Bench-scale SIR-600 ion-exchange column and Cl_2 regeneration for ammonia removal from a simulated mining wastewater

By: Grace Akerele

A thesis submitted under the joint supervision of:

Dr. Roberto M. Narbaitz and Dr. Majid Sartaj

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Department of Civil Engineering

University of Ottawa

Ottawa, Ontario, Canada

Abstract

The Canadian mining industry is one of Canada's largest industrial sectors, creating jobs and a significant contributor to the economy. However, the mining activities can be detrimental to the environment due to the release of pollutants. Mining extensively uses nitrogen-based explosives, creating explosive impacted mining wastewaters (EIMWW) that contains substantial quantities of ammonia which is toxic to fish and thus, it has serious environmental repercussions. Ion-exchange (IE) with zeolite is an effective method for ammonia removal as it is easily automated, has a rapid start-up, is not significantly impacted by cold temperature or toxicity effects. Thus, it is particularly suited for Canadian mines. However, the traditional IE regeneration approach of using high concentration NaCl solutions creates a secondary polluting stream. Chlorine regeneration of ammonia-loaded zeolite appears to be a promising option to avoid such a secondary source of contamination. An evaluation of this option and other alternative regeneration are the main focus of this thesis.

This thesis includes two initiatives. The first is a set of multi-cycle column loading and regeneration tests to investigate the feasibility of a zeolite (SIR-600) column for ammonia removal from a synthetic EIMWW, containing K and Ca as competing ions, coupled with regeneration using different concentration of chlorine solutions and combined salt+chlorine regeneration solutions. NaOCl regeneration was quite effective, but it was slower than salt regeneration. During the NaOCl regeneration, the main mechanism appears to be the oxidation of ammonia to nitrogen gas and hydrogen ions, however the Na in the NaOCl solution also seems to have a role in the regeneration. This results in pH levels around 3 for approximately half the regeneration cycles. In the combined salt+chlorine regeneration, the incorporation of the salt leads to more rapid elusion of the three ions presumbaly because of the higher sodium concentration (205 meq/L Na versus

14 meq/L Na). The long-term total ammonia nitrogen (TAN) uptake of SIR-600 regenerated with a NaOCl and NaOCl-NaCl were fairly similar, they varied within a relatively small range (0.185meq/g - 0.202meq/g). Thus, the various regeneration schemes did not impact the TAN uptake. The only apparent limitation of NaOCl regeneration is that it required a longer duration. However, the NaOCl is very promising because it resulted in very similar TAN uptakes, the SIR-600 showed a higher preference for TAN over K and avoided creating an additional process waste stream.

The second initiative addressed concerns regarding the long-term integrity of SIR-600 arising from its exposure to low pH solutions during the regeneration. Long-term batch tests were performed to expose SIR-600 to low pH conditions (pH=2, pH=3, pH=4) and the characteristics of this IE material were evaluated. The 3-month low batch exposure experiment showed that pH below 4 decreased the TAN uptake capacity by up to 58%. There was no considerable impact on the surface gravimetric analysis (TGA) and Powder x-ray diffraction (PXRD). The exposure to pH=2 and pH=3 led to breakdown of the outer surface of SIR-600 and the creation of fine particles. It also led to decreases in the BET surface area and a decrease in the TAN uptake proportional to the decrease in the BET surface area. Thus, the exposure to pHs below 4 impacts the durability of SIR-600, so SIR-600 may have to be replaced more frequently. However, regeneration with NaOCl solutions still seems very promising as it avoids the creation of a secondary waste stream.

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Lists of Abbreviations

AAS: Atomic Absorption Spectrometer

ACS: American Chemical Society

BET: Brunauer-Emmett-Teller

BV: Bed volume

℃: Celsius Degree

CSL: Chlorine Short Loading

DO: Dissolved oxygen

EIMWW: Explosive impacted mining wastewater

EZ: Exchange zone

FTIR: Fourier-transform infrared spectroscopy

IE: Ion-exchange

PXRD: Powder x-ray diffraction

SAC: Strong-acid cation

SBA: Strong-base anion

SEM: Scanning Electron Microscopy

SSL: Salt Short Loading

TAN: Total ammonia nitrogen

TGA: Thermogravimetric Analyzer

WAC: Weak-acid cation

WBA: Weak-base anion

Nomenclature

A: Exchangeable counter-ions

B: Free ion removed from solution n_B

$C_{breakthrough}$: Breakthrough concentration, meq/L

C_{eff}: Column effluent concentration, meq/L

C_{eq}: Equilibrium aqueous phase contaminant concentration, meq/L

C_{feed}: Column feed water concentration, meq/L

C_i: Initial liquid-phase concentration of ion in the batch tests, meq/L

C_{inf}: Influent concentration for the column tests, meq/L

C_k: liquid-phase concentration of ion k, meq/L'

f_{NH3}: Unionized ammonia fraction, unitless

f_{NH4^+}: Ammonium ion fraction, unitless

K_{AB}: Selectivity coefficient for ion A and ion B

M: Mass of the ion exchange material, g

n_a: Corresponding ionic charge for compound *A*

n_b: Corresponding ionic charge for compound *B*

K_a: Acid disassociation constant

Q_{column}: Ion exchange capacity of the column, meq/g

Q_{eq} : Equilibrium ion exchange capacity for the contaminant in batch tests, meq/g

Qi: Initial solid concentration of ion in batch tests, meq/g

q_T: Sum of solid-phase ion concentrations of all the ions, meq/g

Q_{uptake}: Ion uptake in the column by each gram of IE material

R^2: Coefficient of determination

$R_{ZA.}$: Resin's fixed-ion

V: Volume of the system, L

α_{BA}: Separation factor for ion A and ion B

ΔV: Change in volume, L

Chapter 1: Introduction

Canadian mines are very important to the Canada's well-being, mining and mineral processing contribute $30.9 billion to the Canadian economy annually (Whaley-Martin et al. 2020). However, mining waste disposal has several deleterious impacts on the environment, including land degradation through very large tailings disposal areas, soil contamination, groundwater contamination, and surface water contamination. Acid mine drainage is one of the most severe and widespread environmental problems caused by the mining industry, it is generated by the bio-oxidation of sulfide-bearing materials when exposed to oxygen and water (Forsyth et al. 1995). This drainage has extremely low pHs and high metal concentrations, upon discharge into surface waters it results in biota kills and the coating of stream bottom with metal precipitates (Razo et al. 2004). Another mining related environmental impact is the discharge of ammonia laden wastewaters, which are responsible for fish toxicity and oxygen depletion in receiving waters (Halling-Sørensen & Jørgensen 1993; Souza-Bastos et al. 2017). These wastewaters originate from the degradation of cyanide (used in gold processing) and the use of common nitrate–fuel oil explosives. The focus of this thesis is on the treatment of explosives-impacted mining wastewaters (EIMWW) using ion-exchange (IE) technology as IE has fast start-up times, low cost, simplicity of operation, and the capability to perform well at low temperatures. These make IE particularly suitable for remote Canadian mines (Zhang 2022).

Ammonia removal by IE, particularly zeolites, due to their high affinity for ammonia and low cost, is a well-documented process (Malovanyy et al. 2013; Huang et al. 2015; Zhang et al. 2017; Chatrand et al. 2020). One of the drawbacks of ion-exchange media is that the removal of the target ion may be significantly reduced by the presence of competing ions. For example, clinoptilolite is

a common and inexpensive natural zeolite which is quite effective in ammonium ion (NH_4^+) removal, however it has similar (or possibly higher) preference for the potassium ion (K^+) which often is present in EIMWW. The ion-exchange media's selectivity for NH_4^+ vs. K^+, depends on the media type, the feed concentrations of the ions, and the systems operating conditions. Thus, realistic studies need to incorporate multi-solute waters. The application of SIR-600 (a commercial zeolite) with NaCl (5%) regeneration has proven that IE is an efficient process for the removal of ammonia from EIMWW that contained K^+ and Ca^{2+} (Chartrand 2018; Zhang 2022). The conventional ion-exchange regeneration method is to use 3 to 14% salt regeneration solutions (Rahmani et al. 2004; Zhang 2022), however the used regenerant contains high salt concentrations and a significant amount of NH_4^+-N so it cannot be discharged or reused without further treatment. Thus, a more sustainable alternative regeneration approaches is desired. Only three studies on chlorine regeneration were identified in the literature, and only one used a multi-ion solution and a column IE configuration, which is the most common system configuration for full-scale applications. Zhang (2022) studied the chlorine regeneration of a SIR-600 column loaded with a synthetic EIMWW. While the chlorine regeneration was effective, it had a number of potential drawbacks. First, it led to the generation of gas which restricted the flow of regenerant. Second, it created very low pH conditions (pH~3) which may be detrimental to the IE media. And third, the regeneration was slower than salt regeneration. This thesis will try to address and overcome these limitations.

1.2 Objectives

The main objective of this study was to assess the performance of SIR-600 (a commercially available zeolite) ion-exchange system for the treatment of a synthetic EIMWW (containing

calcium, potassium, and ammonia) in conjunction with chlorine regeneration and combined salt and chorine regeneration. The specific objectives include:

- To evaluate different chlorine regeneration conditions for an SIR 600 IE column used for EIMWW treatment in an attempt to overcome the above mentioned drawbacks. These included conducting multiple loading and regeneration cycles with less concentrated NaOCl solutions and different regenerant flowrates.

- To evaluate the impact of reusing (recycling) the regenerants and of using a combined NaOCl-NaCl regeneration solutions for the same purpose and determine if this could accelerate the regeneration.

- To determine the impact of long-term exposure to low pH solutions on the characteristics of SIR-600.

1.3 Thesis Layout

This thesis consists of six chapters in total. The first chapter being the introduction chapter. It includes background information on the problem at hand, and proposes a method to address these, then it outlines the research objectives. The second chapter is a literature review focusing on the current ammonia removal methods, an in-depth review of the ion-exchange process, the performance of ion-exchange for ammonia removal, and the different regeneration strategies for IE systems. This second chapter concludes with a discussion of research gaps and outlines the proposed research. The third chapter consists of a description of the materials, general procedures and analytical methods used in the experiments conducted. Chapter four is a technical paper

entitled “Chlorine Regeneration of Zeolite Column for Ammonia Removal from an Explosive Impacted Mining Wastewater”**.** This paper investigates the feasibility of the SIR-600 column applications in ammonia removal of the synthetic EIMWW coupled with regeneration using different concentration of chlorine solutions and combined salt+ chlorine regeneration solutions. The fifth chapter presents the results of experiments on the long-term exposure to low pH conditions on the characteristics of the IE material used in this study (SIR-600). The last chapter summarizes the conclusions of the research and points out the possible direction for future work.

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Chapter 2: Literature Review

This literature review will discuss the characteristics of ammonia, the impacts of ammonia in the environment, the wastewater treatment processes capable of ammonia removal, the performance of ion-exchange technology for ammonia removal, and the regeneration of ion-exchange systems. This chapter will conclude with an analysis of the research needs in the treatment of EIMWW by ion-exchange.

