilicate – [Al(OH)]₃(1−x)[SiO₂]ₓ) and sulfate salts alunite (KAl₃(SO₄)₂(OH)₆), and jurbanite (AlOHSO₄). The SI results are discussed in Section 6.4.3.3 and 6.4.3.4 below.

### 6.4.2 Dealumination of Clinoptilolite

Similar to the dissolution of a number of aluminosilicate minerals (Gautier et al. 1994; Oelkers et al. 1994; Carroll and Knauss 2005), the dissolution of the Al-Si leached layer is considered to be proportional to the concentration of partially detached Si tetrahedra at the near surface; these near surface complexes constitute the rate-controlling precursor complex. The partially-detached Si is formed from the removal of adjacent Al atoms, in accord with $n(>\text{Si-O-Al}) + 3n\text{H}⁺ = n(>\text{Si-O-H}) + n\text{Al}^{3+}$, where the Al cation released increased the total Al in the aqueous-precipitation system. The law of mass action is given by:

$$K_4 = \frac{a_{\text{Al}^{3+}}^n X_{>\text{Si-O-H}}^n}{a_{\text{H}^+}^n X_{>\text{Si-O-Al}}^n} \quad \text{(Eq. 6.3)}$$

where $K_4$ corresponds to the equilibrium constant, $n$ refers to the number of liberated Si created by the removal of an Al atom from the surface, and $X_i$ denotes the mole fraction of the subscripted surface species. Taking account of conservation of sites ($X – \text{Si–O–H} + X – \text{Si–O–Al} = 1$), it follows that the surface still contains substantial Al,

$$X_{>\text{Si-O-H}} = (K_4 \frac{a_{\text{H}^+}^n}{a_{\text{Al}^{3+}}})^\frac{1}{n} \quad \text{(Eq. 6.4)}$$
Because \( r_+ \) is proportional to the concentration of the \( > \) Si–O–H precursor complexes (Gislason and Oelkers 2003):

\[
r_+ = k_+ (K_4 \frac{a_{H^+}^3}{a_{Al^{3+}}})^{\frac{1}{n}} = k'_+ \left( \frac{a_{H^+}}{a_{Al^{3+}}} \right)^{\frac{1}{n}}
\]

(Eq. 6.5)

where \( r_+ \) again signifies the steady-state dissolution rate far from equilibrium conditions, \( k_+ \) refers to a rate constant, and \( k'_+ \equiv k + k_4 \frac{1}{n} \). It shows that decreasing aqueous \( Al^{3+} \) activity increases dissolution rates. Wolff-Boenisch et al. (2004) showed that the dissolution rates can be increased by an order of magnitude or more by complexing aqueous \( Al^{3+} \) ions with fluorine. Similarly, Oelkers and Gislason (2001) observed a similar effect of the presence of aqueous oxalate on aluminosilicate dissolution rates.

The sulfate anion can complex aqueous aluminum, forming aluminum-sulfate complexes, by:

\[
Al^{3+} + SO_4^{2-} = Al(SO_4)^{+}
\]

(Eq. 6.6)

and

\[
Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^{+}
\]

(Eq. 6.7)

Figure 6.1b shows the aluminum speciation in an aqueous solution containing sulfate background from Highway 97C ARD as a function of pH. Aqueous sulfate effects \( Al^{3+} \) speciation at \( 1 < pH < 6 \). For highly acid conditions (\( pH < 1.5 \)), \( Al^{3+} \) is the most common aqueous aluminum species. Between \( pH 1.5 \) and \( 5 \), the aluminum-sulfate complexes, \( Al(SO_4)^{2-} \) and \( Al(SO_4)^{+} \) are most common, while at higher pH, aqueous aluminum hydroxide complexes dominate. As aluminosilicate dissolution rates increase with decreased aqueous \( Al^{3+} \) activity (Wolff-Boenisch et al., 2004; Oelkers and Gislason, 2001), the Al dissolution rate should increase when sulfate is present in moderately acidic aqueous solutions. When comparing Figure 6.1a and b, it is obvious that sulfate has a significant impact on the aqueous \( Al^{3+} \) species percentage, with the domination range of \( Al^{3+} \) migrating from \( pH < 4.3 \) (without sulfate) to \( pH < 1 \) (with sulfate).
Figure 6.1 Predictive Al species distribution between pH 0–6 based on Al species calculated with PHREEQC: (a) without considering Highway 97C ARD background, (b) with Highway 97C background incorporated.

This agrees with the observed increase in dealumination with decreasing initial ARD pH (Chapter 5, Section 5.3.1). However, it is hard to quantify the relationship between dealumination and initial ARD pH, since the measurable Al colloid formation depends
on both initial and final ARD pH.

6.4.3 Hydrolysis and Precipitation

Precipitation of solid phases may be the most important chemical process influencing the fate of major constituents (Fe, Al, Mn and Ca), minor elements (Zn, Cu, Mo, Ni, B and Sr) and major anions (sulfate and chloride) in acid rock drainage.

Magnesium and calcium are highly soluble and commonly behave conservatively, only precipitating as efflorescent sulfates (mostly as epsomite and gypsum, respectively) in evaporative pools or margins of acidic effluents and ARD-affected rivers (McGinness 1999; Sanchez-Espana et al. 2005). Conversely, iron and aluminum are much less soluble and precipitate as the pH of the acidic discharges increases (Sanchez-Espana et al. 2005; Sanchez-Espana et al. 2006).

At pH<2, both iron and aluminum are mostly dissolved, and these metals may only precipitate from highly concentrated brines from evaporative pools, where secondary sulfates (e.g., melanterite, copiapite, halotrichite, jarosite, alunogen) eventually become over-saturated (Sanchez-Espana et al. 2006). As pH increases (for example, by partial neutralization during mixing with surface water or sorbents like clinoptilolite), iron is hydrolyzed and precipitates at pH>2.2, whereas Al tends to be hydrolyzed at pH~4.5-5.0 (Bigham and Nordstrom, 2000; Figure 6.1a). The formation of these mineral phases plays an important role in ARD aqueous species, as discussed below.

6.4.3.1 Aqueous Zn Species Distribution

As shown in Figure 6.2, the hydrolysis of zinc is unlikely to occur in the overall tested pH range (2-6), where Zn$^{2+}$ dominates the species distribution. This simplified calculation is based solely on the aqueous pH and total zinc concentration level, with no solid phase interaction or anion complex considered. When the pH of ARD was adjusted before the batch tests by adding NaOH, no precipitates were observed until pH 6 was reached. This proved that zinc hydroxides are not formed with Highway
ARD background when pH<6. So zinc hydroxide, is excluded in the later discussion.

Figure 6.2 Distribution of Zn species as a function of pH, as simulated by PHREEQC (without considering sulfate impact or solid phase interactions)

6.4.3.2 Iron (oxy)hydroxysulfates

The solid formed by precipitation of Fe(III) at pH 2.5-3.5 during mixing and neutralization of the ARD solutions is usually schwertmannite (Sanchez-Espana et al. 2005; Sanchez-Espana et al. 2006). This mineral is a poorly crystallized iron oxyhydroxysulfate whose formation from acid-sulfate waters is described (Bigham et al. 1994; Bigham et al. 1996; Bigham and Nordstrom 2000) by

$$8 \text{Fe}^{3+} + \text{SO}_4^{2-} + 14 \text{H}_2\text{O} \leftrightarrow \text{Fe}_8\text{O}_6(\text{SO}_4)(\text{OH})_4 + 22\text{H}^+$$  \hspace{1cm} (Eq 6.8)

Jarosite is usually assumed to precipitate from very acidic solutions, normally at pH<2. Schwertmannite precipitates near the discharge points at pH 2.5-3.5, whereas ferrihydrite usually forms at pH>5. These three minerals are meta-stable with respect to goethite, the most stable form of Fe(III), at low temperature (Bigham and Nordstrom 2000).

Goethite can also precipitate from ARD, although its presence in the particulate fraction of ARD-containing waters is very minor relative to schwertmannite or
ferrhydrite. Previous works suggest variable sorption of dissolved metals onto the schwertmannite, ferrhydrite and jarosite mineral surfaces (Bigham and Nordstrom 2000). As shown in Chapter 1, Figure 1.1, almost all iron precipitates before sampling with an initial Fe concentration below 2 ppm (Table 6.4 shows the calculated Fe species concentration as an example.) Therefore, iron (oxy)hydrosulfate precipitation is a minor component (Table 6.3) and not discussed in detail.

However, according to the calculation based on PHREEQC, excess Fe would be beneficial for ARD treatment. As compressed air was used to agitate the SBC, the solution is in a stable oxidizing condition which favors almost all iron precipitates. When Fe(III) hydroxide/hydroxsulfate precipitates, it could came co-precipiation of other major heavy metal cations in ARD.

6.4.3.3 Aluminum (oxy)hydroxsulfates

Compared with the Fe(III) solids, the aluminum minerals formed at pH~4.5-5.0 in the ARD are not well characterized. These solids are nearly amorphous to XRD (Appendix A, Figure A3), while being detectable in solids by acid digestion (Chapter 5, Table 5.1) in this study.

According to Bigham and Nordstrom (2000) and Sanchez-Espana et al. (2006), the diffraction pattern, along with their chemical composition, suggest that these Al precipitates probably consist of poorly ordered hydroxsulfates with composition intermediate between hydrobasaluminite and basaluminite. Alunite and aluminite have been also suggested by Sanchez-Espana (2006) to precipitate from waters with high concentrations of Al and sulfate (0.1M and 0.4M, respectively), although both minerals are rarely found as direct precipitates.

Basaluminite forms by dehydration of hydrobasaluminite and is metastable. Basaluminite is a common Al hydroxsulfate in mine drainage environments, although it also tends to be transformed to alunite during maturation or heating (Bigham and Nordstrom, 2000). The hydrolysis of Al$^{3+}$ to form hydrobasaluminite may be written as:

$$4\text{Al}^{3+} + \text{SO}_4^{2-} + 22\text{H}_2\text{O} \leftrightarrow \text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 12\text{H}_2\text{O} + 10\text{H}^+ \quad \text{(Eq. 6.9)}$$
The formation of this mineral during neutralization of ARD can also imply significant removal (by sorption) of toxic trace elements (e.g., Cu, Cr, Zn, U) from the aqueous phase (Sanchez-Espana et al., 2006).

Aluminum hydroxides precipitate when the decrease in pH associated with neutralization of acid mine drainage forces dissolved aluminum out of solution (Stumm and Morgan 1996; Munk and Faure 2004; Ranville et al. 2004). Our results (Chapter 2, Figure 2.4c) show that acidic water is neutralized by mixing with clinoptilolite, resulting in significant precipitation of aluminum hydroxides/hydroxysulfates. This precipitation corresponds to a decrease in dissolved aluminum in ARD. Geochemical modeling (by PHREEQC) matches well with the experimental results (Chapter 5, Table 5.1). Both indicate precipitation of amorphous aluminum hydroxides/hydroxysulfates, which cannot be identified by XRD (Appendix A, Figure A2 and A3).

PHREEQC predicts a fairly high saturation index of 14.68 for alunite, an aluminum hydroxysulfate. However, alunite was not identified in the XRD pattern (Appendix A, Figure A3), and this might be due to the amorphous nature of the precipitate samples. Nordstrom and Ball (1986) reported that the cessation of alunite precipitation and the corresponding onset of gibbsite precipitation are related to the first hydrolysis constant for aluminum, which occurs for pH between 4.6 and 4.9. The precipitation of gibbsite is not accounted for in our predictive model due to the high saturation index for alunite in this sulfate-rich background.