2.1 Ammonia

Ammonia (NH_3) is a colorless gas with distinct odor, it is composed of nitrogen and hydrogen atoms. Ammonia occurs naturally but it is one of the chemicals produced in highest quantities by the chemical industry (New York State Department of Health 2005). Ammonia in water exists either as unionized ammonia (NH_3), also known as ammonia gas, or as the ammonium ion (NH_4^+), the distribution among these two species depends on the temperature and pH. The sum of the two compounds is known as total ammonia nitrogen (TAN). TAN is used very frequently because it is very difficult to measure NH_3 and NH_4^+ separately. The equilibrium equation linking both compounds is as follows:

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \qquad \text{(eq 2.1)}$$

For which the equilibrium constant K_a equals:

$$K_a = \frac{[NH_3]}{[NH_4^+] \cdot [H^+]} \qquad \text{(eq 2.2)}$$

Where $[NH_3]$ is the molar concentration of unionized ammonia; $[NH_4^+]$ is the molar ammonium concentration; and $[H^+]$ is the molar concentration of the hydrogen ion. The value of K_a is a

function of temperature. Equation 2.2 can be rearranged to obtain an expression for unionized ammonia:

$$[NH_3] = K_a \cdot [NH_4^+] \cdot [H^+] \qquad \text{(eq 2.3)}$$

Accordingly, TAN equals

$$TAN = [NH_4^+] + [NH_3] = [NH_4^+] + K_a \cdot [NH_4^+] \cdot [H^+] = [NH_4^+] \cdot (1 + K_a \cdot [H^+]) \qquad \text{(eq 2.4)}$$

Thus, the ammonium ion fraction ($f_{NH_4^+}$) equals

$$f_{NH_4^+} = \frac{[NH_4^+]}{TAN} = \frac{1}{(1 + K_a \cdot [H^+])} \cdot \qquad \text{(eq 2.5)}$$

And the unionized ammonia fraction (f_{NH_3}) equals

$$f_{NH_3} = \frac{[NH_3]}{TAN} = \frac{[NH_4^+] \cdot (K_a \cdot [H^+])}{[NH_4^+] \cdot (1 + K_a \cdot [H^+])} = \frac{K_a \cdot [H^+]}{1 + K_a \cdot [H^+]} \cdot \qquad \text{(eq 2.6)}$$

The equations for these two fractions were used to draw the species distribution as a function of pH at 20°C in Figure 2.1. This figure shows that for pH levels below 7 virtually all of the TAN is in the NH_4^+ form, and as the pH increases further, the $f_{NH_4^+}$ decreases and the f_{NH_3} increases. When the pH equals the pK_a (i.e., -log K_a), the concentrations of the two species are equal. By pH 11, almost all of the TAN is in the form of NH_3. At neutral pH conditions almost all of the ammonia is present as NH_4^+.

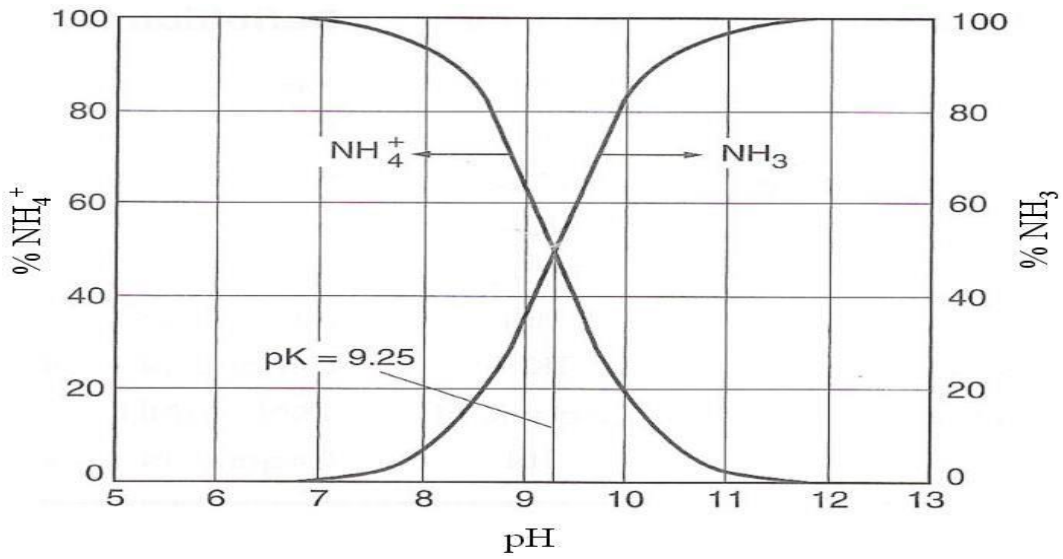

Figure 2-1. Ammonia and ammonium proportions with respect to pH (Source: Kunz and Mukhtar 2016).

Although temperature has an effect, pH is a much larger factor in determining the relative concentrations of two species. Temperature impacts the value of the equilibrium constant, and this is described by the following expression (Environment Canada 2010):

$$pKa = 0.0901821 + \frac{2729.92}{T} \cdot \qquad \text{(eq 2.7)}$$

$$or\ K_a = 10^{\left(0.0901821 + \frac{2729.92}{T}\right)}$$

Where T is the temperature in Kelvin.

2.1.1 Ammonia in the Environment

The primary sources of ammonia in aquatic ecosystems are agricultural runoff containing fertilizers (especially anhydrous ammonia), municipal wastewaters and wastewaters from mines,

food processing and other agriculture activities (Environment Canada 2010). In 2019, approximately 50,400 tonnes of ammonia were released in Canada, mostly from the water and wastewater systems sector (Environment Canada 2019). Mining wastewaters is another source of ammonia pollution, with the large quantities of ammonia generated in mining activities since NH_4NO_3 is a common oxidizing agent in commercial explosives (Forsyth et al. 1995).

The principal detrimental impact of ammonia discharges is fish toxicity caused by even very low unionized ammonia concentrations. For example, the recommended effluent toxicity limit under the Canadian Fisheries Act is set at 1.2 mg TAN/L (equivalent to 0.015 mg NH_3/L) (Environment Canada 2001). The Ministry of Environment and Energy of Ontario (MOEE) has set 0.02 mg NH_3/L as the upper limit of unionized ammonia concentration in water bodies receiving effluents (MOEE 1994). In Ontario, there is no generic TAN effluent discharge concentration limit, during the approval process the above receiving water limit, the degree of dilution and the sensitivity of the receiving water will be considered to assess the necessary degree of treatment that will be required and to set the proposed treatment plant's maximum ammonia discharge levels. In addition, large fluctuations of ammonia can be even more lethal to fish than a steady elevated concentration (Thurston et al. 1981). Many studies on the influence of ammonia on fish have been reported in terms of LC_{50} acute lethality values, i.e., the un-ionized ammonia concentration causing 50% death rate for a specific species in a specified period (Environment Canada and Health Canada 2001). The Canadian mining regulation requires the effluents to be free of toxicity as determined by LC_{50} tests with juvenile rainbow trout within 96 hours (Environment Canada and Health Canada 2001). There is no single identifiable effluent TAN concentration that results in a failed LC_{50} test as other wastewater components may impact the toxicity. In other jurisdictions, there are direct TAN effluent limits, for example in Hungary it is 2 mg TAN/L (Hlavaly et al. 1982).

Another detrimental effect of ammonia discharges into the environment is the depletion of dissolved oxygen (DO) in the receiving water due to nitrification. Nitrification is the conversion of the ammonia to nitrate by the aerobic bacteria. The bacterial oxidation of ammonia requires 4.6 mg of oxygen for every mg of ammonia (Halling-Sørensen & Jorgensen 1993). Therefore, the nitrification process consumes substantial quantities of DO and may reduce its levels to below those required to support aquatic life in the receiving waters. In addition, the temperature variations associated with Canadian seasonal changes affects the ammonia concentration and its conversion to other potential problematic species. First, the decrease of ammonia in receiving waters in the late spring and summer is caused by nitrifying bacteria converting it to nitrite and nitrate which are critical for plant and algal growth. Excessive amounts of nitrate can lead to eutrophication of water bodies, particularly estuaries. However, during the late fall and winter the nitrification process of ammonia is greatly reduced due to the sensitivity of the bacterial community to low temperatures; therefore, ammonia accumulates during the winter (Appl 1999; Ansari et al. 2011). Also, if ammonia is converted to nitrite and nitrate through the nitrification, there is potential for seepage into groundwater sources (Schnobrich et al. 2007; Tutmez & Hatipoglu 2010). This can lead to further problems as groundwaters are frequently used for drinking water sources in rural areas. The ingestion of nitrate-laden groundwater by young infants may result in methemoglobinemia, often referred to as blue baby syndrome, which can lead to death (Comly 1945; Nesslesson 1954). Thus, this further reinforces the notion that ammonia is a leading nuisance in the environment not to be released untreated.

2.2 Treatment of Wastewaters Containing Ammonia

Existing wastewater treatment methods for ammonia removal include: biological treatment, air stripping, reverse osmosis, ion-exchange, adsorption, chemical precipitation, and oxidation processes (Pommen 1983; Dryden & Weatherley 1989; Kurniawan et al. 2006; Bochenek et al. 2011; Ding & Sartaj 2016; Chatrand 2018; Zhang 2022). Although these are potential technologies for the removal of ammonia, it should be noted that the following conditions associated with Canadian mines may limit the suitability of the various technologies. First, most of these mines are located in Northern locations with very cold climate, so the technology needs to operate well under cold temperatures. Second, the operation of the mine and the generation of EIMWW is cyclical in nature so the systems need to be able to work well for fluctuating flows and ammonia concentrations. Third, many of these mines, particularly small mines, do not have dedicated wastewater treatment operators and would prefer to have systems that are automated and require minimum human supervision. Fourth, many of the mines are so remote that there is no road access, supplies either have to be brought in by air or possibly by barge during the summer or possibly by ice roads during the winter. This makes the transportation of chemicals required for wastewater treatment expensive.

Biological nitrification is the most common nitrogen removal process for municipal wastewaters, and it is also used in the treatment of many industrial wastewaters because it is cost-effective. A well designed and operated biological treatment system can achieve more than 90% ammonia removal rate (McCarty 2018). However, the growth rate of a nitrifying organism is slower than that for the heterotrophic bacteria that decompose organic contaminants. And the rate of nitrification is also greatly impacted by temperature so suspended biological nitrification at low temperatures (~5ºC) is difficult (O'Farrel et al. 1973; Zaislev et al. 2008; Widiastuti et al. 2011;

Chartrand 2018). Attached growth systems are capable of nitrification at temperatures as low as 5^{o}C, but only if the concentrations of organics are moderate (COD < 100 mg/L) (Young et al. 2017; Davis 2020). Due to local weather conditions many treatment systems at Canadian mining projects operate at low temperatures and makes biological nitrification more difficult. Furthermore, biological nitrification also has alkalinity requirements to avoid nitrification inhibition and is susceptible to toxicity effects caused by many organic compounds and heavy metals (Metcalf & Eddy 2014). The later may also be an issue in mining wastewaters. Physical/chemical technologies for ammonia removal are not affected by toxicity as biological treatment, however, they also have their potential disadvantages. Air stripping operates well, but requires adjustment to high pHs levels, has high energy consumption, often experiences scaling problems, is less effective with decreasing temperature and may encounter operational challenges with icing. Reverse osmosis, a non–selective process with the removal of other minerals apart from ammonia, has a high energy consumption and membrane fouling is a big concern (Weatherley & Miladinovic 2004; Zhang et al. 2017). Ion-exchange is a chemical treatment process that has great potential for the treatment of EIMWW because it not significantly impacted by low temperatures, it can be easily automated and operated, and is not significantly impacted by flow and concentration fluctuations. Thus, it is the focus of this thesis.

2.3 Ion-Exchange

Ion-exchange (IE) is described as the selective exchange of charged ions in an aqueous phase for an ion attached on a solid phase surface. The IE materials are porous particles that contain ions on the surface of the pore walls, these are known as fixed ions. Attached to these ions are ions with the opposite charge, they are referred to as free-ions or counter ions (Lahav & Green 1998; Mintova &Cejka 2007; Davis 2010; Metcalf & Eddy 2014). The IE process is applicable in the

treatment of industrial wastewater for the removal of a variety of heavy metals and softening of municipal water supplies. Ion-exchange process is regarded as a non-conventional process for municipal water treatment because it is rarely used in large-scale municipal water treatment plants. On the other hand, millions of homes in rural areas of North America use IE units to soften their well water.

2.3.1 Historical Introduction

According to historians, the application of ion-exchange as a water treatment material may date back centuries. For example, in 15 BC Moses sweetened the water of Mariah (Lucy 2003). And in 320 BC Aristotle experimented with sea water to produce fresh water using earthen containers with ion-exchange properties (Wachinski & Etzel 1997). The first systematic study on the IE was by Thompson and Way in the mid-18th century (as reported by Kunin & Myers 1950). They observed ammonia ion adsorption on soil with the release of calcium ions in significant amounts. The exchange was possible by a natural mineral known as zeolites. Most ion-exchange processes performed in the early twentieth century were derived from soils, clays, peat, charred bones and natural zeolites (Torraca 1998; Metcalf & Eddy 2009).

2.3.2 Equilibrium Theory

An ion-exchange material selectively exchanges certain ions in the aqueous phase for counter-ions attached to the fixed ions of the IE material, thus transferring charged molecules from a solution to a solid (i.e., the IE material), while the counter ion originally on the resin surface dissolves in the fluid at the same time. This reaction can be written out through the following equation provided by Harland (1994):

$$n_B R_{z_A} \cdot A^{n_A} + n_A \cdot B^{n_B} \leftrightarrow n_A R_{z_B} \cdot B^{n_B} + n_B A^{n_A} \qquad \text{(eq 2.8)}$$

Where R_{ZA} represents the resin's fixed-ion (functional group); *A is* the exchangeable counter-ions; B is the free ion removed from solution; n_A is the corresponding ionic charge for compound *A;* and n_B is the corresponding ionic charge for compound *B*. The terms on the left represents the ion-exchange material and the target ion in solution, respectively, while the first term on the right represents the IE material loaded with the target ion (i.e., B) and the second term on the right represents the released counter-ion A in solution. The reaction is reversible, a process often referred to as regeneration. The resin will continue exchanging counter-ions until equilibrium is achieved. With the ion-exchange achieving towards equilibrium, there is a necessity for electro-neutrality, meaning that the net charge of the exchange media is zero (Crittenden et al. 2012a).

2.4 Preferential ion uptake quantification

Ion-exchange materials have certain preferences for ions in aqueous solution. The preference is expressed in terms of the selectivity coefficient, the separation factors and selectivity in column tests. The first two will be discussed next, while the selectivity in column tests will be discussed in section 2.5.2.

2.4.1 Selectivity

The IE material's selectivity is determined by the physical and chemical properties of the exchanging ion and those of the ion-exchanger media. The selectivity of an IE material is defined by its affinity or preference for one type of ion over another type of ion (Crittenden et al. 2012b). In a binary system described by eq. 2.8 the selectivity can be quantified using a selectivity coefficient K_A^B and a separation factor $\alpha_{B^{A\cdot}}$ (Clifford et al. 2012).

$$K_A^B = \frac{(A^+)^n (RB^{n+})}{(RA)^n (B^{n+})} \qquad \text{(eq 2.9)}$$

Where: *A* and *B* represent the aqueous phase equivalent concentrations of respective counter-ions; while *RA* and *RB* represent the solid phase equivalent concentration of respective counter-ions; n is the valence charge of exchanging ion (Davis 2010).

The separation factors are not constant, they are influenced by the exchangeable ions, the characteristics of the IE material, relative concentrations of ions, temperature, reaction period, etc. (Crittenden et al. 2012a).

2.5 Natural Zeolites

Natural zeolites originate mostly from kaolinite and montmorillonite minerals. Although these natural zeolite materials exhibit low capacities and poor abrasion characteristics, they were used in considerable quantities in water treatment and for industrial air separation, drying and purification prior to the development of synthetic zeolites and synthetic resins. In general, the ions in the aqueous-phase solution can either be exchanged for the cation and anion. Many natural zeolites have a low-cost and they are readily available in the form of zeolite-rock, and they include different counter ions that are readily exchangeable for other like-charged ions in a contact solution (Montegut et al. 2016). The most commonly used natural zeolite types for large-scale applications include, but are not limited to, chabazite, faujasite and clinoptilolite (Chartrand et al. 2020).

Figure 2-2 shows that natural zeolites have porous structures composed of interlacing aluminosilicates attached by covalent bonds to oxygen atoms forming tetrahedral structures which are then linked into a three-dimensional crystalline structure (Gordes Zeolites 2014; Smith & Smith 2015).

Zeolites appear as cation exchangers because they have a net negative charge on the surface as a result of the substitution of Si by Al, which is compensated by alkaline and earth alkaline metal cations (Weatherley & Miladinovic 2004).

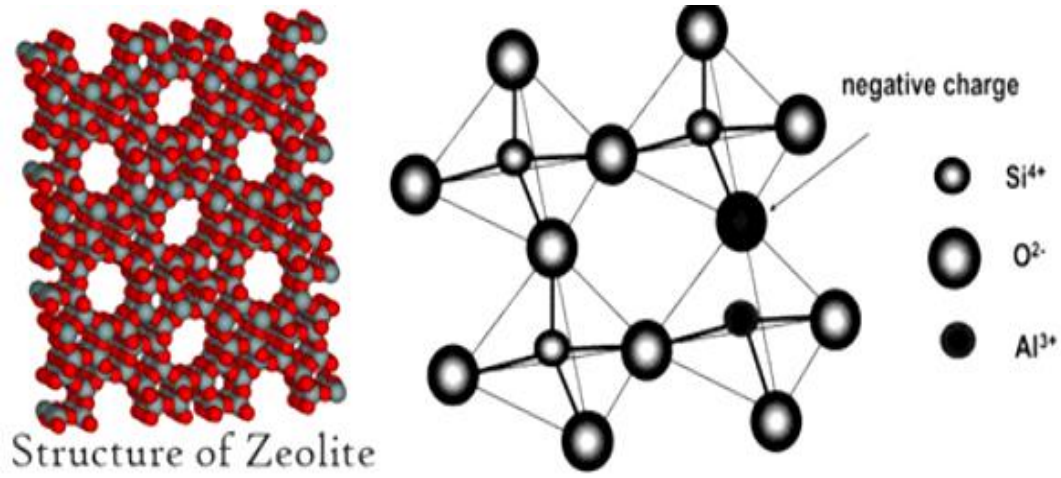

Figure 2-2. Potential Zeolite Structural Matrix (Gordes Zeolites 2014).

These structures can have variances in their atomic make-up which lead to different mineral configurations and different size pores within the matrix. Despite these variations, all zeolites share the same general atomic formula $(Na^+, K^+, Ca^{2+})_6(Si^{4+}, Al^{3+})_{36}O_{72} \cdot 2H_2O$ (Curkovic et al. 1997; Margeta et al. 2013; Huang et al. 2015; Casadellà et al. 2016).

2.5.1 Synthetic Zeolites

The first known synthetic ion-exchange developed was from natural zeolite materials (Kunin & Myers 1950). Synthetic zeolites are derived from processed clays, ash and natural zeolites (Huang et al. 2018). Compared to natural zeolites, synthetic zeolites show higher ammonium adsorption capacity (>15 mg/g), due to a higher proportion of sodium and other cations, higher specific area and larger total pore volume (Lin et al. 2013; Zhou et al. 2015). Furthermore, synthetic zeolites

have the advantage that the Si:Al ratio can be modified to control the ion exchange properties (Harland 1994). For example, the hydrophobic type of synthetic zeolites with high Si/Al ratios are better for the removal of organic compounds from water due to their appropriate pore size while the hydrophilic type zeolites with relatively low Si/Al ratios are regarded as cation (e.g., NH_4^+) exchangers in water treatment (Ellis & Korth 1993; Kawai et al. 1994; Taty-costodes et al. 2005; Rossner & Knappe 2008). However, since synthetic zeolites are manufactured products, they are more costly than natural zeolites. It should be also noted that most synthetic zeolite studies evaluated the NH_4^+ uptake from single solute solutions. There only has been very limited work studied with synthetic zeolites for ammonia removal from wastewaters (Montegut et al. 2016), and the NH_4^+ uptake will not be as good from real wastewaters because of the competition among cations.

2.5.2 Synthetic Ion-Exchange Resins

The discovery of resin backbones led to the development of crosslinked polystyrene resins by D'Alelio in 1945 and it was the basis of modern-day synthetic ion-exchangers (Kunin & Myers 1950). Synthetic IE resins, unlike aluminosilicate zeolites, are highly resistant to regenerant solutions of mineral acids and are mostly utilized for their large exchange capacity and ease regeneration (Chartrand 2018; Huang et al.2018). The exchange mechanisms for synthetic resins consisting of a network of cross-linked polymers modified to remove both cations and anions. They are prepared with polystyrene or polyacrylic crosslinked with divinylbenzene polymer. The pore structure on the type of synthetic resins formed depends on the exchanging ions, the ionic strength, the temperature, and the degree of crosslinking (high cross-linking leads to lower surface area or low cross-linking leads to more surface area) (Davis 2020).

The classification of synthetic resins is by functional groups bonded to the polymer backbone, there are four ion-exchange resins categories: strong-acid cation resins (SAC); weak-acid cation resins (WAC); strong-base anion resins (SBA); weak-base anion resins (WBA). The acid cation exchanger has a negative fixed ion as functional group and target the uptake of positively charged counter-ions; the basic anion exchanger has a positive fixed ion as functional group and target the removal of negatively charged counter-ions (Chartrand 2018; Davis 2020). The strong–acid exchangers (SAC), typically have sulfonate groups at the exchange sites. SAC exchangers will give up a proton over a wide pH range (1 to 14). Strong-acid resin regeneration requires a regeneration solution with a very high concentration of the exchangeable ion so as to provide the driving force for exchange to take place (Harland et al. 1994). The functional group of WAC resins is usually carboxylate. The weak acid cation exchange resins, which are mostly used in softening and dealkalization, will not give up a proton unless the pH is greater than 6. Strong base anion exchange resins generally feature quaternary amine groups as their fixed group, they can operate at a pH below 13 so it appears that their performance is essentially independent of pH. SBA are mostly used in the treatment of water contaminated with nitrate and arsenic and they are generally regenerated with chloride solutions (Kawai et al. 1994). For the removal of ammonia, one can use (strong or weak) acid cation exchangers (Jorgensen & Weatherley 2003; Malovanyy et al. 2013). SAC resins are not particularly effective for the removal of NH_4^+ from wastewaters because SAC resins have a much higher selectivity for divalent ions, such as Ca^{2+} and Mg^{2+}, which are also present in wastewaters. (Chartrand 2018; Huang et al.2018; Han et al. 2021).

2.5.3 Natural Zeolite Selectivity

Clinoptilolite, a natural zeolite, is well documented for the removal of ammonia from aqueous solutions (Ames 1960; Weatherley & Miladinovic 2004; Li et al. 2010; Montégut et al. 2016; Huang et al. 2017; Chartrand 2018; Zhang 2022). Its framework structure consists of four-and five-tetrahedral ring channels with 3 to 8 Å channel diameters and a porosity of about 34% (Vaughan 1978). The cation exchange capacity (CEC) is the mass/equivalence of cations that can be accommodated by the zeolites. Note that other zeolites, such as chabazite and mordenite, also adsorb ammonia and are governed by the same principle of clinoptilolite for ion sieving and ion-exchange capacity, but they do not have the same structure as clinoptilolite (Hedström 2001). Clinoptilolite is the commonly suggested zeolite type for wastewater treatment application because of its high CEC (>18.95 meq/g), and affinity for ammonium (Hedström 2001).

The general order of cation selectivity for clinoptilolite was extensively studied (Ames 1960) and the general selectivity order is:

$$Cs^{+}>Rb^{+}>K^{+}>NH_4^{+}>Ba^{2+}>Na^{+}>Ca^{2+}>Fe^{2+}>Al^{3+}>Mg^{2+}>Li^{+} \quad \text{(eq. 2.10)}$$

Several subsequent studies have confirmed the position of NH_4^{+} in the preference sequence shown in eq. 2.10 (Rahmani et al. 2004; Leyva-Ramos et al. 2004; Guo et al. 2008). It should be noted that potassium is slightly preferred by this IE material over ammonium in accordance with the cation preference sequence (Chartrand 2018). Furthermore, for practical application of IE materials in real wastewater where other cations are present, there is a competition in the wastewater for exchange sites between ammonium ions and other cations, resulting in a lower ammonium exchange compared to if only an ammonium solution would have been applied (Koon & Kaufmann 1975). It should also be acknowledged that the above selectivity order is a general

order which can be impacted by the relative concentrations of the ions involved (Ames 1960; Koon & Kaufman 1975; Leyva-Ramos et al. 2004; Guo et al. 2008; Widiastuti et al. 2011; Zhang 2022).