The sulfate anion can complex aqueous aluminum, forming aluminum-sulfate complexes, Figure 6.1b shows the aluminum speciation in an aqueous solution containing 0.1 M Na₂SO₄ and 10⁻⁶ M Al as a function of pH. Aqueous sulfate results in Al³⁺ speciation at 1 < pH < 6. For highly acidic conditions (pH < 1.5), Al³⁺ is the most common aqueous aluminum species. Between pH 1.5 and 5, the aluminum-sulfate complexes, Al(SO₄)²⁻ and Al(SO₄)⁺, are the most common species, while at higher pH, aqueous aluminum hydroxide complexes dominate.

The predicted hydrolysis of Al in the presence of sulfate anions (in ARD) in our test is shown in Figure 6.1b. This differs from the predicted hydrolysis in deionized
water (Figure 6.1a). In our test, where precipitates were already observed at a pH of about 4, instead of pH ~4.9 in deionized water. Our finding is supported by Georgantas and Grigoropoulou (2007) who found that up to pH≈4, hydroxide addition does not significantly increase the pH, indicating that the added hydroxide ions immediately bind to Al ions. At pH≈4, a sharp increase in solution pH is recorded, indicating that the hydroxide ions remain in the sulfate-rich solution, and white flocs of aluminum hydroxide are observed (Georgantas and Grigoropoulou 2007).

6.4.3.4 Saturation Indices (SI) and Solubility Equilibrium

The saturation index (SI) describes the extent to which a particular solution is supersaturated or under-saturated with respect to a particular solid phase. Note that the saturation index only indicates what happens thermodynamically, not the rate at which the process proceeds. A mineral with SI<0 may dissolve very slowly or not at all, depending on the reaction kinetics (Drever, 1997). If SI>0, the mineral might precipitate, but cannot dissolve. If the saturation index is close to zero, the mineral may not react at all, or may react reversibly, meaning that the mineral may dissolve or precipitate. How fast the precipitation occurs is in question. However, SI can be an important indicator in geochemical interpretation of water chemistry.

The saturation indices and activities utilized in this work were calculated using the PHREEQC computer code based on $SI = \log(IAP/Keq)$, where IAP is the ion activity product calculated from measured solution concentrations after activity and speciation calculations were performed and Keq is the equilibrium constant.

The following is an illustration of how to apply SI using PHREEQC to predict the possible precipitate formation:

Step 1: Input of original ARD concentration as background. (Table 6.1)

Step 2: Calculate the leached aluminum from clinoptilolite, based on the colloid collected (Table 6.2). Combine the leached aluminum and original aqueous aluminum into the total available aluminum concentration.

Step 3: Compare the experimental results in Table 6.2 and the predicted precipitates in Table 6.3.
Step 4: Specific prediction of sulfate species (Table 6.4) as a supplement to choose the possible precipitates in Table 6.2.

Step 5: Predict potential precipitates for ARD with lower initial pH (pH at 2), which indicates that no or minor precipitation occurs.

Table 6.1 Composition of solution 1 (ARD with initial pH 2.6 assigned in the input file)

<table>
<thead>
<tr>
<th>pe*</th>
<th>6.08</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp</td>
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</tr>
<tr>
<td>pH</td>
<td>2.6</td>
</tr>
<tr>
<td>Al</td>
<td>8.12e-04 mol/L</td>
</tr>
<tr>
<td>Ca</td>
<td>4.94e-3 mol/L</td>
</tr>
<tr>
<td>Cu</td>
<td>8.06e-07 mol/L</td>
</tr>
<tr>
<td>K</td>
<td>1.15e-4 mol/L</td>
</tr>
<tr>
<td>Mn</td>
<td>1.93e-04 mol/L</td>
</tr>
<tr>
<td>Na</td>
<td>7.79e-03 mol/L</td>
</tr>
<tr>
<td>S</td>
<td>5.60e-02 mol/L</td>
</tr>
<tr>
<td>Si</td>
<td>1.44e-03 mol/L</td>
</tr>
<tr>
<td>Zn</td>
<td>2.2e-04 mol/L</td>
</tr>
</tbody>
</table>

* pe = -log , where {e-} is the activity of electrons.

Similar to Table 6.1, other initial solutions are assigned various initial compositions; then the final pH is designated for solutions with measured final compositions. Zn and Al in the colloid phase are calculated according to Table 6.2, and these are added to the final aqueous species concentrations, after which the saturation indices of the solution are recalculated.

Table 6.2 Zn and Al measured in collected colloid

<table>
<thead>
<tr>
<th>initial pH</th>
<th>colloid collected (g)</th>
<th>Zn in colloid (g/g)</th>
<th>Al in colloid (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4.10</td>
<td>3.90E-03</td>
<td>1.75E-01</td>
</tr>
<tr>
<td>4</td>
<td>10.4</td>
<td>3.30E-03</td>
<td>1.85E-01</td>
</tr>
<tr>
<td>5</td>
<td>13.4</td>
<td>2.80E-03</td>
<td>1.60E-01</td>
</tr>
</tbody>
</table>

The detailed calculation results for the final solution for an initial pH 5 are listed in Table 6.3:
Table 6.3 PHREEQC calculated saturation indices in final ARD solutions (for batch test with initial pH 5)

<table>
<thead>
<tr>
<th>Non aqueous phase</th>
<th>SI</th>
<th>logIAP</th>
<th>logKT</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃(a)</td>
<td>1.44</td>
<td>12.85</td>
<td>11.4</td>
<td>Al(OH)₃</td>
</tr>
<tr>
<td>Albite</td>
<td>1.68</td>
<td>-16.91</td>
<td>-18.59</td>
<td>NaAlSi₂O₈</td>
</tr>
<tr>
<td>Alunite</td>
<td>14.68</td>
<td>14.43</td>
<td>-0.25</td>
<td>KAl₃(SO₄)₂(OH)₆</td>
</tr>
<tr>
<td>Anglesite</td>
<td>-1.17</td>
<td>-9.01</td>
<td>-7.84</td>
<td></td>
</tr>
<tr>
<td>Anhydrite</td>
<td>-0.67</td>
<td>-5</td>
<td>-4.34</td>
<td>CaSO₄</td>
</tr>
<tr>
<td>Anorthite</td>
<td>-0.03</td>
<td>-20.01</td>
<td>-19.98</td>
<td>Ca₃Al₂Si₂O₈</td>
</tr>
<tr>
<td>Cd(OH)₂</td>
<td>-8.92</td>
<td>4.73</td>
<td>13.65</td>
<td>Cd(OH)₂</td>
</tr>
<tr>
<td>CdSiO₃</td>
<td>-7.77</td>
<td>1.67</td>
<td>9.44</td>
<td>CdSiO₃</td>
</tr>
<tr>
<td>CdSO₄</td>
<td>-8.2</td>
<td>-7.96</td>
<td>0.24</td>
<td>CdSO₄</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>0.59</td>
<td>-3.06</td>
<td>-3.66</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Chlorite (14A)</td>
<td>-18.74</td>
<td>53.1</td>
<td>71.84</td>
<td>Mg₅Al₁Si₃O₁₀(OH)₈</td>
</tr>
<tr>
<td>Chrysoite</td>
<td>-17.52</td>
<td>15.83</td>
<td>33.35</td>
<td>Mg₃Si₂O₅(OH)₄</td>
</tr>
<tr>
<td>Fe(OH)₃(a)</td>
<td>1.57</td>
<td>6.46</td>
<td>4.89</td>
<td>Fe(OH)₃</td>
</tr>
<tr>
<td>Fluorite</td>
<td>-9.47</td>
<td>-20.18</td>
<td>-10.71</td>
<td>CaF₂</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>4.22</td>
<td>12.85</td>
<td>8.63</td>
<td>Al(OH)₃</td>
</tr>
<tr>
<td>Goethite</td>
<td>7.14</td>
<td>6.47</td>
<td>-0.67</td>
<td>FeOOH</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-0.42</td>
<td>-5</td>
<td>-4.58</td>
<td>CaSO₄·2H₂O</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>-31.66</td>
<td>12.86</td>
<td>44.52</td>
<td>H₂</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>-1.75</td>
<td>0</td>
<td>1.75</td>
<td>H₂O</td>
</tr>
<tr>
<td>Halite</td>
<td>-5.8</td>
<td>-4.24</td>
<td>1.56</td>
<td>NaCl</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>-13.41</td>
<td>49.91</td>
<td>63.33</td>
<td>Mn₃O₄</td>
</tr>
<tr>
<td>Hematite</td>
<td>16.24</td>
<td>12.93</td>
<td>-3.3</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Jarosite-K</td>
<td>3.78</td>
<td>-4.72</td>
<td>-8.5</td>
<td>KFe₃(SO₄)₂(OH)₆</td>
</tr>
<tr>
<td>Manganite</td>
<td>-3.42</td>
<td>21.92</td>
<td>25.34</td>
<td>MnOOH</td>
</tr>
<tr>
<td>Melanterite</td>
<td>-6.52</td>
<td>-8.85</td>
<td>-2.32</td>
<td>FeSO₄·7H₂O</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>-22.9</td>
<td>-25.72</td>
<td>-2.82</td>
<td>O₂</td>
</tr>
<tr>
<td>Pb(OH)₂</td>
<td>-4.79</td>
<td>3.68</td>
<td>8.47</td>
<td>Pb(OH)₂</td>
</tr>
<tr>
<td>Pyrochroite</td>
<td>-9.14</td>
<td>6.06</td>
<td>15.2</td>
<td>Mn₃(OH)₂</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>-5.08</td>
<td>37.78</td>
<td>42.87</td>
<td>MnO₂·H₂O</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.04</td>
<td>-3.06</td>
<td>-4.1</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>-10.56</td>
<td>5.44</td>
<td>16</td>
<td>Mg₅Si₃O₇·5OH·3H₂O</td>
</tr>
<tr>
<td>Sepiolite(d)</td>
<td>-13.22</td>
<td>5.44</td>
<td>18.66</td>
<td>Mg₅Si₃O₇·5OH·3H₂O</td>
</tr>
<tr>
<td>SiO₂(a)</td>
<td>-0.28</td>
<td>-3.06</td>
<td>-2.79</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Talc</td>
<td>-12.76</td>
<td>9.7</td>
<td>22.46</td>
<td>Mg₅Si₃O₁₀(OH)₂</td>
</tr>
<tr>
<td>Willemite</td>
<td>-5.29</td>
<td>10.8</td>
<td>16.09</td>
<td>Zn₂SiO₄</td>
</tr>
<tr>
<td>Zn(OH)₂(e)</td>
<td>-4.57</td>
<td>6.93</td>
<td>11.5</td>
<td>Zn(OH)₂</td>
</tr>
</tbody>
</table>

The bolded rows have positive saturation index (SI) values, implying that these are possible precipitates. However, the total Fe concentration is too low (shaded italics in Table 6.4) to get measurable Fe-associated precipitates. So Alunite is the most possible precipitate in this solution.
As seen above, the most possible precipitate is alunite (high positive SI value, with the Al% (mass basis) at ~19%, close to the observed 16-18.5% in Table 6.3, considering the amorphous colloid captured and the co-precipitates involved). Another mineral with high positive SI value is gibbsite. However, iron hydroxysulfate is less likely, due to the low total Fe concentration. The aqueous sulfate species are listed in Table 6.4:

Table 6.4 Sulfate species distribution in ARD (for the same conditions as in Table 6.3)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molality</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSO₄⁺</td>
<td>2.59E-02</td>
<td>2.01E-02</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.22E-02</td>
<td>8.09E-03</td>
</tr>
<tr>
<td>Al(SO₄)₂⁺</td>
<td>6.34E-03</td>
<td>4.93E-03</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>1.78E-03</td>
<td>1.82E-03</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>7.65E-04</td>
<td>7.84E-04</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>3.71E-04</td>
<td>3.80E-04</td>
</tr>
<tr>
<td>NaSO₄⁻</td>
<td>2.89E-04</td>
<td>2.25E-04</td>
</tr>
<tr>
<td>Zn(SO₄)₂⁻</td>
<td>7.31E-05</td>
<td>2.69E-05</td>
</tr>
<tr>
<td>MnSO₄</td>
<td>3.43E-05</td>
<td>3.52E-05</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>1.77E-05</td>
<td>1.82E-05</td>
</tr>
<tr>
<td>KSO₄⁻</td>
<td>5.80E-06</td>
<td>4.52E-06</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>4.19E-06</td>
<td>3.26E-06</td>
</tr>
<tr>
<td>CdSO₄</td>
<td>2.91E-06</td>
<td>2.98E-06</td>
</tr>
<tr>
<td>Cd(SO₄)₂⁻</td>
<td>7.63E-07</td>
<td>2.80E-07</td>
</tr>
<tr>
<td>PbSO₄</td>
<td>5.32E-07</td>
<td>5.46E-07</td>
</tr>
<tr>
<td>LiSO₄⁻</td>
<td>5.04E-07</td>
<td>3.92E-07</td>
</tr>
<tr>
<td>FeSO₄⁻</td>
<td>2.09E-07</td>
<td>2.15E-07</td>
</tr>
<tr>
<td>Pb(SO₄)₂⁻</td>
<td>6.30E-08</td>
<td>2.32E-08</td>
</tr>
<tr>
<td>CaHSO₄⁺</td>
<td>6.21E-08</td>
<td>4.83E-08</td>
</tr>
<tr>
<td>FeSO₄⁺</td>
<td>3.42E-08</td>
<td>2.67E-08</td>
</tr>
<tr>
<td>AlHSO₄⁺</td>
<td>2.27E-08</td>
<td>8.35E-09</td>
</tr>
<tr>
<td>Fe(SO₄)₂⁻</td>
<td>5.85E-09</td>
<td>4.55E-09</td>
</tr>
<tr>
<td>FeHSO₄⁺</td>
<td>8.92E-12</td>
<td>6.94E-12</td>
</tr>
<tr>
<td>FeHSO₄⁺⁺</td>
<td>9.90E-13</td>
<td>3.64E-13</td>
</tr>
</tbody>
</table>

The shaded rows show that the Fe species concentration is so low that no Fe precipitates are obtained, despite the positive saturation index (SI).

The aluminum species are less likely to precipitate at pH 3, given the same composition. The corresponding SI calculation is shown in Table 6.5. This shows that
there are less likely to be precipitates for this composition, with SI values being low for most minerals. However, at higher Fe concentration, hematite precipitation is possible, corresponding to the brown precipitates observed in the field during sampling (Chapter 1, Figure 1.1).
Table 6.5 PHREEQC calculated saturation indices in final ARD solutions (assign final pH 3 to the model, simulating the test with initial pH 2, where no precipitates captured)

<table>
<thead>
<tr>
<th>Non aqueous phase</th>
<th>SI</th>
<th>logIAP</th>
<th>logKT</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)$_3$(a)</td>
<td>-5.41</td>
<td>6</td>
<td>11.4</td>
<td>Al(OH)$_3$</td>
</tr>
<tr>
<td>Albite</td>
<td>-7.46</td>
<td>-26.06</td>
<td>-18.59</td>
<td>NaAlSi$_3$O$_8$</td>
</tr>
<tr>
<td>Alunite</td>
<td>1.01</td>
<td>0.76</td>
<td>-0.25</td>
<td>KAl$_3$(SO$_4$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>Anglesite</td>
<td>-1.18</td>
<td>-9.02</td>
<td>-7.84</td>
<td>PbSO$_4$</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>-0.67</td>
<td>-5.01</td>
<td>-4.34</td>
<td>CaSO$_4$</td>
</tr>
<tr>
<td>Anorthite</td>
<td>-18.32</td>
<td>-38.3</td>
<td>-19.98</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
</tr>
<tr>
<td>Cd(OH)$_2$</td>
<td>-13.51</td>
<td>0.14</td>
<td>13.65</td>
<td>Cd(OH)$_2$</td>
</tr>
<tr>
<td>CdSiO$_3$</td>
<td>-12.37</td>
<td>-2.93</td>
<td>9.44</td>
<td>CdSiO$_3$</td>
</tr>
<tr>
<td>CdSO$_4$</td>
<td>-8.2</td>
<td>-7.97</td>
<td>0.24</td>
<td>CdSO$_4$</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>0.59</td>
<td>-3.06</td>
<td>-3.66</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Chrysotile</td>
<td>-31.3</td>
<td>2.05</td>
<td>33.35</td>
<td>Mg$_3$Si$_2$O$_4$(OH)$_4$</td>
</tr>
<tr>
<td>Fe(OH)$_3$(a)</td>
<td>-3.92</td>
<td>0.98</td>
<td>4.89</td>
<td>Fe(OH)$_3$</td>
</tr>
<tr>
<td>Fluorite</td>
<td>-9.56</td>
<td>-20.28</td>
<td>-10.71</td>
<td>CaF$_2$</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>-2.63</td>
<td>6</td>
<td>8.63</td>
<td>Al(OH)$_3$</td>
</tr>
<tr>
<td>Goethite</td>
<td>1.65</td>
<td>0.98</td>
<td>-0.67</td>
<td>FeOOH</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-0.43</td>
<td>-5.01</td>
<td>-4.58</td>
<td>CaSO$_4$:2H$_2$O</td>
</tr>
<tr>
<td>H$_2$(g)</td>
<td>-27.06</td>
<td>17.46</td>
<td>44.52</td>
<td>H$_2$</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>-1.75</td>
<td>0</td>
<td>1.75</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>Halite</td>
<td>-5.8</td>
<td>-4.24</td>
<td>1.56</td>
<td>NaCl</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>-31.79</td>
<td>31.53</td>
<td>63.33</td>
<td>Mn$_3$O$_4$</td>
</tr>
<tr>
<td>Hematite</td>
<td>5.26</td>
<td>1.95</td>
<td>-3.3</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>K-mica</td>
<td>-6.28</td>
<td>7.78</td>
<td>14.06</td>
<td>KAl$_3$Si$_2$O$_4$(OH)$_2$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-2.37</td>
<td>5.87</td>
<td>8.24</td>
<td>Al$_2$Si$_2$O$_4$(OH)$_4$</td>
</tr>
<tr>
<td>Manganite</td>
<td>-10.31</td>
<td>15.03</td>
<td>25.34</td>
<td>MnOOH</td>
</tr>
<tr>
<td>Melanterite</td>
<td>-5.13</td>
<td>-7.45</td>
<td>-2.32</td>
<td>FeSO$_4$:7H$_2$O</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>-32.1</td>
<td>-34.92</td>
<td>-2.82</td>
<td>O$_2$</td>
</tr>
<tr>
<td>Pb(OH)$_2$</td>
<td>-9.38</td>
<td>-0.91</td>
<td>8.47</td>
<td>Pb(OH)$_2$</td>
</tr>
<tr>
<td>Pyrochroite</td>
<td>-13.73</td>
<td>1.47</td>
<td>15.2</td>
<td>Mn(OH)$_2$</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>-14.28</td>
<td>28.59</td>
<td>42.87</td>
<td>MnO$_2$:H$_2$O</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.04</td>
<td>-3.06</td>
<td>-4.1</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>SiO$_2$(a)</td>
<td>-0.28</td>
<td>-3.06</td>
<td>-2.79</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Willemite</td>
<td>-14.47</td>
<td>1.62</td>
<td>16.09</td>
<td>Zn$_2$SiO$_4$</td>
</tr>
<tr>
<td>Zn(OH)$_2$(e)</td>
<td>-9.16</td>
<td>2.34</td>
<td>11.5</td>
<td>Zn(OH)$_2$</td>
</tr>
</tbody>
</table>

The bolded rows have positive saturation index (SI) values, implying these are possible precipitates; however, the total Fe concentration is too low (shaded italic in Table 6.4) to get measurable Fe-associated precipitates. Meanwhile, alunite shows a very low positive SI, that is, the precipitation is very little.
6.4.4 Sorption at Mineral/Water Interface and Effect of pH

According to Appelo and Postma (1993), the sorption processes depend on (a) surface area and number of sorption “sites”, (b) relative attraction of aqueous species to sorption sites on mineral/water interfaces, where mineral surfaces can have permanent structural charge and/or variable charge.

The empirical-fitting sorption isotherms, Freundlich and Langmuir, are included in Chapter 2. In PHREEQC (Parkhurst and Appelo 1999), clinoptilolite sorption is considered as ion exchange due to its permanent charged surface, meanwhile, sorption onto Fe, Mn, Al, Ti, Si oxides and hydroxides, carbonates, sulfides are considered as surface complexation. However, the ion exchange and surface complexation were not investigated separately in these two empirical models.

6.4.4.1 Ion Exchange

The ion exchange model involves small cationic species (Ca$^{2+}$, Na$^+$, NH$_4^+$, Al$^{3+}$, etc.). Assuming the exchangers have fixed cation exchange capacity (CEC), PHREEQC designates the exchanged species sorbed onto the exchangeable sites, either by adjusting sorbed concentrations in response to a fixed aqueous composition, or by adjusting both sorbed and aqueous compositions.

Unlike certain well-studied clay minerals, the unit uptake by clinoptilolite varies for different clinoptilolites, as shown in Appendix D, Table D2-D4. The ion selectivity relevant to the Si/Al ratio, also varies, as summarized in Table D5. The zinc uptake capacity for the same clinoptilolite, which could also vary ten-fold, depends on the aqueous solution backgrounds. It is likely that due to the variable conditions, the clinoptilolite components vary over a vast range. So the reported data also vary too much to be consolidated as modeling use. Since, there is no good theoretical data to be used to calculate unit zinc uptake onto clinoptilolite, the experimental data were used for parameter fitting. Tests of single target cation with pH controlled are required to obtain the ion exchange equilibrium constant and kinetic data. The ion exchange calculation approach by PHREEQC is given in Appendix D.2.
The selectivity preference on exchangers, is generally divalents > monovalents (Appendix D, Table D7). Ions with greater ionic radius (and consequently lower hydrated radius) are preferred: hence Ba > Ca, Cs > Na, heavy metals > Ca. The hydrated radius and Gibbs free energy of cations are partly listed in Appendix C, Table C.2

6.4.4.2 Surface Complexation

As mentioned in previous section, surface complexation has been considered as the dominant mechanism on Fe, Mn, Al, Ti, Si oxides and hydroxides, carbonates, sulfides, etc. (Appelo & Postma, 1993). The principle of surface complexation is to fully consider variable charge surfaces as individual charge on sorption sites and total surface charge. Vary as a function of solution composition. Surface charge depends on the sorption/surface binding of potential determining ions, such as $\text{H}^+$, and surface complexes also affect surface charge. Details are given in Appendix D.3.