2.6. Batch and column IE system operation

Ion-exchange processes can either be operated in batch or continuous mode. Batch tests are widely applied in IE research because they are fast and only require simple equipment and multiple tests can be conducted simultaneously. In a batch reactor, the adsorbent is stirred with the water (containing the target ion) until the reaction is complete. The spent ion-exchange adsorbent is removed by settling or filtering and afterwards regenerated.

The continuous mode systems generally consist of columns packed with IE material, they are the most common type of IE systems used in full-scale applications. To incorporate the dynamic nature of the IE columns into full-scale designs, designers generally perform small scale laboratory column tests (Crittenden et al. 2012b; Wachinski 2017). Within the column the exchange occurs in a portion of the IE material at a time, this portion which is referred to as the exchange zone (EZ). For downflow columns the EZ moves down the column during the loading phase. Figure 2-3 (a) shows a downflow IE column and the EZ moving down during four different stages of the loading phase. The zone ahead of the EZ, shown in white, contains IE without the target ions. With time as the column slowly gets saturated ($\forall_2$), the EZ moves down in the same direction as the liquid flow. The zone upstream of the EZ, denoted by closely spaced horizontal lines, is called the saturated zone. Within this zone the IE material is in equilibrium with the feed solution. During the early stages of the column run ($\forall_1$) the saturated zone is very small, with time and it expands and at $\forall_4$ it comprises almost all of the entire column (Treybal 1981; Davis 2020). Figure 2-3 (b) shows the target ion concentration in the IE column's effluent, known as the breakthrough curve.

In the early stages of operation, before the EZ reaches the bottom of the column (i.e., $\forall_1$ and $\forall_2$), the column's effluent contains no target ions. Once EZ reaches the bottom of the column, the target ion starts appearing in the column's effluent, this is the start of the breakthrough. The effluent target ion concentration increases with time as the EZ moves down the column. The maximum allowed effluent concentration is called the breakpoint or breakthrough concentration (V3 in Figure 2-3 (b)). Normally the column is operated until the breakthrough concentration is reached and then it is removed out of operation and the ion-exchange material is regenerated. If instead the column was operated further, the target ion effluent will continue to increase (V4 in Figure 2-3) until it reaches the feed concentration. At this point, the ion-exchange material within the column is fully saturated, this means effluent concentration of the target compound is in equilibrium with the influent, because the exchange of the adsorbent is equilibrium with the feed (Treybal 1981; Wachinski 2017; Davis 2020). The ion uptake capacity within a column can be calculated using the following mass balance equation:

$$q = \frac{\Sigma(Cinf - Ceff)\Delta V}{M} \qquad \text{(eq 2.11)}$$

Where q is the ion uptake of the IE material (meq/g of IE material), V is the volume of liquid treated (L) up to time t; C_{inf} is the influent concentration (meq/L); C_{eff} is the effluent concentration (meq/L) which changes with V (and time); and M is the mass of the IE material in the column (g).

The IE column systems generally incorporate at least two columns, one is off-line being regenerated while the other treats (or others treat) the feed water. Furthermore, the kinetics of ion exchange are relatively rapid and the breakthrough concentration in IE columns are generally reached in less than a day and often as low as few hours (Wachinski 2017).

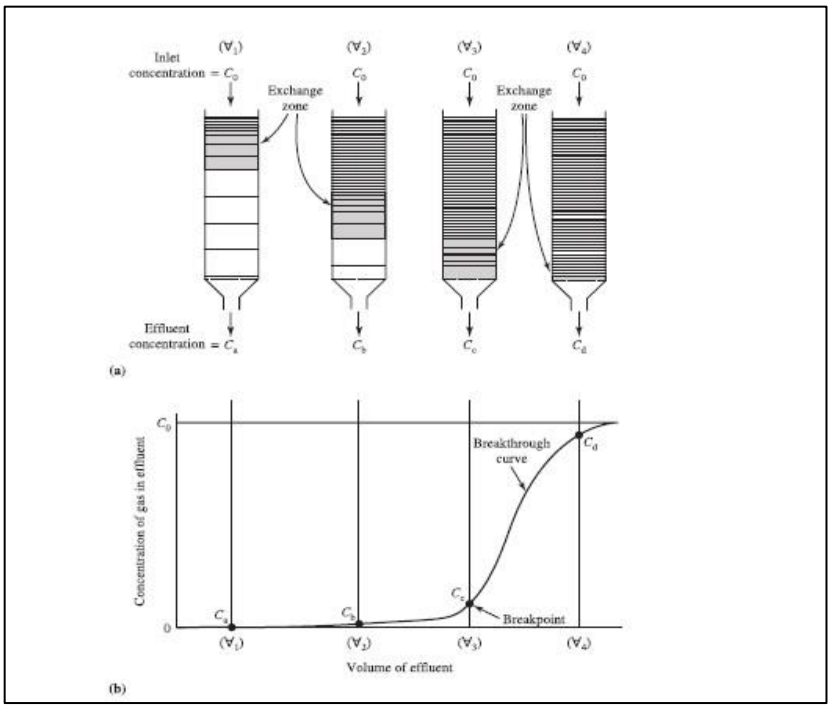

Figure 2-3. Ion exchange process in column (a) and breakthrough (Source: Treybal 1968 as cited by Davis 2020)

2.6.1 Ion preference in column tests

In column tests, the length of the time before the breakthrough of the target ion depends primarily on the total ion uptake capacity of the IE material, the IE material's selectivity, the IE material's particle size, the concentration of the competing ions in the feed, the effectiveness of the previous regeneration, the flowrate, the column's empty bed contact time (EBCT), etc. In practical applications the wastewater being treated usually contains numerous ions, but the available sites on the IE material are limited. As a result, the competition between different ions exists in such a multi-component environment. Thus, if the ion-exchange media has higher selectivity for the target ion, the longer is the length of the run. In such systems, the selectivity is generally assessed in terms of the ion uptakes (or solid phase concentrations or ions accumulated on the IE material)

of the various ions. The ion uptakes are calculated by the integral equation and the trapezoidal rule equation (eq. 2-11).

If the column is operated until it is saturated (i.e., it reaches equilibrium state) the solid-phase concentration of a specific ion could be estimated by the following equation (Crittenden et al., 2012b):

$$q_i = \frac{q_T C_i}{\sum_{k=1}^{N} \alpha_i^k \, c_k} \qquad \text{(eq. 2.12)}$$

Where q_i represents the solid-phase concentration of ion i, eq/g of IE material; q_T is the sum of solid-phase ion concentrations of all the ions, eq/g of IE material; C_i is the liquid phase concentration of ion i in the feed, eq/L; C_k is the liquid-phase concentration of ion k in the feed, eq/L; *N* is the number of different ions present; and α_i^k represents separation factor for ion i over ion k (Crittenden et al., 2012b). As noted in section 2.4.1 the separation factors are not constant, they are influenced by the exchangeable ions, the characteristics of the IE material, relative concentrations of ions, temperature, etc. (Crittenden et al. 2012a). Thus, eq. 2.12 is just an estimate. In addition, most columns are not operated to reach equilibrium conditions (saturation). Accordingly, rather than predicting the values of q_i using equation 2.12 the more common approach is to conduct multicomponent experiments, calculate the uptake of the ions, and use the ratios of the ions uptake to quantify the selectivity.

2.7 Ammonia removal by zeolite columns

There has been previous research on the removal of ammonia by ion-exchange media, however most of this research was based on the treatment of single–solute ammonia, which is not very practical as ammonia removal is greatly impacted by competing cations such as K^+ and Ca^{2+} that are found in practically every wastewater (Chartrand 2020; Zhang 2022). Ion-exchange using zeolites has shown to be effective in the removal of ammonia from challenging waters (Koon & Kaufman 1975; Cooney et al. 1999; Semmens et al. 1975; Svetich 1993; Huang et al. 2015; Vocciante et al. 2018; Chartrand et al. 2020; Han et al. 2021). Accordingly, this review will focus on ammonia removal from multi-solute solutions. In addition, most of the published research comprises of batch studies, however full-scale IE applications are mostly continuous-flow column systems. Thus, the discussion in the remainder of this section will focus on studies on TAN removal by IE columns regenerated by NaCl solutions, which is the standard regeneration approach, other regeneration approaches will be discussed later.

Table 2.1 presents a summary of selected zeolite column studies on the removal of TAN ammonia removal from multi-solute real and synthetic wastewaters. These studies have approximately 20 mg/L TAN feed concentrations, for which there is more data in the literature, to allow for comparisons of the breakthrough times and breakthrough TAN loadings achieve with different zeolites, column designs and operating conditions. Table 2.1 also includes data for the latest work from our group (Zhang 2022). As discussed in a previous subsection, the ion-exchange column breakthroughs (and accompanying loadings) are a function of the characteristics of the zeolite used, the zeolite particle size, the feed cation concentrations, the desired breakthrough level, the column's EBCT, the column's flowrate, and the characteristics of the regeneration (Chartrand 2020; Zhang 2022). For example, smaller IE particle size, lower target ion feed concentration,

higher breakthrough levels, longer empty bed contact times and lower flowrates result in longer runs and higher ion uptakes. Thus, the lower the flowrate (in terms bed volumes (BVs) per unit time), the longer the empty bed contact time (EBCT), the longer the breakthrough time and the higher the loading achieved (Schoeman et al.1986). From the data in Table 2-1, it can be observed that the equilibrium TAN loadings for selected clinoptilolite vary from 0.062 to 0.27meqTAN/g at the equilibrium states for multi-component solutions. The TAN uptake for SIR-600, a commercial natural zeolite, falls within the range of the studies using clinoptilolite, so SIR-600 is likely a clinoptilolite (Zhang 2022). Note this is in spite that the SIR-600 particles are larger and the flowrate is the largest, which should lead to lower uptakes. The only full-scale facility application, which was operated for a long time, achieved TAN loading of 0.1 meqTAN/g, which is in the middle of the range (Svetich 1993).

2.8 Regeneration

Regeneration is the renewal and restoration of resins once they have reached saturation or the breakpoint. Zeolites regeneration can also be described as the process where the cations or anions (counter ions) are restored on the spent IE material, this is generally accomplished by the application of salt regenerant (NaCl, KCl, $CaCl_2$) solutions. For strong- and weak acid cation resin exchangers HCl regenerant can also be applied (Crittenden et al., 2012b). In the case of salt regeneration, the regeneration with the Na form of the clinoptilolite is considered the preferrable to calcium solutions. This is because the calcium ion is larger than the sodium ion, it cannot approach the exchange sites as closely as sodium, which is smaller and migrates faster through the zeolite channels (Koon and Kaufmann 1975; Hedstörm 2001). Thus, calcium form of clinoptilolite leads to a lower ammonium exchange capacity than untreated clinoptilolite in terms of cation size

(Hlavay et al. 1982). Another potential reason for the NaCl regeneration preference over CaCl regeneration is the possible calcium precipitation as $CaCO_3$ at high pH, and the precipitates block surface ion-exchange material (Koon and Kaufmann 1975; Hedstorm 2001). For ammonia removal applications it is not desirable to use KCl solutions because K^+ will be the counterion, and since the clinoptilolite may have a greater preference for K than TAN then the TAN uptakes will be lower than those achievable with a NaCl regenerant.

Table 2-1 Selected clinoptilolite used in column tests for multiple regeneration.

Reference	Koon and Kaufman (1975)	Cooney (1999)	Schoeman (1986)	Schoeman (1986)	Svetich (1993)	Vocciante et al (2018)	Zhang (2022)
WW type	Tertiary treatment of municipal wastewater	Tertiary treatment of municipal wastewater	Underground mine water	Spiked tap water	Tertiary treatment of municipal wastewater (Full-scale)	Groundwater	Synthetic EIMWW
IE media	Clinoptilolite (Hector, USA)	Clinoptilolite (Australia)	Clinoptilolite (Pratley, SA)	Clinoptilolite (Pratley, SA)	Clinoptilolite (Ash Meadows, USA)	Clinoptilolite S.U.	SIR-600 (USA)
Regeneration solution	2% NaCl pH=12.5	3.5% NaCl pH=10	0.59 % NaCl pH=12	0.59% NaCl pH=12.5	3% NaCl pH~9	NEINR.	5% NaCl pH=10
C^{TAN}_{in} (mg NH_4-N/L)	20	30	20	24.5	25	17	21
C^{K}_{in} (mg K/L)	0.9	15	14	15	NR	41	30
C^{Ca}_{in} (mg Ca/L)	26	12	87	32	NR	177	80
Other cation in feed	Na, Mg	Mg	Na, Mg	Na, Mg	Na, Mg	Na, Ca, Mg, K, Sr, Fe, Ni	None
Particle size(mm)	0.3-0.84	0.82	0.5-1.0	0.25-0.7	0.42-0.84	NR	0.4-1.68
Downflow/upflow	downflow	downflow	downflow	downflow	horizontal	downflow	downflow
Flow (BV/h)	20	8	5	15	8.2	NR	26
column's empty bed contact time(h)	3.5	20	26	4	21	NR	4
Breakthrough level (mg TAN-N/L)	1	5	2	2	2	2	2
BV to breakthrough	70	160	130-200	55	169	70	92
TAN uptake (meq N/g) @ breakthrough	0.18	0.22	0.257	0.062	0.20	NR	0.16

NEINN = new EI material, not regenerated.
NR = not reported.
BV = empty bed volume.
S.U. = source unspecified.

Many approaches have been applied for zeolites regeneration used for ammonia removal. These include the use of NaCl, $CaCl_2$, and brine/NaOH solutions. In column applications, the NaCl regeneration effect can be controlled by three factors: the regeneration concentration, the regenerant flow rate, and the regenerant mass applied divided per unit IE volume (Crittenden et al. 2012b). The effectiveness of NaCl regeneration has been proven by many studies that NaCl solution can effectively desorb NH_4-N from zeolite (Koon and Kaufman 1975, Rahmani et al. 2004; Chartrand 2018). High concentration NaCl solutions (e.g., 3 to 14% NaCl or 30,000 to 140,000 mg NaCl/L) are the most common regenerants for IE material regeneration (Crittenden et al. 2012b). However, the improvement is relatively small when the NaCl concentration increased from 5% to 10% (Chartrand 2018). NaCl + NaOH regeneration solution with pHs as high as 12.5 have been shown to be more effective than the same concentration of NaCl, however the resulting high pH leads to a more rapid deterioration of the zeolite (Koon and Kaufmann 1975; Schoeman 1986). The management of the used NaCl regeneration solution is considered as an environmental issue because; a) NaCl regeneration solutions cannot be discharged directly because the high salt concentrations; and b) they cannot be reused without first removing the NH_4^+-N. Thus, these environmental concerns are motivations to find alternative regeneration methods.

2.8.1 Alternative regeneration methods

The use of the brine and NaOH regeneration solution coupled with air stripping of the regenerant avoided the accumulation of NH_4-N in the used regenerant solution and permitted regenerant reuse (Hlavay et al. 1982; Schoeman et al. 1986). This reduces regenerant costs and minimizes the problem of brine disposal. Thus, using this regeneration set-up clinoptilolite may theoretically be reused indefinitely (Ames 1960). This approach has been used for a full-scale application (Svetich 1993) and is presented in Metcalf and Eddy, the standard wastewater treatment design textbook

(Metcalf and Eddy 2014). However, this approach normally requires great quantities of chemical reagents to raise the pH (Schoeman et al. 1986). In addition, the effectiveness with including air stripping is highly sensitive to temperature as the Henry's Law constant decreases with decreasing temperature. Accordingly, it is not appropriate for cold Canadian climates.

An alternative is biological regeneration, which actually is a combination of chemical and biological regeneration and has primarily been developed to decrease the brine solution at regeneration or to improve the conventional nitrification-denitrification process (Hedstorm 2001). However, the biological regeneration leads to the formation of biofilm attached on the zeolite which could affect the longevity of the IE material, on the ammonium exchange capacity. In addition, the kinetics of nitrification are slow, thus this approach is not very practical. Han et al. (2021) also pointed out that the biological regeneration is generally not as efficient or fast as other methods, especially under low temperatures.

Another alternative regeneration methods that have been applied is electrochemical regeneration (Lei et al. 2009; Li et al. 2010). The combination of IE technology with electrochemical regeneration has been developed with the aim of improving both technologies simultaneously. Some researchers have utilized electrochemical method to regenerate loaded zeolites and have reported that the NH_4^+ exchanged by zeolite can be effectively oxidized to nitrogen gas using electrified anode and cathode in the presence of chloride ions (Lei et al. 2009; Li et al. 2010). They found that electrochemical regeneration is very effective in oxidizing and converting Cl^- ion into Cl_2, the Cl_2 oxidizes the ammonia converting it to nitrogen gas which escapes into the atmosphere. Thus, the electrochemically treated regenerant can be reused avoiding the disposal of the used regenerant, avoiding a secondary source of pollution (Li et al. 2010). This has been marketed under the name AMMEL by Current Water Technologies Inc.

(http://www.currentwatertechnologies.com). However, the complex equipment and relatively high-energy consumption are needed for zeolite electrochemical regeneration, which may increase the costs of project operation and wastewater treatment (Lei et al. 2009; Huang et al. 2015). In addition, as its main mechanism is the oxidation of ammonia by chlorine, regeneration using chlorine solutions may be just as effective. This topic will be discussed next

2.8.2 Chlorine Regeneration

Chlorine disinfection is an effective method for inactivating most bacteria and viruses, and since its implementation (in conjunction with filtration) there has been a sharp decline in the number of water borne epidemics (Environment Canada 2010). Water and wastewaters frequently contain ammonia and when chlorine is added a number of different reactions occur.

Chlorine can be added to water using chlorine gas ($Cl_{2(g)}$) or solid calcium hypochlorite ($Ca(OCl)_2$) or liquid sodium hypochlorite (NaOCl), commonly called bleach. These three sources lead to the formation of free chlorine, which is the sum of the hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). The following are the reactions involved (Metcalf & Eddy 2014):

i) Chlorine Gas

$$Cl_2 + H_20 \leftrightarrow \mathrm{HOCl} + H^+ + Cl^- \qquad \text{(eq 2.13)}$$

ii) Sodium hypochlorite (NaOCl)

$$\mathrm{NaOCl} + H_20 \leftrightarrow \mathrm{Na} + + \mathrm{HOCl} + \mathrm{OH} \qquad \text{(eq 2.14)}$$

Hypochlorous acid and hypochlorite ion are related by the following equation:

$$\mathrm{HOCl} \leftrightarrow H^+ + \mathrm{OCl} \qquad \text{(eq 2.15)}$$

So the distribution between HOCl and OCl- is pH dependent. At 20^{o}C the pK_i of the ionization reaction is $2.62*10^{-8}$, so 76% of the chlorine at pH=7 will be in the form of HOCl but at pH=10 the principal species will be OCl^- (99.6 %).

The process of the chlorination is demonstrated by Figure 2-4. The reactions and the products are largely determined by the chlorine to nitrogen ratio. Owing to its strong oxidizing power, the free chlorine reacts with ammonia to generate monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) by the following reactions (Metcalf & Eddy 2014):

$$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O \qquad \text{(eq 2.16)}$$

$$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O \qquad \text{(eq 2.17)}$$

If the chlorine to ammonia nitrogen molar ratio is up to 1:1 (or 5:1 based on a mass basis) monochloramine is formed and some dichloramine is formed (Davis 2020). If there is additional chlorine introduced, more dichloramine is formed and trichloramine (NCl_3) is generated by the reaction below (Metcalf & Eddy, 2014):

$$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O \qquad (eq. 2.18)$$

NH_2Cl, $NHCl_2$, and NCl_3 are also known as chloramines (Metcalf & Eddy 2014). Combined chlorine consists of the chloramines plus other chlorinated compounds, such as chlorinated organic compounds.

When the mass ratio approaches 7.6:1 (about 1.5 on a molar basis) the majority of the chloramine will be oxidized to nitrogen gas. This point is called the chlorination breakpoint, further chlorine additions will lead to increasing free chlorine concentrations (Metcalf & Eddy 2014). Note that a small portion of combined chlorine residual is still left behind as shown in Figure 2-4.

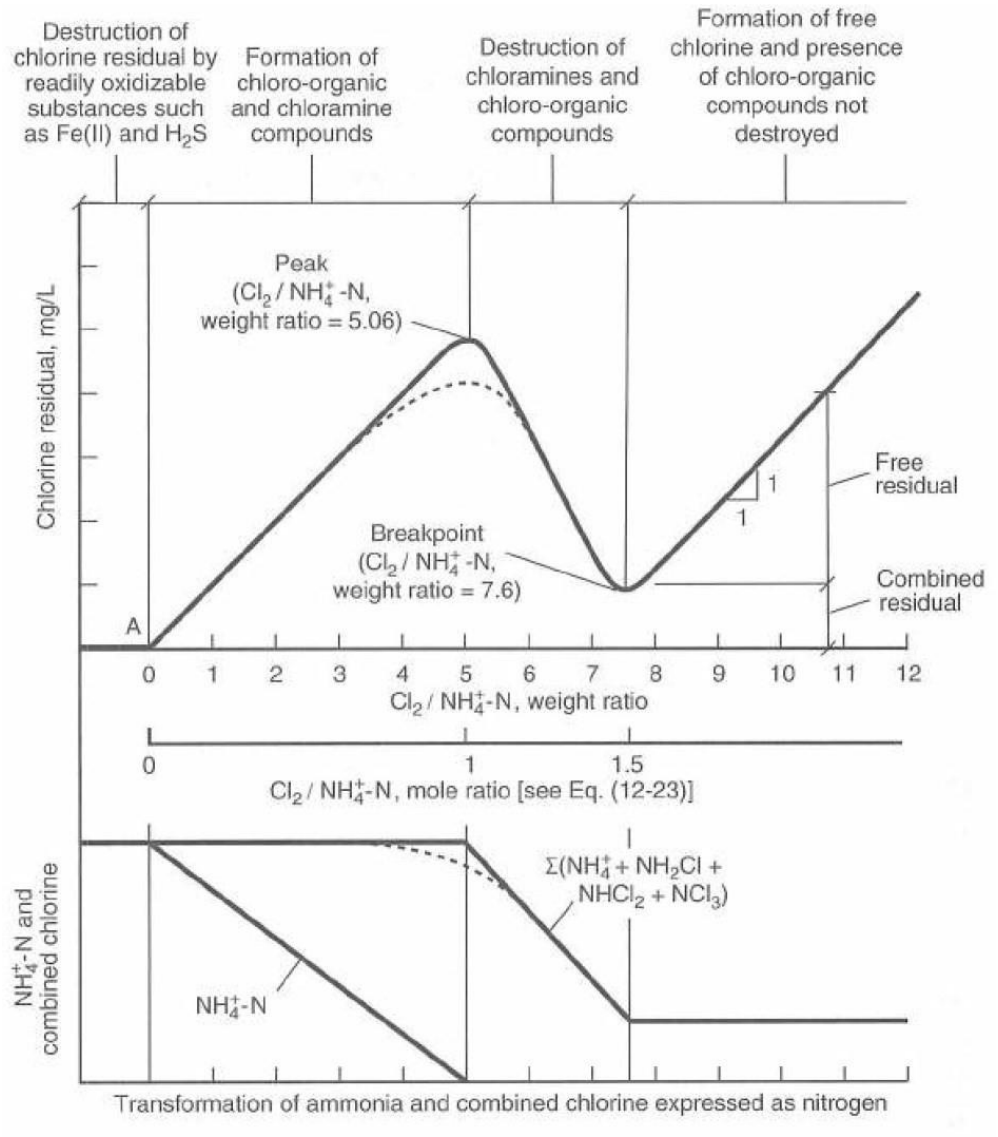

Figure 2-4 Chlorine Break-point Stoichiometry (Metcalf & Eddy 2014).