Surface complexation is the major control onto hydroxides, as mentioned above. Aluminum hydroxides and Iron hydroxides are two major potentially-formed surfaces, in addition to clinoptilolite, occurring as colloids and precipitates with very high surface areas.

The impact of pH on sorption to clinoptilolite is likely insignificant, based on our test results (Figure 6.3a). On the contrary, sorption to iron hydroxide and aluminum hydroxide is highly pH dependent (Figure 6.3b). So the sorption to clinoptilolite was assumed to be independent of pH to minimize the empirical parameters and to give better fit for sorption on hydroxides.
Figure 6.3 pH-dependent sorption of Zn on (a) clinoptilolite and (b) colloid

Overall, as stated above, it is feasible to use the PHREEQC model for the combined surface complexation of zinc onto aluminum hydroxysulfate and ion exchange of Zn\Na on clinoptilolite. However, there is lack of theoretical data of the surface complexation (Zn onto Aluminum hydroxysulfate) and ion exchange (Zn\Na on clinoptilolite), the latter is widely studied, reported data vary dramatically (Appendix D, Table D2-D5).

Our current experimental data are also insufficient to set up a predictive model for the surface complexation part of ARD remediation. As the tests were performed to select optimal conditions, the pHs and the background ions were not controlled at a constant level to isolate multiple factors. More tests with controlled pH and simplified (known) background ions are therefore required in the future to obtain the surface
complexation parameters.

Additional information on mass transfer and pore chemistry are discussed in Appendix D.4. The mass transfer regime in SBC and the temperature fluctuation are discussed in Appendix B.

Overall, the composition of the mine water is calculated with clinoptilolite dealumination and the aluminum hydroxysulfate precipitate formation considered. Additional problems, like possible coating of the clinoptilolite by hydroxide crusts, as well as the kinetics of the formation of hydroxide (considered as occurring simultaneously) are ignored.

### 6.5 Conclusions

- The PHREEQC model is useful in considering the Zn uptake on clinoptilolite and surface uptake, given the initial Zn concentration and pH.
- The model was able to be implemented and applied to the ARD treatment process, considering the sulfate impact on aluminum/iron species distribution.
- Saturated indices of minerals are consistent with observed precipitation.
- Amorphous aluminum hydroxide formation observed in the preliminary experimental tests was confirmed by the model.
- High Zn removal amount is observed for an initial pH 3 with extended time, due to higher dealumination at low initial pH and formation of more aluminum hydroxide at moderate equilibrium pH.
- Zn uptake by clinoptilolite and amorphous aluminum hydroxide are affected by both pH and the amount of amorphous precipitates formation.
- The model is helpful in a qualitative sense, but in order to be fully predictive, further tests to measure certain properties, such as the adsorption capacity and the kinetics of surface complexation of the formed precipitates are necessary, due to the lack of these in the existing database.
Chapter 7 Overall Conclusions and Recommendations

7.1 Uptake Studies

- Natural clinoptilolite was found to be capable of removing heavy metals from solution.
- The rate of metal uptake by natural clinoptilolite was influenced by initial solution pH, initial solution concentration and particle size.
- Zn adsorbed rapidly onto clinoptilolite during the first 25 min in the slurry bubble column for all particle sizes studied, while the pH increased over time during batch tests with fresh sorbent each time. The uptake approached equilibrium in a time of 60 min.
- Zinc uptake on clinoptilolite increased with increasing initial Zn concentration. There was also a slight increase with decreasing particle size. The Langmuir isotherm model fitted the zinc uptake tests well with 0.960~0.980 $R^2$ values. The removal capacities were 0.615 mg/g for the 300-500 μm particles tested.
- Decreasing the particle size distribution of natural clinoptilolite resulted in higher heavy metal removal rates and efficiencies. However, as the contact time increased from 1 h to 2 h (bringing the system closer to equilibrium), there was a decrease in the effect of particle size on adsorption. Thus the impact of particle size should be insignificant providing that there is sufficient agitation time.
- The initial pH significantly affected the adsorption performance. Higher aqueous pH resulted in higher zinc adsorption for the initial range, pH 2 to 5, tested.
- Clinoptilolite proved to be an effective adsorbent for removing Zn from ARD. After 8 adsorption stages in series, the Zn concentration could be decreased from 100 ppm to as low as 0.8 ppm.
• Cation pre-treatment resulted in an increase in the rate and capacity of natural clinoptilolite for heavy metals. Exposure of natural clinoptilolite to NaCl enhanced its ability to remove significant amounts of heavy metals from solution.

7.2 Loaded Clinoptilolite Regeneration Studies

• After zinc is taken up from natural acid rock drainage by clinoptilolite, the loaded clinoptilolite can be regenerated, by removal of the loaded zinc from loaded clinoptilolite to a regenerant. It was possible to regenerate natural zeolite using 20 g NaCl per kg regenerant solution.
• The Langmuir isotherm model gave a fair fit to the experimental results.
• Satisfactory treatment was achieved using 20 g/kg NaCl solution in distilled water, adjusted to a pH of 3.
• Good regeneration was achieved after 1 h agitation in the slurry bubble column, with a regenerant/sorbent ratio of 10 g/g. Tests with the regenerated clinoptilolite revealed promising Zn removal capacity.

7.3 Regeneration Cycles Studies

• The regeneration process was investigated, with various test conditions, including concentrations and the sorbent/regenerant ratio, in order to assist with process optimization.
• Regeneration resulted in a decrease in the adsorption capacity of natural clinoptilolite over cycles. The adsorption capacity of natural zeolite for zinc decreased by approximately 16% over 3 cycles of uptake/regeneration. This may have been caused by the clogging of pores.
• Zinc accumulated in clinoptilolite over cycles, leading to a decrease in uptake performance. However, three continuous desorption-only cycles could rejuvenate the clinoptilolite to a level close to that of the fresh sample, and the following 10 cycles had performance similar to that of the first 10 cycles.
• When tap water was used to prepare regenerant solutions, the performance was
similar to deionized water. It therefore seems that the regeneration test is not very sensitive to the trace amounts of impurities from tap water, given the existence of numerous cations and anions in ARD.

- Tests of reusing the regenerant solutions over cycles were performed to minimize the liquid waste volume.

### 7.4 Dealumination of Clinoptilolite and Its Impact

- The removal of heavy metals from solution was not only due to adsorption and ion exchange by clinoptilolite, but also due to the aluminum hydrolysis during the process.
- There was evidence of zinc removal due to the formation of aluminum hydroxides. So co-precipitation and/or sorption by aluminum hydroxide plays a role in total zinc removal from ARD.
- Excess Al appears in the aqueous phase from clinoptilolite.
- The zinc uptake by Al hydroxide/colloid was analyzed to evaluate the dealumination and the hydrolysis impact on ARD remediation.

### 7.5 Aqueous Species Modeling

- The PHREEQC model is useful in considering the Zn uptake on clinoptilolite and surface uptake, given the initial Zn concentration and pH.
- The model could be implemented and applied to the ARD treatment process, considering the sulfate impact on aluminum/iron species distribution.
- Saturated indices of minerals are consistent with observed precipitation.
- Amorphous aluminum hydroxide formation observed in the preliminary experimental tests was confirmed by the model.
- High Zn removal is observed for an initial pH 3 with extended time, due to higher dealumination at low initial pH and formation of more aluminum hydroxide at moderate equilibrium pH.
- Zn uptakes by clinoptilolite and amorphous aluminum hydroxide are affected by
both pH and the amount of amorphous precipitates formation.

- The model is helpful in a qualitative sense, but in order to be fully predictive, further tests to measure certain properties, such as the adsorption capacity and the kinetics of surface complexation of the formed precipitates are necessary, due to the lack of these in the existing database.

7.6 Recommendations

- Only natural clinoptilolite as received or homogenized by NaCl solution was used in this study; while other pre-treatment methods like thermal pre-treatment, acid and/or chemical pretreatment, microwave pretreatment were not investigated. Those pretreatment methods might increase the capacity and efficiency of natural clinoptilolite in treating ARD according to some previous studies with natural zeolite and surrogate ARD.

- Extra surface characterization and/or sorption capacity information of relevant minerals contained in ARD are needed to achieve better predictions of different ARD performance by the PHREEQC model.

- Further research and studies are needed in this area to fully utilize the natural zeolite technology on a large scale.
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Appendices

Appendix A Clinoptilolite as Sorbent in Acid Drainage Treatment

The ion-exchange performance of natural clinoptilolite depends on several factors, including the framework structure, ion size and shape, concentration charge density of anionic framework, ionic charge and composition of the external electrolyte solution. Meanwhile, the ion size/shape, charge, etc. are greatly affected by the potential complexes formed with certain aqueous anions, as outlined in Appendix D.

As shown in Table A1, the chemical compositions of various clinoptilolites are similar, although the performance varies (Wang and Peng 2010).
Table A1 Chemical composition of Bear River clinoptilolite and other natural clinoptilolites in the world

<table>
<thead>
<tr>
<th>Clinoptilolite</th>
<th>Chemical Composition (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>Bear River (US) clinoptilolite</td>
<td>67.14</td>
<td>12.45</td>
</tr>
<tr>
<td>Canmark Clinoptilolite</td>
<td>66.53</td>
<td>12.30</td>
</tr>
<tr>
<td>Turkey clinoptilolite</td>
<td>70.90</td>
<td>12.40</td>
</tr>
<tr>
<td>Iranian clinoptilolite</td>
<td>70.00</td>
<td>10.46</td>
</tr>
<tr>
<td>Cuban clinoptilolite</td>
<td>62.36</td>
<td>13.14</td>
</tr>
<tr>
<td>Turkish clinoptilolite</td>
<td>69.72</td>
<td>11.74</td>
</tr>
<tr>
<td>Chinese clinoptilolite</td>
<td>65.52</td>
<td>9.89</td>
</tr>
<tr>
<td>Chilean clinoptilolite</td>
<td>67.00</td>
<td>13.00</td>
</tr>
<tr>
<td>Turkish clinoptilolite</td>
<td>69.31</td>
<td>13.11</td>
</tr>
<tr>
<td>Croatian clinoptilolite</td>
<td>64.93</td>
<td>13.39</td>
</tr>
<tr>
<td>Iranian clinoptilolite</td>
<td>66.5</td>
<td>11.81</td>
</tr>
<tr>
<td>Chinese clinoptilolite</td>
<td>68.27</td>
<td>7.48</td>
</tr>
<tr>
<td>Turkish clinoptilolite</td>
<td>70.00</td>
<td>14.00</td>
</tr>
<tr>
<td>Chinese clinoptilolite</td>
<td>69.5</td>
<td>11.05</td>
</tr>
<tr>
<td>Ukrainian clinoptilolite</td>
<td>67.29</td>
<td>12.32</td>
</tr>
<tr>
<td>Slovakian clinoptilolite</td>
<td>67.16</td>
<td>12.30</td>
</tr>
<tr>
<td>Croatian clinoptilolite</td>
<td>55.80</td>
<td>13.32</td>
</tr>
<tr>
<td>Ukraine clinoptilolite</td>
<td>66.7</td>
<td>12.3</td>
</tr>
<tr>
<td>Australian clinoptilolite</td>
<td>68.26</td>
<td>12.99</td>
</tr>
</tbody>
</table>
Figure A1 shows the X-ray diffraction of Canmark clinoptilolite from a preliminary study (Cui et al., 2006); A2 and A3 shows the X-ray diffraction of Bear River clinoptilolite in this study, before zinc uptake and after 10 regeneration cycles, respectively. Acid digestion of the latter sample shows significant Al hydroxides in the amorphous phase, while could not be identified by XRD. Meanwhile, the accumulated NaCl in the clinoptilolite is significant, which was identified as Halite.