As the chloramines are oxidized into nitrogen gas with further chlorine additions, the overall reaction is as follows (Metcalf & Eddy 2014):

$$2NH_4 + 3HOCl \leftrightarrow N_2 + 3\,H_2O + 3HCl + 2H^+ \qquad (eq.2.19)$$

In drinking water treatment, frequently chlorine doses beyond the breakpoint are added to have a small residual free chlorine in the water within the distribution system. Breakpoint chlorination has also been applied in full-scale municipal and industrial wastewater treatment (Stone 1978). This disinfection is intended to protect downstream swimmers and the chlorine is normally only applied during warm seasons. It is also important to reduce the total residual chlorine levels of the effluent as free chlorine even at low levels is toxic to fish. In Canada, the National Municipal Wastewater Effluent Standards require all municipal wastewater effluents to have free chlorine concentrations below 0.02 mg/L (Minister of Fisheries and Oceans Canada 2012b). Also, this method is generally not considered for industrial wastewaters that contain stronger reducing agents, such as ferrous iron, that causes high chlorine demands (Metcalf & Eddy 2014; Moran 2018). This method is only appropriate when the concentration of stronger reducing agents' level is low (Woodard 2001; Metcalf & Eddy 2014; Moran 2018).

2.8.3 Chlorine Regeneration of Ion-Exchange Materials used for Ammonia Removal

An alternative hypochlorite regeneration solution was studied for the purpose of removing ammonia loaded on the zeolite (Zhang et al. 2017; Huang et al. 2015; Zhang 2022). Huang et al. (2015) assessed the overall influence of sodium hypochlorite regeneration on the regeneration of Chinese zeolites-used in the treatment of synthetic swine wastewater containing 320-1120 mg/L NH_4-N. Their batch loading experiments used very large zeolite doses, many of them used 160 g zeolite/L. In the experiments, the capacity of the IE material was approximately 2 mg NH_4-N/g (0.11 meq TAN/g), which is comparable to those achieved by column operations (Table 2-1). Furthermore, multiple-cycle chlorine regenerations did not significantly affect the zeolite's NH_4^+ removal efficiency (Huang et al. 2015). Zhang et al. (2017) conducted batch experiments using a

Chinese zeolite for the removal of ammonia from single-solute ammonia solutions. They speculated that regeneration using hypochlorite solutions resulted in the oxidation of the adsorbed NH_4^+ to N_2. Zhang et al. 2017 found that a combined NaOCl -NaCl regenerant solution achieved a higher zeolite regeneration efficiency (80.3%) than using NaCl or NaOCl alone (67.7% and 74.5%, respectively). The higher efficiency of the NaOCl -NaCl regenerant solution was probably due to the high concentration of NaCl that accelerated the ion elution from the zeolite.

Zhang (2022) studied both batch and column chlorine regeneration approaches for using a commercial natural zeolite (Resintech SIR-600), for the removal of ammonia from a synthetic EIMWW (20 mg/L NH_4-N; 80 mg/L Ca; and 30mg/L K). The chlorine regeneration mechanism should primarily impact the sites that were occupied by ammonium, as the chlorine should not impact the sites with K^+ and Ca^{2+}. Thus, this type of regeneration should lead to decreased uptakes of the cations present in the synthetic EIMWW (i.e., K^+ and Ca^{2+}). His batch loading and regeneration tests used a 100 mg free Cl_2/L solution whose pH was raised to 10 to convert the NH_4^+ to NH_3 and in the process enhancing desorption. The batch tests showed that after 5 cycles the IE material's TAN uptake was 0.24 meq/g, and it was approximately 80% of that obtained using a 5% NaCl solution, a standard regeneration solution. However, due to the lower calcium and potassium uptakes of the chlorine regenerated SIR-600, chlorine regeneration resulted in a much greater TAN selectivity. Zhang (2022) also conducted column studies using a 1000 mg free Cl_2/L regeneration solution. These 6 h-long column loading runs achieved 20% higher TAN uptakes than batch tests. Thus, this indicated that the results in batch tests were not directly transferrable to the more practical continuous flow column operation. Zhang (2022) also observed that gas bubbles were generated during the 1000 mg/L free Cl_2 regeneration, from that he inferred that the hypochlorite ions in column operation can oxidize absorbed NH_4^+ to N_2. This is consistent

with the breakpoint chlorination reactions and the claims of Huang et al. (2015). According to Huang et al. (2015) the reaction can be described by the following equation:

$$2NH_4 + 3HClO \leftrightarrow N_2 \uparrow + 3H_2O + 5H^+ + 3Cl^- \quad \text{(eq 2.20)}$$

This is the breakpoint chlorination equation described in section 2.6.3, and for it to be completed the Cl_2:N molar ratio needs to at least a 1.5 (or 7.5 Cl:N mass ratio). To make sure the reaction goes to completion, Huang et al. (2015) recommended an 8:1 mass Cl:N ratio at the neutral pH level. According to Huang et al. (2015), this process achieved effective and rapid (less than 10 minutes in their batch tests) zeolites regeneration without secondary pollution if the residual chlorine is removed. Zhang (2022) did not directly apply eq 2.20 because the chlorine was adjusted to pH =10, the free chlorine is present as OCl^- instead of HOCl so it yields a somewhat different (in this case Cl:N atomic ratio is 1:5) as shown below:

$$2NH_4 + 3ClO^- \leftrightarrow N_2 \uparrow + 3Cl^- + 3H_2O + 2H^+ \quad \text{(eq 2.21)}$$

He also compared the Ca, TAN plus K uptakes and found that the Na in the NaOCl regeneration solution had a smaller but significant role in the regeneration.

Although chlorine regeneration of the EIMWW loaded column was effective, Zhang (2022) raised three concerns. First, regeneration produced many gas bubbles, presumably N_2, which limited the regenerant flowrate. Second, as indicated by the H^+ in the right-hand side of eq. 2.21 the reaction leads to a lowering of the pH. Indeed, Zhang (2022) observed that for a significant period of time the pH of the regeneration solution decreased to approximately 3. This raised concern about the

long-term durability of the IE media. Third, for the single set chlorine regeneration conditions evaluated, chlorine regeneration was significantly slower than salt regeneration (Zhang, 2022). Accordingly, additional column studies need to be undertaken to assess if by changing the operating conditions chlorine regeneration could be accelerated and the other two concerns can be addressed.

2.9 Research Summary and Knowledge Gap

At mines, ammonia is introduced into the waste stream through the application of by the common nitrate-fuel oil (ANFO) explosives. The EIMWWs need to be treated to reduce ammonia levels to acceptable levels. The application of ion-exchange is an appropriate technology for the removal of ammonia from explosive impacted wastewaters produced at remote northern Canadian mines because its operation can be automated, not significantly impacted by low temperature, and require little overall supervision. The IE ammonia removals are significantly impacted by competing ions such as potassium in the wastewater and the type of regeneration method used (Chartrand 2018). The standard salt regeneration of ammonia loaded ion-exchange materials, could lead to a secondary source of pollution. A number of different regeneration methods have been investigated but they have some limitations. Chlorine regeneration of TAN-loaded zeolites converts the ammonia to nitrogen gas so it is removed from the system and thus it can be reused. As practically all of the chlorine is oxidized to chloride and the used regenerant does not contain high salt concentrations it avoids creating a secondary waste stream, thus this technology seems promising.

Presently, there have been only three studies on chlorine regeneration of zeolites used for TAN removal. They had successful results but only two involved multi-solute wastewaters and only one used an ion-exchange column, the more common full-scale IE system setup. The study by Zhang

(2022), only evaluated one set of column chlorine regeneration conditions and the regeneration was rather slow. During the chlorine regeneration the pH decreased to approximately 3, so there are potential concerns about the IE materials long-term durability and performance. Thus, there is a need to evaluate alternative chlorine regeneration conditions, possibly also adding a salt, to shorten the necessary regeneration cycles. Also, there is a need for further research on the characteristics and TAN removal capacities of the zeolite after long-term exposure to low pH solutions.

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Chapter 3: Experimental Materials & Methods

The overall objective of this thesis is to assess and optimize the performance of an ion-exchange (IE) column system for the removal ammonia from a synthetic explosive derived mining wastewater (EIMWW) which unlike conventional systems uses chlorine to regenerate the ion-exchange media. EIMWW contains K and Ca, in addition to ammonia, as the main competing ions. The thesis has two initiatives. The first initiative is the study of the performance of a column system, and it consists of column loading experiments followed by column regeneration experiments using chlorine, salt, and combined chlorine+salt regeneration solutions. The second initiative evaluates the impact of low pH conditions (encountered during chlorine regeneration) on the integrity and characteristics of the ion-exchange media through a series of batch exposure experiments. This chapter discusses material, analytical methods, experimental methods, and the experimental plan used in this thesis.

3.1 Materials

3.1.1 Ion-Exchange media

The IE material selected for this research, was the SIR-600 produced by ResinTech (ResinTech Inc., Candem, NJ). It was selected based on the suggestion of the industrial partner, Dowclear Environmental Inc., and the fact that this was the continuation of the research work by two former graduate students (Z. Chartrand 2018, and T. Zhang 2022) who used the same material. SIR-600 is a natural zeolite marketed for ammonia and cesium removal (ResinTech Inc. 2022). Chartrand (2018) showed that SIR-600 behaved similarly to clinoptilolite for the removal of TAN, so it is presumed that it is a clinoptilolite. Table 3-1 presents some basic information about SIR-600.

Table 3-1. SIR-600 technical properties (ResinTech Inc 2020)

Material structure	Zeolite
Functional group	Aluminosilicate
Ionic form as shipped	Na^+, K^+
Total Capacity Sodium form	>0.6meq/ml
Moisture retention	< 10 %
Screen Size Distribution (US mesh)	12 to 40
< 300µm	1 %
Shipping weight	60 lbs/ft^3

3.1.2 Chemicals

The chemicals used in the preparation of the synthetic EIMWW wastewater included ACS grade ammonium chloride, potassium chloride and calcium chloride hexahydrate (Fisher Scientific, Waltham, MA). The chlorine regeneration solutions were prepared by dilution of a commercial bleach (No Name) using distilled water. The salt regeneration solutions were prepared with NaCl (ACS grade, Fisher Scientific, Waltham, MA). TAN was analysed with Rochelle Salt (Potassium Sodium Tartrate) (RICCA, Arlington, TX) solution. For the metals analysis, 0.1% La and 0.1% HNO_3 was used (ACS grade, Fisher Scientific, Waltham, MA).

3.1.3 Synthetic Explosive Impacted Mining Wastewater (EIMWW)

The EIMWW was prepared by dissolving ammonium chloride, potassium chloride and calcium chloride hexahydrate to distilled water to produce a solution with approximately 20mgTAN/L, 30mg K/L and 80mg Ca/L (1.43 meq TAN /L, 0.769 meq K/L and 4.0 meq Ca/L). The concentrations of these three key ions are very similar to those reported as typical for underground mines in South Africa by Schoeman (1986). The solution was prepared in a 40L tank with magnetic stirring bar to provide mixing and was covered by tank lid to avoid any potential contamination. A new EIMWW solution was created for each column loading experiment.