![Figure A1 X-ray diffraction pattern of Canmark clinoptilolite in preliminary study (Cui et al. 2006)](image)
Figure A2  X-ray diffraction pattern of Bear River clinoptilolite in this study. The vertical lines are the peaks identified as clinoptilolite-Na.

Figure A3  X-ray diffraction pattern of Bear River clinoptilolite after 10 regeneration cycles. The lines of Halite (NaCl) and of Cristobalite (SiO₂) are marked. The remaining vertical lines are the peak identified as clinoptilolite-Na.
Appendix B Slurry Bubble Column

The behaviour of the gas-liquid-solid systems has been studied for a long time (Shah 1979). These systems can be considered as bubbly flows with the presence of solids, or, as liquid–solid fluidized beds with presence of gas bubbles. (Mena et al. 2005)

The presence of solids affect the gas-liquid mixture in many different ways: bubble formation (Yoo et al. 1997; Luo et al. 1998; Fan et al. 1999), bubble rise (Bly and Worden 1992; Luo et al. 1997; Fan et al. 1999), axial (Gandhi et al. 1999) and radial (Ohkawa et al. 1997) profiles, mixing and dispersion (Smith and Ruether 1985; Matsumoto et al. 1989), mass transfer (Sanchez et al. 2005), voidage and flow regimes (Mena et al. 2005). Despite the extensive research, our knowledge about the possible effects of solids on gas–liquid systems is far from satisfactory. Even less understood are the physical mechanisms underlying the known macroscopic effects.

Hydrodynamic and mass transfer characteristics in SBC strongly depend on the following factors as shown in Table B1: (1) gas/liquid/solid physicochemical properties: gas nature (molecular weight), liquid nature (aqueous, organic, and mixture), liquid physical properties (density, viscosity, surface tension, vapor pressure, foaming characteristics), and solid particle nature (density and size); (2) operating variables: system pressure and temperature (affecting gas density), superficial gas velocity, superficial liquid velocity, and solid concentration; (3) reactor size and geometry: internals, geometry, height/diameter ratio; and (4) gas distributor: type/size and number of orifices (Lemoine et al. 2008).
Table B1 Categories and variables influencing hydrodynamic and mass transfer parameters (Lemoine et al. 2008)

<table>
<thead>
<tr>
<th>Geometrical variables</th>
<th>Operating variables</th>
<th>Physicochemical variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter</td>
<td>Superficial gas velocity</td>
<td>Liquid viscosity</td>
</tr>
<tr>
<td>Column internals</td>
<td>Temperature</td>
<td>Liquid density</td>
</tr>
<tr>
<td>Sparger type and design</td>
<td>Gas partial pressure</td>
<td>Gas density</td>
</tr>
<tr>
<td>Number of orifices</td>
<td>Solid concentration</td>
<td>Liquid surface tension</td>
</tr>
<tr>
<td>Orifice diameter</td>
<td>Liquid concentration</td>
<td>Gas diffusion coefficient in the liquid</td>
</tr>
<tr>
<td>Particle size</td>
<td></td>
<td>Particle density</td>
</tr>
</tbody>
</table>

In bubble column reactors, there are two principal flow regimes: homogeneous and heterogeneous (Figure B1) (Deckwer 1992; Kastanek et al. 1993; Molerus 1993).

The homogeneous regime is produced by plates with small and closely spaced orifices at low gas flow rates. The bubbles generated at the plate are small, almost spherical and monodisperse, and rise roughly vertically with small vertical and horizontal fluctuations. Coalescence and break-up are negligible and no large-scale liquid circulation occurs in the bed. The long-time radial profiles of voidage and liquid velocity are flat. The heterogeneous regime is produced either by plates with small and closely spaced orifices at high gas flow rates, or by distributor plates with large orifices at any gas flow rate (pure heterogeneous regime). This regime is characterized by a wide bubble size distribution, due to generation of large and highly non-uniform bubbles. Bubble coalescence is promoted and macro-scale circulation of
the liquid phase are present. The long-time radial profiles are roughly parabolic with a maximum at the centre. (Mena et al. 2005)

The major batch uptake tests were performed with 2.0 kg ARD and 200 g 600-850 μm clinoptilolite. The air flow to mobilize the liquid–solid slurry was metered by a rotameter (Figure 2.1). The static bed depth was 335 mm. All experiments were carried out at 15±2 °C and at three superficial air velocities, 0.08, 0.11 and 0.23 m/s. At all three velocities tested, all of the particles were in suspension and the voidage difference was not significant, which suggests transitional or heterogeneous regime (HeR) for the lower and higher velocities, as depicted in Figure B2.

![Figure B2](image)

Figure B2 Typical graph of (voidage $e$)–(gas flow rate $q$) dependence $e=e(q)$. Homogeneous regime loses stability in inflection point where regime transition begins. (Mena et al. 2005)

As listed in Chapter 2, Table 2.1, the solid content varied from 1.3% ~ 20.4% as the clinoptilolite amount varied between 50g~800g. As seen in figure B3, when the solid content was low, the voidage increase with it; when the solid content was high, voidage decreases with it. When the gas flow rate was high, the voidage changed insignificantly with increasing gas flow rate. Mena et al. (2005) also reported the impact of solid content on voidage and mean bubble speed (Figure B4).
Figure B3 voidage $e$ vs. gas flow rate $q$

(a) low solid content $c$ increases voidage. $c=0$ vol% (water) (■), 1 vol% (♦), 3 vol% (▲), 5 vol% (■) and (b) higher solid content $c$ decreases voidage. 5 vol% (■), 10 vol% (♦), 15 vol% (▲), 20 vol% (♦), 25 vol% (*) and 30 vol% (-).  
(Mena et al. 2005)

Figure B4 effect of solid content $c$ on (a) voidage $e$ and (b) mean bubble speed $u$.
(Mena et al. 2005)

Both preliminary tests (Figure B5) by Cui et al. (2006) and our work (Figure B6) show minimal zinc uptake for the three superficial air velocities investigated: 0.08, 0.11 and 0.23 m/s. This implies that 0.08 m/s is sufficient to achieve sufficient mass transfer, and this value was therefore applied through the rest of the project.
Figure B5 Zn adsorption at different times and superficial gas velocities in preliminary tests (Cui et al., 2006)

Figure B6 Zn adsorption at different times and superficial gas velocities

This test is with original unspiked ARD, i.e. with an initial Zinc concentration of ~15 ppm
Various temperatures (7, 16, 25°C) were also tested in the early stage of this study to check the impact of temperature fluctuations. As shown in Figure B7, the three temperatures tested shows minor differences, so the small temperature fluctuations encountered in this study were neglected.

Figure B7 Zn adsorption at different times and temperatures

This test is carried out with original unspiked ARD, i.e. an initial Zinc concentration of about 15 ppm
Appendix C Aqueous Species in Acid Rock Drainage

C.1 The pH Impact on Aqueous Metal Concentration

When mixed with ARD, clinoptilolite increases the aqueous pH from 2.6~3.0 to 4.8~8.1 depending on the solid/liquid ratio. The aqueous metal concentration changes determined in this study involve both solid uptake and potential precipitation.

To verify the pH impact on aqueous metal concentration, 1M NaOH was used to titrate the ARD to a certain pH. As shown in Table C1, Fe and Al almost all precipitated when the pH increased to 6, while Mn still existed in the aqueous phases.

Table C1 Aqueous metal concentrations (ppm) in ARD with pH titrated to designated level

<table>
<thead>
<tr>
<th>pH</th>
<th>2.8</th>
<th>6</th>
<th>6.5</th>
<th>7</th>
<th>7.5</th>
<th>8</th>
<th>8.5</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>5.09</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Al</td>
<td>23.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Mn</td>
<td>8.51</td>
<td>8.03</td>
<td>8.03</td>
<td>7.94</td>
<td>7.22</td>
<td>7.13</td>
<td>5.84</td>
<td></td>
</tr>
</tbody>
</table>

C.2 Cation Sizes

Hydrated radius and free energy of hydration are considered to be relevant with respect to the metal selectivity. The radius and hydration energies of Cu, H, Pb and Zn are summarized in Table C2 (Asthagiri et al. 2004)

Table C2 Radius and hydration energies of cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Hydrated radius (Å)</th>
<th>Unhydrated radius (Å)</th>
<th>Free Energy of hydration (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>4.19</td>
<td>0.73</td>
<td>-2021.9</td>
</tr>
<tr>
<td>H$^+$</td>
<td>2.80</td>
<td>1.15</td>
<td>-1063.0</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>4.01</td>
<td>1.32</td>
<td>-1435.6</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>4.30</td>
<td>0.74</td>
<td>-1969.2</td>
</tr>
</tbody>
</table>
Appendix D Cation Uptake by Zeolite or Hydroxides

According to Appelo and Postma (1993), the sorption processes depend on (a) surface area and number of sorption “sites”, (b) relative attraction of aqueous species to sorption sites on mineral/water interfaces, where mineral surfaces can have permanent structural charge and/or variable charge.

D.1 Sorption Isotherm

The widely used Langmuir adsorption model:

\[ q = \frac{bK_c}{1 + K_c} \]

provides better fits than linear interpolation/fits, here b and K_c are adjustable parameters.

The assumptions of this model are (a) a fixed number of sorption sites of equal affinity (b) Speciation distribution, pH, competing ions, redox states are all neglected.

The Freundlich adsorption model also provides good fits helped by having two f 2 adjustable parameters, compared with on in the linear model. In this case,

\[ q = Ac^\beta \]

where A and \( \beta \) are adjustable parameters usually with 0 < \( \beta \) < 1.

This assumes a log-normal distribution of Langmuir K parameters (i.e. affinities), as in the Langmuir model, species distribution, pH, competing ions, redox states are ignored.

Besides the above-mentioned empirical-fitting sorption isotherm models, thermodynamic speciation based sorption models are mainly of two type, both included in this study: (a) ion exchange, where sorption occurs on permanent charge surfaces, like smectites, zeolites, etc., and (b) surface complexation, which occurs on Fe, Mn, Al, Ti, Si oxides and hydroxides, carbonates, sulfides, etc.
D.2 Ion Exchange

The ion exchange model involves small cationic species (Ca$^{2+}$, Na$^+$, NH$_4^+$, Al$^{3+}$, etc.). Assuming the exchangers have fixed cation exchange capacity (CEC), PHREEQC designates the exchanged species sorbed onto the exchangeable sites, either by adjusting sorbed concentrations in response to a fixed aqueous composition, or by adjusting both sorbed and aqueous compositions. Three keywords are used in PHREEQC to define the exchange processes: EXCHANGE_MASTER_SPECIES (component data), EXCHANGE_SPECIES (species thermodynamic data) and EXCHANGE; the first two of these are usually found in phreeqc.dat and wateq4f.dat (from Appelo's User Guide) but can be modified in user-created input files. The last is user-specified to define the amount and composition of an “exchanger” phase. “SAVE” and “USE” keywords can be applied to indicate “EXCHANGE” phase compositions.

The amount of exchanger (e.g. moles of X) was calculated from CEC (cation exchange capacity, usually expressed in meq/100g of soil):

$$X^- = \frac{CEC}{(100/\text{sw})(\theta/(1-\theta))} = \frac{CEC}{100(\theta/\rho_B)}$$

where sw is the specific dry weight of soil (kg/L of soil), q is the porosity and $\rho_B$ is the bulk density of the soil in kg/L.

The ARD composition is provided in Chapter 2, Table 2.2. The measured ARD solution is entered in PHREEQC. Solution pe was then calculated for equilibrium with atmospheric O$_2$, as compressed air was used for agitation of the SBC during the contacting time. Sulfate is used to charge balance the solution. Next “Save” the resulting solution composition as solution 1.

In a new simulation, find the composition of an exchanger clinoptilolite-Na that would be at equilibrium with solution 1 (fixed composition).

The amount and direction of exchange depend on the ratio of ions in solution (and other solution properties) and the characteristics of the exchanger, as described by Appelo & Postma (1993).
The selectivity preference on exchangers, is generally divalents > monovalents (Appendix D, Table D7). Ions with greater ionic radius (and consequently lower hydrated radius) are preferred: hence Ba > Ca, Cs > Na, heavy metals > Ca. The hydrated radius and Gibbs free energy of cations are partly listed in Appendix C, Table C.2

Unlike certain well-studied clay minerals, the unit uptake by clinoptilolite are widely studied (Table D1), but varies for different clinoptilolites, as shown in D2-D4. The ion selectivity relevant to the Si/Al ratio, also varies, as summarized in Table D5. The zinc uptake capacity for the same clinoptilolite, could also vary ten-fold depends on the aqueous solution backgrounds. Since, there is no good theoretical data to be used to calculate unit zinc uptake onto clinoptilolite, the experimental data were used for parameter fitting.

Table D1 Environmental applications of natural zeolites

<table>
<thead>
<tr>
<th>Wastewater treatment</th>
<th>References</th>
</tr>
</thead>
</table>

Wang and Peng (2010) reviewed various clinoptilolites used as sorbents, and summarized the CEC and ammonium adsorption capacity of these clinoptilolites from...
various sources. As seen in Table D2, these clinoptilolite differ significantly, despite their similar chemical components (Table A1). The single cation uptake performance also varies (Table D3).

Table D2 CEC and sorption capacity of several natural clinoptilolites in the world (Wang and Peng 2010)

<table>
<thead>
<tr>
<th>Source</th>
<th>Ammonium adsorption capacity (mg/g)</th>
<th>CEC (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turkey clinoptilolite</td>
<td>5.2-8.1</td>
<td>1.6–1.8</td>
</tr>
<tr>
<td>Turkey clinoptilolite</td>
<td>5.7-7.7</td>
<td>1.84</td>
</tr>
<tr>
<td>Chinese clinoptilolite</td>
<td>2.7-3.2</td>
<td>1.03</td>
</tr>
<tr>
<td>Chilean clinoptilolite</td>
<td>11.4-14.8</td>
<td>2.05</td>
</tr>
<tr>
<td>Croatia clinoptilolite</td>
<td>7.7-17.6</td>
<td>1.45</td>
</tr>
<tr>
<td>Iranian clinoptilolite</td>
<td>17.8</td>
<td>1.20</td>
</tr>
<tr>
<td>Ukraine clinoptilolite</td>
<td>6.6-21.5</td>
<td>0.64</td>
</tr>
</tbody>
</table>
Table D3 Single cation uptake capacity of clinoptilolite
(Wang and Peng 2010)

<table>
<thead>
<tr>
<th>Material</th>
<th>Metal</th>
<th>Adsorption (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sardinian clinoptilolite</td>
<td>Cu²⁺</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Cd²⁺</td>
<td>0.05–0.19</td>
</tr>
<tr>
<td></td>
<td>Pb²⁺</td>
<td>0.27–1.2</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>0.1</td>
</tr>
<tr>
<td>Turkish clinoptilolite</td>
<td>Pb²⁺</td>
<td>0.299–0.730</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>0.108–0.251</td>
</tr>
<tr>
<td></td>
<td>Cu²⁺</td>
<td>0.022–0.227</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺</td>
<td>0.017–0.173</td>
</tr>
<tr>
<td>Greek clinoptilolite</td>
<td>Cr³⁺</td>
<td>0.237</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>0.106</td>
</tr>
<tr>
<td></td>
<td>Cu²⁺</td>
<td>0.186</td>
</tr>
<tr>
<td></td>
<td>Cd²⁺</td>
<td>0.082</td>
</tr>
<tr>
<td>Mexican clinoptilolite</td>
<td>Pb²⁺</td>
<td>1.4</td>
</tr>
<tr>
<td>Ukraine clinoptilolite</td>
<td>Pb²⁺</td>
<td>0.134</td>
</tr>
<tr>
<td></td>
<td>Cu²⁺</td>
<td>0.405</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺</td>
<td>0.222</td>
</tr>
<tr>
<td></td>
<td>Cd²⁺</td>
<td>0.0375</td>
</tr>
<tr>
<td>Turkish clinoptilolite</td>
<td>Co²⁺</td>
<td>0.448</td>
</tr>
<tr>
<td></td>
<td>Cu²⁺</td>
<td>0.282</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>0.268</td>
</tr>
<tr>
<td></td>
<td>Mn²⁺</td>
<td>0.153</td>
</tr>
</tbody>
</table>
Table D4 Kinetics of single cation uptake by clinoptilolite
(Wang and Peng 2010)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Metal ion</th>
<th>Reaction order</th>
<th>First-order rate constant (min⁻¹)</th>
<th>Second-order rate constant (g/mg h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinoptilolite</td>
<td>Cd²⁺</td>
<td>First-order</td>
<td>0.0137</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pb²⁺</td>
<td>First-order</td>
<td>0.0532</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺</td>
<td>First-order</td>
<td>0.0158</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cu²⁺</td>
<td>First-order</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>First-order</td>
<td>0.021</td>
<td>-</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Pb²⁺</td>
<td>First-order</td>
<td>2.9 e⁻⁴</td>
<td>-</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Pb²⁺</td>
<td>First-order</td>
<td>0.0053</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺</td>
<td>First-order</td>
<td>0.1419</td>
<td>-</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Pb²⁺</td>
<td>First-order</td>
<td>3.5 e⁻⁴</td>
<td>-</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Cu²⁺</td>
<td>Second-order</td>
<td>0.00113</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cd²⁺</td>
<td>Second-order</td>
<td>0.0226</td>
<td>-</td>
</tr>
</tbody>
</table>

The ion exchange selectivity appears to be related to the Si/Al ratio of the sorbent mineral and the mineral structures (Table D5 and D6).

The order of aluminum hydroxide selectivity was:
phosphate ≫ sulfate > carbonate > nitrate > chloride.  (Georgantas, 2007)
Table D5 Ion exchange selectivity of heavy metal ions (zeolites with various Si/Al ratios)
(Wang and Peng 2010)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Selectivity</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinoptilolite</td>
<td>Pb$^{2+}$ &gt; Ag$^{+}$ &gt; Cd$^{2+}$ &gt; Zn$^{2+}$ &gt; Cu$^{2+}$</td>
<td>2.7-5.3</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Pb$^{2+}$ &gt; Zn$^{2+}$ &gt; Cu$^{2+}$ &gt; Ni$^{2+}$</td>
<td>4.9</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Pb$^{2+}$ &gt; Cd$^{2+}$ &gt; Zn$^{2+}$ &gt; Cu$^{2+}$</td>
<td>4.2</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Pb$^{2+}$ &gt; Cd$^{2+}$ &gt; Cu$^{2+}$ &gt; Co$^{2+}$ &gt; Cr$^{3+}$ &gt; Zn$^{2+}$ &gt; Ni$^{2+}$ &gt; Hg$^{2+}$</td>
<td>-</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Mn$^{2+}$ &gt; Cu$^{2+}$ &gt; Co$^{2+}$ &gt; Zn$^{2+}$ &gt; Ni$^{2+}$</td>
<td>4.4-5.5</td>
</tr>
<tr>
<td>Scolecite</td>
<td>Cu$^{2+}$ &gt; Zn$^{2+}$ &gt; Pb$^{2+}$ &gt; Ni$^{2+}$ &gt; Co$^{2+}$ &gt; Cd$^{2+}$</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Table D6 Relative binding strength of metals on different sorbents for clay minerals, zeolites and hydroxides
(Bunzl et al. 1976)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative binding strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay minerals, zeolites</td>
<td>Cu&gt;Pb&gt;Ni&gt;Zn&gt;Hg&gt;Cd</td>
</tr>
<tr>
<td>Fe, Mn-oxides and -hydroxides</td>
<td>Pb&gt;Cr=Cu&gt;Zn&gt;Na&gt;Cd&gt;Co&gt;Mn</td>
</tr>
<tr>
<td>Organic matters (in general)</td>
<td>Pb&gt;Cu&gt;Na&gt;Cd&gt;Co&gt;Zn&gt;Fe&gt;Mn</td>
</tr>
<tr>
<td>Humic- and Fulvic acids</td>
<td>Pb&gt;Cu=Zn=Fe</td>
</tr>
<tr>
<td>Peat</td>
<td>Cu&gt;Pb&gt;Na&gt; Cd</td>
</tr>
<tr>
<td>Degraded peat</td>
<td>Cu&gt;Cd&gt;Zn&gt;Pb&gt; Mn</td>
</tr>
</tbody>
</table>

Table D7 Values for exchange coefficients with respect to Na$^+$ (Gaines-Thomas convention, equivalent fractions are used for exchangeable cations).
(Bruggenwert and Kamphorst, 1982; Appelo & Postma, 1993)

Equation: \[ \text{Na}^+ + 1/i \text{I}_t \rightarrow \text{Na} - \text{X} + 1/i \text{I}^+ \] with \[ K_{\text{Na}^+} = \frac{[\text{Na}-\text{X}][\text{I}^+]^{1/i}}{[1-xi]^{1/i}[\text{Na}^+]} \]

<table>
<thead>
<tr>
<th>Ion I$^+$</th>
<th>$K_{\text{Na}^+}$</th>
<th>Ion I$^{2+}$</th>
<th>$K_{\text{Na}^+}$</th>
<th>Ion I$^{3+}$</th>
<th>$K_{\text{Na}^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>1.2 (0.95-1.2)</td>
<td>Mg$^{2+}$</td>
<td>0.5 (0.4-0.6)</td>
<td>Al$^{3+}$</td>
<td>0.6 (0.5-0.9)</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.2 (0.15-0.25)</td>
<td>Ca$^{2+}$</td>
<td>0.4 (0.3-0.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.25 (0.2-0.3)</td>
<td>Sr$^{2+}$</td>
<td>0.35 (0.3-0.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>0.10</td>
<td>Ba$^{2+}$</td>
<td>0.35 (0.2-0.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>0.08</td>
<td>Mn$^{2+}$</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td></td>
<td>Ni$^{2+}$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td></td>
<td>Cu$^{2+}$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.4 (0.3-0.6)</td>
<td>Cd$^{2+}$</td>
<td>0.4 (0.3-0.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Langmuir and Freundlich isotherm models were fitted with the zinc uptake experimental data (Chapter 2, Table 2.4). These data were collected from batch tests with initial pH 3 and various initial zinc concentrations where no significant colloid formation was observed (i.e. the most of zinc uptake resulted from sorption onto clinoptilolite).