3.2 Analytical Methods

3.2.1 Measurement of Ammonia

Ammonia was measured by direct nesslerization standard methods 4500-NH_3, it uses the Nessler reagent that consists of mercuric iodide, potassium iodide, sodium hydroxide, and water (American Public Health Association 1992). The detailed procedure consisted of adding 0.125 mL of Rochelle salt solution to each 10mL sample in a beaker and mixing them well by shaking the beaker before adding 0.10 mL of Nessler reagent allowing to react for 10 minutes. The stabilizing Rochelle salt (Potassium Sodium Tartrate) is added to prevent precipitation after the addition of the Nessler reagent. Once reaction was completed, the sample's absorbance was measured on a spectrophotometer (DR600, HACH, Loveland, CO) at a wavelength of 425nm. If TAN is present in the solution, it will turn yellow, and the concentration is proportional to the colour intensity which was measured using the spectrophotometer. Before analyzing the first real sample, a calibration curve was established and verified with every set of measurements. In this thesis, a blank sample consisting of 10-mL distilled water, was used to zero the spectrophotometer, then TAN standards with concentrations ranging 1 to 5 mg NH_3-N/L were used to build the calibration

curve. To ensure the reliability of the calibration curve, it was based on triplicate analysis of six different standards. Figure 3-1 shows an example of a typical calibration curve.

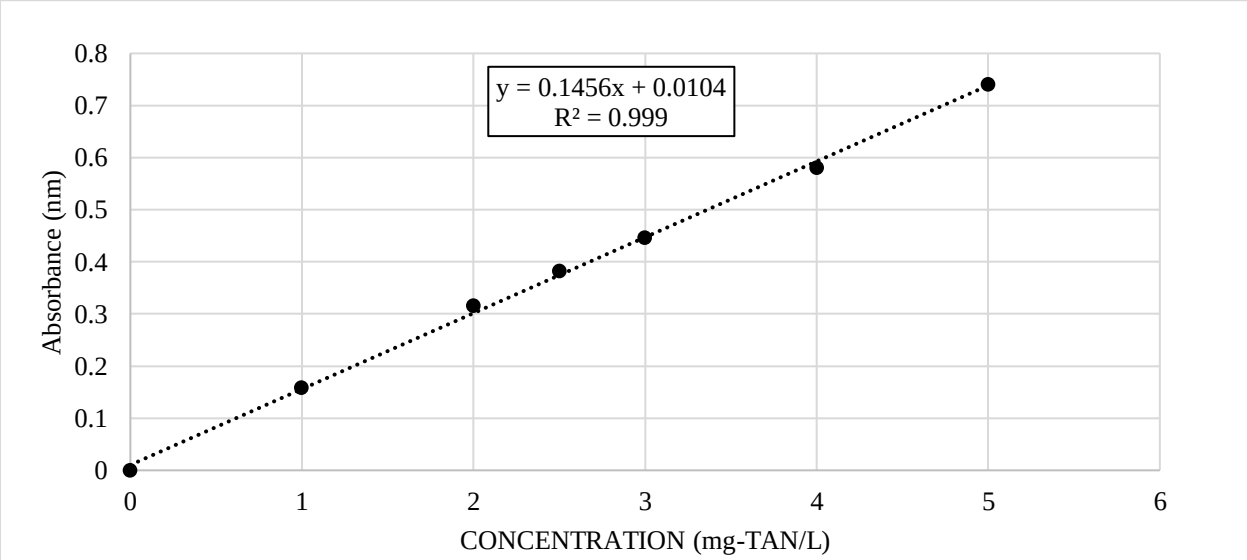

Figure 3-1. Calibration curve of Nesslerization.

3.2.2 pH

pH was measured with a pH probe connected to a portable benchtop meter (HQ40d, HACH, Loveland, CO). The probe was calibrated using stock buffer solutions of the following pH's: 4.0, 7.0 and 10.0 (Oakton Buffer Pack, Virginia, USA).

3.2.3 Chlorine Measurements

The free and total chlorine concentrations of the chlorine regeneration solutions were measured by the Hach methods 8021 for free chlorine and 8167 for total chlorine, respectively (Hach 2021a, Hach 2021b). It consists of adding DPD free/total chlorine reagent pillows (Hach, Loveland, CO) to the samples, mixing them and measuring the resulting colour intensity with a spectrometer (DR6000, Hach, Loveland, CO) using its built-in calibrations.

3.2.4 Temperature

All experiments were conducted at room temperature. The solution temperature was measured with Sartorius pHBasic meter (Sartorius, Goettingen, Germany) with a temperature sensor-integrated probe (PY-P11-2S, Sartorius, Goettingen, Germany).

3.2.5 Metal Analysis

The potassium, sodium and calcium concentrations were measured using Standard Methods 3111B (American Public Health Association 2017) and a flame atomic absorption spectrometer (PinAAcle 500, PerkinElmer, Waltham, MA, United States) located at the Dept. of Civil Engineering of the University of Ottawa. 0.1% Lanthanum solution and 1mL was added to the 100 mL samples, standards, and blanks to avoid the possible ionization and chemical interference; 0.1% HNO_3 solution and 1mL was added to insure the dissolution of the metals. Before using the AA spectrometer, the burner head of this instrument was adjusted to assure optimal alignment. Then, the flame was turned on and two drops of diluted nitric acid solution was sipped up the analyzer's capillary sampling tube for cleaning purposes. The blank sample was prepared with deionized water. Three standards (usually 2 ppm, 6 ppm, and 10 ppm) were used to build calibration curves for the calcium and potassium measurements. The option of "nonlinear through zero" was chosen for the instrument's automatically generated calibration curves. To fit the range of the calibration curve, the samples were diluted to be in the 0-10 mg/L range. A calibration curve was created each time experimental measurements were taken, and standards were prepared freshly prior to each analytical session. To prevent cross contaminations, the capillary tube was inserted into deionized water to run for a few seconds between samples, standards, or blanks, and it was wiped with a Kimwipe tissue afterwards. Testing showed that when several standards covering a wide range of concentrations (e.g., 1 to 12 mg/L) were used it often resulted in an

unfavorable S shaped curve, which has the tendency to over or underestimate the values and ultimately reduce the accuracy of readings. When plotting the calibration curve, the AA's software will ensure that the curve is fitted to every point by assuming there is no error in the calibration standards. Therefore, using standards covering a wide range of concentrations leads to a curved calibration curve, leading to errors in the measurements.

To ensure linearity only three standards (usually 2 ppm, 6 ppm, and 10 ppm) were used to build calibration curves for the calcium, potassium and sodium measurements. To fit the range of the calibration curve, the samples were diluted to be in the 0-10 mg/L range. To assure that the calibration did not drift, the standard was also checked twice after 10 samples were tested.

3.2.5.1 Potassium

The potassium was measured using a potassium LuminaTM hollow cathode lamp (PerkinElmer, Waltham, MA, United States) installed in the AAS for this analysis. The operation conditions selected were wavelength = 769.90nm, slit width 0.7 nm, acetylene gas flow rate = 2.5L/min and air flow rate = 10 L/min. The potassium standard solutions were prepared using potassium chloride (ACS grade, Fisher Scientific, Waltham, MA). New standards were prepared before analysis of every set of samples.

3.2.5.2 Sodium

Sodium analyses were determined using the AAS with a sodium hollow (Na) cathode lamp (N3050139XX Lumina™ 2, PerkinElmer, Waltham, MA, United States). The key operating conditions were wavelength = 422.67 nm, slit width = 0.7 nm, acetylene flow rate = 2.7 L/min and air flowrate = 10 L/min. The sodium standard solutions were prepared using NaCl (ACS grade,

Fisher Scientific, Waltham, MA). New standards were prepared before analysis of every set of samples.

3.2.5.3 Calcium

For the calcium analysis, a calcium LuminaTM hollow cathode lamp (PerkinElmer, Waltham, MA, United States) was installed in the AAS. The key operating conditions were wavelength = 422.67 nm, slit width = 0.7 nm, acetylene gas flow rate = 2.7 L/min and air flowrate = 10 L/min. The calcium standard solutions were prepared using calcium chloride hexahydrate (ACS grade, Fisher Scientific, Waltham, MA). New standards were prepared before analysis of every set of samples.

3.2.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was conducted of the samples of the long-term low pH solution exposure tests, it was performed at the Advanced Research Center of the University of Ottawa. The SIR-600 samples included a control and pH = 2, pH = 3 and pH =4 exposed samples. The SEM tests were performed with the field emission SEM (JMS7500F, JEOL Ltd, Tokyo, Japan).

3.2.7 Sieve analysis

Sieve analysis of the samples of the long-term low pH solution exposure tests was conducted in Geotechnical Laboratories of the Civil Engineering Department of the University of Ottawa. The experimental procedure was adapted from ASTM method D6913/D6913M-17 (ASTM 2017). Approximately 50g of dried SIR-600 were loaded on top of a stacked series of pre-weighed sieves (12, 16, 20, 40 and US mesh). The sieve was shaken with a sieve shaker (SS-8R, Gilson company, Lewis Center, OH) for 10 minutes. At the end of the 10 minutes, each sieve was re-weighed to

obtain the mass of SIR-600 retained in them. The sieve analysis was performed on the control SIR-600 sample and samples exposed to different pH solutions.

3.2.8 BET

The BET surface area tests were performed in the Chemistry and Biomolecular Science Department of the University of Ottawa using N_2 adsorption-based surface area analyzer (ASAP 2020, Micromeritics, Norcross, GA). The samples were analyzed at 77K. Again, a control SIR-600 sample, and samples exposed to different pH solutions were analyzed.

3.2.9 Thermogravimetric Analyzer (TGA)

The TGA tests were performed in the Civil Engineering Department of the University of Sherbrooke using a differential scanning calorimetry analyzer (20-750^o C; 10^o C/min) for the control SIR-600 sample and samples exposed to different pH solutions were analyzed.

3.2.10 PXRD

Powder x-ray diffraction (XRD) was conducted at the Science, Technology, Engineering and Mathematics (STEM) complex of the University of Ottawa. The SIR-600 samples included a control and pH = 2, pH = 3 and pH =4 exposed samples. The XRD tests were performed with the Rigaku Ultima IV Diffractometer (I R Technology Services Pvt. Ltd, Mumbai, India)

3.3 Column Experiments

3.3.1 Column Loading Experiments

As this thesis is an expansion of Zhang's (2022) investigation into chlorine regeneration of SIR-600 loaded with EIMWW, it used the same EIMWW composition, the same column, the same column loading conditions, and the same media as Zhang (2022). The experimental column set-up is shown in Figure 3-2, it included a 2.2 cm ID, 100cm long clear glass column (ACE Glass, NJ) which was packed with 96.1 g of Resintech SIR-600. The bed depth was 30.5 cm and the bed volume (BV) was 116 cm^3. During the column loading experiments EIMWW was pumped by a high-pressure liquid metering pump (Optos Model3, Eldex, Napa, CA) from a 40L feed reservoir to the column. The line enters the column well above the media and flows downward through the media. The feed flowrate was at approximately 50mL/min or 25.8 BV/h. The effluent flowrate was checked periodically by weighing the mass of the collected effluent in one minute, and if there were deviations the pump was adjusted accordingly. The pump was very accurate and adjustments were seldom required. The loading cycles were 6 h long. Multiple loading-regeneration cycles were performed to establish stable operation.

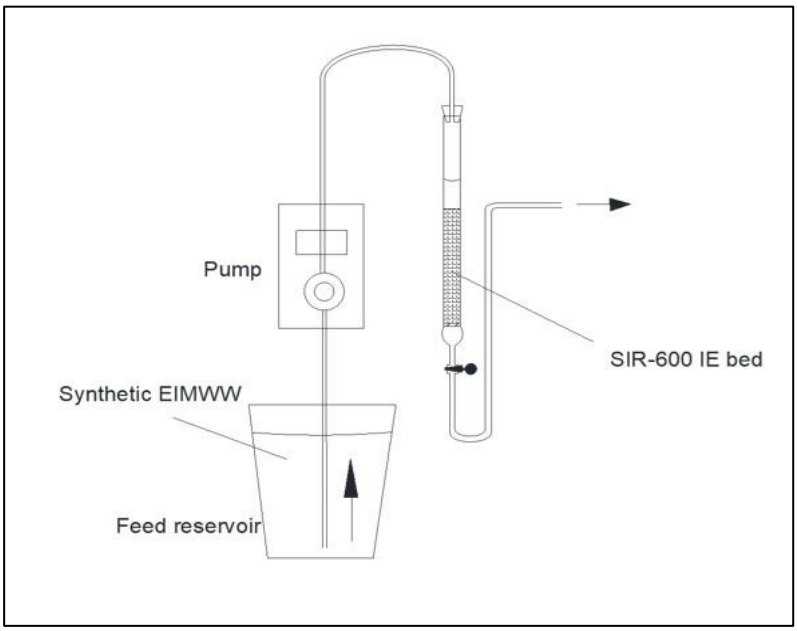

Figure 3-2 The schematic diagram of the column experimental setup (Source: adapted from Zhang 2022).