D.3 Surface Complexation

As mentioned above, surface complexation has been considered as the dominant mechanism on Fe, Mn, Al, Ti, Si oxides and hydroxides, carbonates, sulfides, etc. (Appelo & Postma, 1993) The principle of surface complexation is to fully consider variable charge surfaces as individual charge on sorption sites and total surface charge vary as a function of solution composition. Surface charge depends on the sorption/surface binding of potential determining ions, such as $\text{H}^+$, and surface complexes also affect surface charge.

The aluminum/ferrous hydroxide surfaces have silanol $\text{Si-OH}$ and/or aluminol $\text{Al-OH}$ groups, where in acid solutions, surface protonation occurs ($\text{Si-OH}_2^-$ and $\text{Al-OH}_2^-$), and in basic solutions, deprotonation occurs ($\text{Si-O}^-$ and $\text{Al-O}^-$) (Sposito, 1984). Hence the surface complexation is significantly affected by pH, and pH "edges" are formed for cation sorption, with increasing cation surface complexation at higher pH.
According to Sposito (1984), sorption of Pb onto iron hydroxide results in an inner-sphere complex, which is less affected by aqueous anion concentration, while sorption of Ba onto iron hydroxide results in an outer-sphere complex, less uptake with higher aqueous anion concentration. However, the surface complex mechanism of zinc onto aluminum hydroxide is unclear in previous studies, so the sorption capacity is estimated based on experimental data.

Accounting for the electrostatic work required to transport species through the “diffuse layer” (similar to an activity coefficient correction), Gouy-Chapman double-layer theory is applied in PHREEQC. A charged surface attracts a diffuse cloud of ions, preferentially enriched in counter-ions. The cation/anion imbalance in the cloud gradually decreases away from the surface. The distribution of charge near a surface seeks to minimize energy (charge separation) and maximize entropy. The double-layer model assumes a surface layer of charge and uniform potential \( \Phi \) throughout the layer and a “diffuse” layer with exponentially decreasing potential away from the surface layer.

The charge density of the surface layer is determined by the sum of protonated and deprotonated sites and sorbed charged complexes:

\[
\sigma = \frac{F}{AS} \sum m_s \nu_s
\]

where \( F \) is the Faraday constant (96,490 C/mol), \( A \) is the specific surface area (m\(^2\)/g), \( S \) is the solid concentration (g/L), whereas \( m_s \) and \( \nu_s \) are the molar concentrations and charges of surface species.

According to Gouy-Chapman theory, for a symmetrical electrolyte:

\[
\sigma = \left(8000RT \varepsilon \varepsilon_0 m\right)^{1/2} \sinh \left(\frac{ZF\Phi}{2RT}\right)
\]

where \( R \) is the gas const. (8.314 J/mol/K), \( T \) is absolute temperature (K), \( m \) is molar...
concentration, \( e \) is the dielectric constant of water (78.5 at 25 Celsius), \( e_0 \) is the permittivity of free space (8.854x10-12 C/V/m), \( Z \) is the valence.

Surface complexation equations are as follows:

1st deprotonation reaction:
\[
\text{SOH}^+ + \text{H}^+ \rightleftharpoons \text{SOH}^0
\]
\[
K_{a1}^{\text{app}} = \frac{[\text{SOH}^0]}{[\text{SOH}^+]} \left( \frac{[\text{H}^+]}{[\text{H}^+] + [\text{H}_2\text{O}]} \right)
\]

2nd deprotonation reaction:
\[
\text{SOH}^0 \rightleftharpoons \text{SO}^- + \text{H}^+ 
\]
\[
K_{a2}^{\text{app}} = \frac{[\text{SO}^-]}{[\text{SOH}^0]} \left( \frac{[\text{H}^+]}{[\text{H}^+] + [\text{H}_2\text{O}]} \right)
\]

divalent cation complexation:
\[
\text{SOH}^0 + M^{2+} \rightleftharpoons \text{SOM}^+ + \text{H}^+ 
\]
\[
K_{M}^{\text{app}} = \frac{[\text{SOM}^+]}{[\text{SOH}^0]} \left( \frac{[\text{H}^+]}{[\text{H}^+] + [\text{H}_2\text{O}]} \right)
\]

For all surface reactions:
\[
\Delta G_{\text{total}} = \Delta G_{\text{intrinsic}} + \Delta G_{\text{coulombic}} = \Delta G_{\text{intrinsic}} + \Delta ZF\Psi
\]
\[
K_{\text{app}} = K_{\text{int}} \exp \left( \frac{-\Delta ZF\Psi}{RT} \right)
\]

where \( DZ \) is the net change in the charge number of the surface species.
Three keywords were used in PHREEQC to define the processes: SURFACE_MASTER_SPECIES, SURFACE_SPECIES and SURFACE. The first two are found in phreeqc.dat and wateq4f.dat (for hydrous ferrous oxide, HFO, with both weak and strong sorption sites; data from Dzombak & Morel, 1990), and the last is user-specified to define amount and composition of a “surface” phase.

Surface complexation is the major control onto hydroxides, as mentioned above. Aluminum hydroxides and Iron hydroxides are two major potentially-formed surfaces, in addition to clinoptilolite, occurring as colloids and precipitates with very high surface areas.
D.4 Mass Transfer and Pore Chemistry

SBC filled with clinoptilolite was modeled as equilibrated with the 20 g/kg NaCl solution. Then acid mine drainage of a certain composition was added. NaCl was considered as not being rate-limiting in this study given the vigorous agitation, while ion exchange and surface complexation are surface-reaction controlled, and likely rate-limits in this study. (Christoffersen et al., 1978)

The distribution of the (pore) concentrations within the SBC column was calculated (by inverse model with double diffusive layer theory), taking into account the cation exchange and/or surface complexation. Selectivity coefficients are taken from the exemplary data of the WATEQ4F.dat data set.

The determination of the process where the reaction happens (clinoptilolite surfaces, pore/channel and colloid surfaces) is an important aspect.

The basic idea is to reconstruct the physical/chemical evolution of the solution from its chemical composition, to figure which formation the solution may have passed through after its remediation to change its chemical composition as the result of reactions with mineral and gas phases (dissolution, precipitation, degassing) in a way that accounts for the composition of the water from the SBC.

The key term in PHREEQC is "Inverse Modeling". The primary solutions (ARD) and the final product (treated ARD) have to be defined as SOLUTION, as well as the mineral (clinoptilolite, etc.) and gas phases as PHASES.

For modeling purposes, the process involved in this water treatment approach is modeled as conducting these acid waters through clinoptilolite surfaces and pores. This process causes an increase in pH. Furthermore it can result in super-saturation of other minerals which can precipitate spontaneously. The high sulfate concentrations combined with increasing aqueous cations from the ion-exchange and aluminosilicate dissolution may exceed certain mineral solubility products. Iron minerals are also supersaturated as a result of these reactions (if initial iron is abundant), and consequently amorphous hydroxide precipitates spontaneously.

At the beginning of the modeling, the zeolite pores are considered to be filled
with NaCl solution (as a result of regeneration) or just air and pore water (as air-dry minerals). Then, the acid mine water is added and compressed air is sparged. The composition of the mine water is calculated, alumino-silicate dissolution and precipitate formation are considered. Additional problems, like possible coating of the clinoptilolite by hydroxide crusts, as well as the kinetics of the formation of hydroxide (considered as simultaneously) are ignored. The mass transfer regime in SBC and the temperature fluctuation are discussed in Appendix B.
Appendix E Experimental Equipment, Instrumentation and Methodology

Methods and materials are described in this appendix, including the test conditions and configuration.

Natural ARD from Highway 97C (Chapter 1, Figure 1.2) was collected in 20 L and 25 L bottles and sealed. Approximately 35 ARD sample bottles were collected from the field in both July 2005 (designated as A) and 2008 (labelled B). The metal comparison of samples A and B are compared in Table E4. The difference between the two batch samples is small, reflecting the similar collecting season and lack of change over a 3-year period. Reddish brown iron precipitates were observed in the field; this removal of iron resulted in low Fe concentration in the ARD samples collected. Changes of sample composition during storage were negligible (shown in the last two columns of Table E4). It is considered that the microbial activity was low due to the lack of Fe and Cu, especially Fe, in these samples.

The major chemical compositions of the ARD are listed in Table 2.2. This ARD was used to as background solution to determine the effectiveness of clinoptilolite in a slurry bubble column. The zinc concentrations were varied by adding zinc chloride to simulate the seasonal zinc fluctuation in actual ARD from Highway 97C. The initial pH was adjusted with HCl or NaOH to achieve designated values. pH was measured by a pH-meter with a glass pH electrode before and after the experiment; the pH-meter was calibrated with buffer solutions of pH 3.0, 7.0, 10.0.

Sodium chloride (NaCl) solution was used as regenerant; regenerant concentrations tested were 10, 20, 30 and 40 g/kg, prepared from solids and used in desorption and regeneration tests.

Standard solutions for metal analysis using the atomic absorption spectrometer (AAS) and ICP-AES were prepared from standard metal solutions from Fischer Scientific. AAS was used for most of the batch test solutions when only the Zn
concentration was determined. ICP was used to determine multiple metal concentrations. Differences between the Zn concentrations from the two analytical methods were small (between 3 and 8% for the same sample).

Natural clinoptilolite from Bear River Zeolite (USA) was used in this study. The samples were used as received with no chemical modifications, except where specified. The chemical compositions of the clinoptilolite are listed in Table 2.1.

Mineralogical analysis of the clinoptilolite samples before and after tests were carried out using X-Ray Diffraction (XRD). (Appendix A)

Appendix A also shows the properties of other clinoptilolites in the literature, and Appendix D shows the cation uptake performance of some these clinoptilolites.

A schematic of the three-phase slurry bubble column used in this work to treat ARD from the Highway construction is shown in Figure 2.1. The reactor consists of a Perspex (acrylic) column of height 1.4 m and internal diameter 90 mm. The distributor plate has 57 evenly spaced holes of 6 mm diameter with a 38 mm mesh screen below to prevent particles from falling through the orifices. The plenum chamber of internal diameter 90 mm below the distributor was filled with plastic spheres of diameter 9 mm to provide a uniform flow of gas to the distributor plate. The air flow is adjustable through a Float Style flow meter as specified in each test. More discussion of the SBC is provided in Appendix B.

Sorption of zinc was investigated in preliminary batch experiments in the slurry bubble column (Figure 2.1).

Batch uptake tests were conducted with different amounts of clinoptilolite contacted with natural ARD containing prescribed concentrations of zinc. If necessary, the initial pH was adjusted by adding 0.1 N HCl or NaOH. Then the mixture was agitated in a slurry bubble column by air bubbles for 1 hour to approach equilibrium (2 h tests were performed to justify the time necessary to achieve equilibrium, showing 2-5% difference with an additional hour).

Based on the results of preliminary work (Cui et al., 2006), contact time, temperature, agitating air velocity, initial solution pH, solid-to-liquid ratio, and initial metal cation concentration may affect metal adsorption of zeolites.
The regeneration of used sorbent by NaCl solution is further explored, extending previous work (Lai 2005; Li 2005; Li et al. 2005; Cui et al. 2006). This was followed by the uptake/regeneration cycles with various conditions.

The test condition combinations are summarized in Tables E1, E2 and E3 for zinc uptake, removal and regeneration cycles, respectively. Test details are described in corresponding chapters (Chapters 2, 3 and 4) of the thesis.

The original test configurations were also set based on the following hypotheses:

1. The total amount of zinc in the system, i.e. in the aqueous phase and solid phase, during operation remained constant. This was later confirmed by the mass balance verification.

2. Based on previous studies (Inglezakis et al. 2001; Lai 2005; Li et al. 2008), clinoptilolite is considered to be long-term stable in ARD with pH 3 or higher, i.e. there is negligible leaching of structural Al or Si.

3. Zinc adsorption is likely related to the BET surface area of the sorbent, and likely to be most favorable on sorbents with high BET surface areas such as synthetic zeolites. The most significant ambient property observed in the literature is the pH of the aqueous phase (Peric et al. 2004; Athanasiadis and Helmreich 2005; Oren and Kaya 2006; Chang et al. 2007).

4. For the aqueous species, the sorption occurring on suspended particles finer than 54 µm (typical filter cut-off size for AAS samples) is neglected, although those suspended particles might flocculate/precipitate later.

5. For simplicity in the current tests, breakage of zeolite particles during agitation is not considered, since it has not been significantly observed during previous work.

Some of these hypotheses are updated in later chapters based on the test results, as discussed in those chapters.

Metal and metalloid concentrations in the samples collected from the different experiments were determined by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) or TS 220 Atomic Absorption Spectrometry (AAS) or ICP-AES. The stock solutions of the metal ions for standards preparation were prepared from
corresponding chloride salts in deionised water. Duplicates or triplicates were analyzed in the tests for quality control purpose. The error ranges in reanalysis error, repeatability and reproducibility are specified in Table 4.1.

Samples were prepared for analysis by adding 0.5 % (v/v) HNO₃ to ensure that any precipitate is dissolved. The AAS is generally used to analyze relatively low metal concentrations, using standard solutions of the respective metals in the range 0.1 – 5 mg/kg. Deionised water was used for all dilution purposes.

Zeolite uptake efficiency was calculated from the equation:

\[
Uptake,(mg \, g) = \frac{m_{ARD}(C_0 - C_t)}{m_{clinoptilolite}}
\]

(Eq. E1)

where \(C_0\) is initial contaminant concentration (mg/kg), and \(C_t\) is contaminant concentration at time \(t\) (mg/kg). Uptake is the adsorbed quantity of metal ion per gram clinoptilolite (mg/g); \(m_{ARD}\) is the mass of metal solution (kg), and \(m_{clinoptilolite}\) is the dry weight of clinoptilolite (g). The desorption was determined in a similar manner.
<table>
<thead>
<tr>
<th>No.</th>
<th>Subprocess</th>
<th>Required Functionality</th>
<th>Test Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1a</td>
<td>Adsorption</td>
<td>Kinetics test; Batch operation time effect</td>
<td>Batch test with time of 5, 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>2.1b</td>
<td>Adsorption</td>
<td>Isotherm test</td>
<td>Equilibrium (120mins) with initial spiked Zinc concentration of 200ppm, 100ppm, 50ppm, 20ppm, 10ppm</td>
</tr>
<tr>
<td>2.2</td>
<td>Adsorption</td>
<td>Particle size effect</td>
<td>Batch test with particle size of 300-500 μm, 500-600 μm, 600-850 μm, 850-1400 μm</td>
</tr>
<tr>
<td>2.3</td>
<td>Adsorption</td>
<td>Solid/liquid ratio effect</td>
<td>Batch test with clinoptilolite amount 50 g, 200 g, 400 g, 600 g, 800 g</td>
</tr>
<tr>
<td>2.4</td>
<td>Adsorption</td>
<td>pH effect</td>
<td>Batch test with pH adjusted to 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>2.5</td>
<td>Adsorption</td>
<td>Temperature effect</td>
<td>Batch test with temperature at 10℃, 16℃, 20℃</td>
</tr>
<tr>
<td>2.6</td>
<td>Adsorption</td>
<td>Gas superficial velocity</td>
<td>0.08 m/s, 0.11 m/s and 0.23 m/s</td>
</tr>
</tbody>
</table>
Table E2 Zinc removal from loaded clinoptilolite to NaCl regenerant batch test condition summary

<table>
<thead>
<tr>
<th>No.</th>
<th>Sub process</th>
<th>Required Functionality</th>
<th>Test Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Desorption</td>
<td>Kinetics test; Batch operation time effect</td>
<td>Kinetics: time of 5, 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>3.2</td>
<td>Desorption</td>
<td>Particle size effect Batch test with particle size of 300-500 μm, 500-600 μm, 600-850 μm, 850-1400 μm</td>
<td>Kinetics: time of 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>3.3</td>
<td>Desorption</td>
<td>Solid/liquid ratio effect Batch test with contaminated clinoptilolite amount 800 g, 400 g, 200 g</td>
<td>Kinetics: time of 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>3.4</td>
<td>Desorption</td>
<td>pH effect Batch test with pH adjusted to 2, 3, 4, 5, 6</td>
<td>Kinetics: time of 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>3.5</td>
<td>Desorption</td>
<td>NaCl concentration Batch test with NaCl concentration 10, 20, 30, 40 g/kg</td>
<td>Kinetics: time of 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>3.6</td>
<td>Desorption</td>
<td>Temperature effect Batch test with temperature at 10°C, 16°C, 20°C</td>
<td>Kinetics: time of 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
<tr>
<td>3.7</td>
<td>Desorption</td>
<td>Gas superficial velocity 0.08 m/s, 0.11 m/s and 0.23 m/s</td>
<td>Kinetics: time of 10, 20, 40, 60, 120, 180 minutes</td>
</tr>
</tbody>
</table>
Table E3 Zinc uptake/removal cycles (regeneration cycles) batch test condition summary

<table>
<thead>
<tr>
<th>No.</th>
<th>Sub process</th>
<th>Required Functionality</th>
<th>Test Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Regeneration cycles</td>
<td>Feasibility test</td>
<td>Batch test with clinoptilolite regeneration check</td>
</tr>
<tr>
<td>4.2</td>
<td>Regeneration cycles</td>
<td>Desorption time effect</td>
<td>Regeneration for 1h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Regeneration for 2h</td>
</tr>
<tr>
<td>4.3</td>
<td>Regeneration cycles</td>
<td>Tap water vs. deionized water</td>
<td>Batch test with clinoptilolite regeneration check</td>
</tr>
<tr>
<td>4.4</td>
<td>Regeneration cycles</td>
<td>Rejuvenation by continuous desorption</td>
<td>Batch test with clinoptilolite regeneration check</td>
</tr>
<tr>
<td>Metal</td>
<td>Concentration (ppm)</td>
<td>Concentration (ppm)</td>
<td>Concentration (ppm)</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td></td>
<td>Sample A obtained</td>
<td>Sample B obtained</td>
<td>Sample B obtained</td>
</tr>
<tr>
<td></td>
<td>February 2008</td>
<td>April 2010</td>
<td>June 2011</td>
</tr>
<tr>
<td>Aluminum (Al)-Dissolved</td>
<td>21.9</td>
<td>19.4</td>
<td>18.8</td>
</tr>
<tr>
<td>Antimony (Sb)-Dissolved</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Arsenic (As)-Dissolved</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Barium (Ba)-Dissolved</td>
<td>0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Beryllium (Be)-Dissolved</td>
<td>0.0053</td>
<td>&lt;0.0050</td>
<td>&lt;0.0050</td>
</tr>
<tr>
<td>Bismuth (Bi)-Dissolved</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Boron (B)-Dissolved</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Cadmium (Cd)-Dissolved</td>
<td>0.126</td>
<td>0.123</td>
<td>0.115</td>
</tr>
<tr>
<td>Calcium (Ca)-Dissolved</td>
<td>198</td>
<td>187</td>
<td>192</td>
</tr>
<tr>
<td>Chromium (Cr)-Dissolved</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Cobalt (Co)-Dissolved</td>
<td>0.175</td>
<td>0.179</td>
<td>0.173</td>
</tr>
<tr>
<td>Copper (Cu)-Dissolved</td>
<td>0.386</td>
<td>0.344</td>
<td>0.368</td>
</tr>
<tr>
<td>Iron (Fe)-Dissolved</td>
<td>0.537</td>
<td>0.382</td>
<td>0.332</td>
</tr>
<tr>
<td>Lead (Pb)-Dissolved</td>
<td>0.186</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
</tr>
<tr>
<td>Lithium (Li)-Dissolved</td>
<td>0.121</td>
<td>0.133</td>
<td>0.125</td>
</tr>
<tr>
<td>Magnesium (Mg)-Dissolved</td>
<td>47.0</td>
<td>48.2</td>
<td>50.4</td>
</tr>
<tr>
<td>Manganese (Mn)-Dissolved</td>
<td>10.6</td>
<td>9.56</td>
<td>9.43</td>
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<tr>
<td>Molybdenum</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
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<tr>
<td>(Mo)-Dissolved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel (Ni)-Dissolved</td>
<td>0.887</td>
<td>0.850</td>
<td>0.933</td>
</tr>
<tr>
<td>Phosphorus (P)-Dissolved</td>
<td>&lt;0.30</td>
<td>&lt;0.30</td>
<td>&lt;0.30</td>
</tr>
<tr>
<td>Potassium (K)-Dissolved</td>
<td>4.5</td>
<td>5.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Selenium (Se)-Dissolved</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Silicon (Si)-Dissolved</td>
<td>40.4</td>
<td>37.4</td>
<td>39.2</td>
</tr>
<tr>
<td>Silver (Ag)-Dissolved</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Sodium (Na)-Dissolved</td>
<td>179</td>
<td>168</td>
<td>171</td>
</tr>
<tr>
<td>Strontium (Sr)-Dissolved</td>
<td>0.640</td>
<td>0.539</td>
<td>0.566</td>
</tr>
<tr>
<td>Thallium (Tl)-Dissolved</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Tin (Sn)-Dissolved</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
</tr>
<tr>
<td>Titanium (Ti)-Dissolved</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Vanadium (V)-Dissolved</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
</tr>
<tr>
<td>Zinc (Zn)-Dissolved</td>
<td>14.4</td>
<td>13.8</td>
<td>13.3</td>
</tr>
</tbody>
</table>
Figure E1 Slurry bubble column in this study
Appendix F Implications for Continuous Process based on Clinoptilolite Capture

Design of a continuous or semi-continuous system and scale-up of the bubble columns would be necessary to implement the process considered in this thesis in a practical field application.

Although the construction of slurry bubble columns is simple, accurate and successful scale-up and optimization would require an improved understanding of multiphase fluid dynamics, due to complex hydrodynamics and its impact on transport characteristics.

In general, semi-batch mode and continuous mode could be considered for the slurry bubble column process. In continuous operation, the gas and the suspension flow co-currently upward into the column and most of the suspension leaving the column is recycled to the feed tank. On the other hand, in the semi-batch mode there is no liquid throughput, with the gas being bubbled upward into the column (Pino et al., 1992). Figure F1 shows a possible configuration of the continuous process which could be used.

Mixing characteristics are major concerns in the design and scale-up of bubble column reactors for this study. Scale-up rules and dimensional analysis are relevant to regime analysis. The regime analysis is then followed by setting-up appropriate models with the hydrodynamics (e.g. Deckwer and Shumpe, 1993).
Figure F1: Schematic showing a possible configuration for a continuous steady state process for clinoptilolite capture of acid rock drainage
L1: acid rock drainage; S1: clinoptilolite; S0: make-up solid; G: compressed air;
S2: used clinoptilolite; L2: treated ARD;
LN1: NaCl solution; LN0: make-up solution;
S3: regenerated clinoptilolite; LN2: used NaCl solution;