During the loading experiments effluent samples were collected at various predetermined intervals for chemical analysis. The ion uptakes by the IE media were calculated by integrating mass of ions removed from water which was determined by the breakthrough curve. The integral ion mass balance using trapezoidal rule to calculate the integral yields the following equation for the ion uptakes

$$q_{column} = \frac{1}{M}\sum_{i=2}^{n}\left(C_{feed} - \frac{C_{eff_i} + C_{eff_{i-1}}}{2}\right)\cdot(V_i - V_{i-1}) \quad \text{(eq. 4-2)}$$

where q_{column} is the uptake for a given species that has been achieved by the IE material within a column at a given time (mg or meq contaminant / g ion-exchange media); M is the dry mass of IE material present in the column (g); C_{feed} is the influent concentration (mg or meq/L); C_{eff_i} is the

effluent pollutant concentration at sample time i (mg or meq/L); $C_{eff_{i-1}}$ is the effluent pollutant concentration at sample time i-1 (mg or meq/L); and $V_i - V_{i-1}$ is the volume of EIMWW treated during step i(L). Next, the regeneration methods will be described.

3.3.2 Column Regeneration Experiments

The regenerations were conducted by passing the regeneration solution in the downflow mode, the same as in the loading cycle. During the regenerations a different pump was used in order to avoid damaging the high precision, high pressure liquid metering pump. The regeneration pump was a peristaltic pump (Masterflex L/S variable-speed economy drive, Cole-Parmer, Vernon Hills, IL). The regenerant flow rate was set at the pre-selected value for the given experiment, they were either approximately 16 mL/min or 50mL/min. In an attempt to optimize the chlorine regeneration experiments were conducted using different strength chlorine or chlorine-salt solutions, different flowrates and different duration regeneration phases.

Three different hypochlorite regeneration solutions, two salt+chlorine regeneration solutions and a salt regeneration solution were evaluated. The regeneration test conditions are presented in Table 3-2, the first set of regeneration conditions using 1000ppm Cl_2 regenerant solution, called R1000 and was chosen based on the results by Zhang (2022). The objective of the R1000 runs was to determine if the performance was similar to those reported by Zhang (2022) for the same operating conditions. The other various regeneration conditions were selected based on the results of the previous experiments and their justification will be presented as part of chapter 4. These tests served as the basis for the comparison of all regeneration solutions, and the performance of each regenerants was evaluated by the ion uptake of zeolite in the next cycle.

Table 3-2: Experimental set up for regeneration cycles.

TEST NAME	Prior regeneration solution	Post regeneration solution	Regenerant flowrate (mL/min)	Regeneration duration (h)	Water used to prepare regeneration solution
R1000 -1	R1000 ppm Cl_2	R1000 ppm Cl_2	16.1	4	Recycled regenerant
R1000-2	R1000 ppm Cl_2	R1000 ppm Cl_2	16.2	4	Recycled regenerant
R1000-3	R1000 ppm Cl_2	R1000 ppm Cl_2	16.3	4	Recycled regenerant
F250 -1	R1000 ppm Cl_2	F250ppm Cl_2	16.2	4	Distilled water
F250-2	F250ppm Cl_2	F250ppm Cl_2	16.2	4	Distilled water
R250-1	F250 ppm Cl_2	R250ppm Cl_2	49.9	5	Recycled regenerant
R250 -2	R250 ppm Cl_2	R250ppm Cl_2	49.2	5	Recycled regenerant
1.2%NaCl + R250	R250ppm Cl_2	R250 +1.2% NaCl	49.3	5	Recycled regenerant
1.2%NaCl + R250-2	R250 +1.2% NaCl	R250 +1.2% NaCl	49.3	5	Recycled regenerant
1.2%NaCl + R1000	R250 +1.2% NaCl	R1000 + 1.2% NaCl	16.0	4	Recycled regenerant
1.2%NaCl + R1000	R100 +1.2% NaCl	R1000 + 1.2% NaCl	16.0	4	Recycled regenerant
1.2% NaCl	R1000 + 1.2% NaCl	**1**.2% NaCl	16.0	2	Distilled water

3.4 Low-pH Exposure IE Material Durability Tests

During the chlorine regeneration tests it was observed that the pH decreased from pH 10 to approximately pH 3, this raised questions at to the impact of these low pH conditions on the durability and performance of the media. Thus, a set of SIR-600 long-term low-pH batch exposure experiments were conducted and their impact on the SIR-600 was characterized in terms of particle size distribution analysis, scanning electron microscope images, BET surface area analysis, surface gravimetric analysis (TGA), PXRD as well as TAN uptake. The exposure tests consisted of adding 50 g of SIR-600 to a 1 L glass bottle, filling it with water of chosen pHs, sealing them and then rotated in an end-over-end bottle tumbler for three months. The tumbler rotated at approximately 10 rpm, thus it provides gentle particle mixing so as to minimize particle attrition. After the three months the SIR-600 was recovered using vacuum filtration through 0.45 μm membrane filter (GN-6, Pall, Port Washington, NY), and then dried in an oven (~ 105ºC) for 24 hours. Then the cooled samples were characterized. The contact solutions consisted of solutions whose pH were adjusted to pH = 2, 3 and 4. In addition, there was another set of bottles with 50g of SIR-600 and 1 L of distilled water to act as controls, to help see if changes arose from the contact period with water and if there was particle attrition through the mixing. The acidic solution with a pH=2 was prepared by adding 2.04 mL with use of an automatic pipette (Labnet Biopette, Brockville, Canada) of 0.1 M solution of sulfuric acid. The pH=3 and pH=4 solutions were prepared using universal buffer mixtures, i.e., combinations of sulfuric acid with citric acid (ACS grade**,** Fisher Scientific, Waltham, MA). Table 3-3 shows the universal buffer mixtures for the adjustment of the pH (3 and 4). The characterization techniques utilized were described in the analytical methods sections. The TAN uptake capacity of the low pH exposed samples was evaluated, these tests are described in the next subsection.

Table 3-3: The universal buffer mixtures (Handbook of Chemistry & Physics, 2004).

0.2 M Na_2HPO_4 (mL)	**0.1 M citric acid (mL)**	**pH**
20.55	79.45	3.0
38.55	61.45	4.0

3.4.1 Batch TAN loading/uptake test

Batch loading tests were performed using the control SIR-600 and low-pH exposed SIR-600 samples from the three-month exposure tests. A schematic of these experiments is presented in Figure 3-3. First, 0.24 g of media were added to a clean 100 mL clear glass bottles, then filled with the synthetic EIMWW solutions. To prevent the loss of ammonia due to volatilization, the bottles were filled with the solution to the top without headspace. The threaded necks of the bottles were covered with Teflon tape so that the screw-on caps provided a good seal. Then, the bottles were placed into the end-over-end tumbler and rotated for 48 hours to provide gentle mixing and insure equilibrium. Then, the contents of the bottle were vacuum filtered through a 0.45 um membrane filter (Cole-Parmer PTFE Membrane, Quebec, Canada), the filtrate was then analyzed for the TAN, Ca and K concentrations.

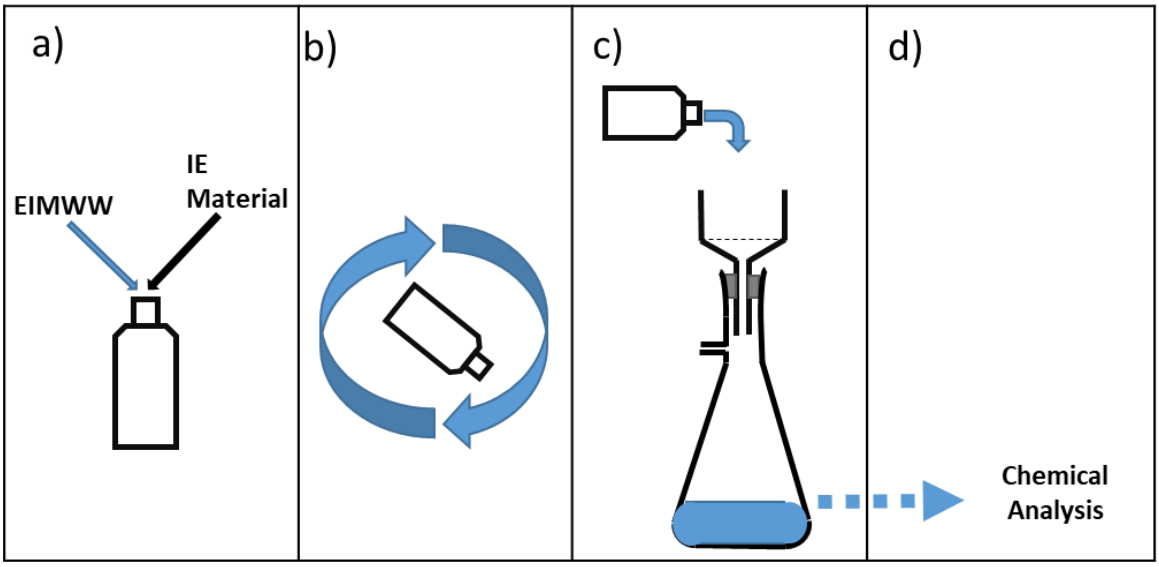

Figure 3-3. The schematic of batch loading phase. A) Prepare EIMWW and SIR-600 in bottles; B) Mixing in tumbler; C) Filtration; D) Chemical analysis. (Source: adapted from Chartrand et al. 2020).

The target ion concentration in the filtrate is considered as the equilibrium liquid phase concentration, C_{eq}. One can find the solid phase concentration at equilibrium (Q_{eq}) by using the following mass balance equation between the initial and final conditions for the solid-phase and liquid phase concentrations of this target ion.

$$Q_{eq} = \frac{(C_{\text{in}} - C_{\text{eq}})\,\text{V}}{M} \qquad \text{(eq. 3.2)}$$

Where Qeq is the ion uptake of the SIR-600 (meq/g), V is the volume of liquid treated (L); Cin is the influent ion concentration (meq/L); Ceq is the effluent ion concentration (meq/L); and M is the mass of SIR-600 (g). The ammonium, K^+ and Ca^{2+} concentrations of the liquid were then analyzed. The experiments were conducted in duplicate at room temperature (~220C), and the average results were reported

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Chapter 4: Chlorine Regeneration of a Zeolite Column for Ammonia Removal from an Explosive Impacted Mining Wastewater

Abstract

There has only been limited research on ammonia removal by zeolites followed by chlorine regeneration. To better simulate full-scale applications, this study used a continuous flow zeolite ion-exchange column system to assess the feasibility of chlorine regeneration of a zeolite used for the removal of ammonia from a synthetic explosive impacted mining wastewater (EIMWW). Also, the performance of several ion-exchange regeneration solutions (NaOCl and NaOCl-NaCl) was investigated and compared with a salt regeneration. The column's TAN (total ammonia nitrogen) uptake for the zeolite regenerated with a NaOCl and NaOCl-NaCl was fairly similar (0.19 meq/g - 0.23 meq/g), thus, these various regeneration schemes did not significantly impact the TAN uptake. It was also found that effluent pH, total chlorine level, and free chlorine level during the chlorine regeneration were positively related, seemingly confirming that the ammonia is oxidized to nitrogen gas and producing hydrogen ions. The NaOCl regeneration took longer to complete than the NaOCl-NaCl regenerations, however NaOCl regeneration is still promising because it does not generate a secondary waste stream as with NaOCl-NaCl regenerations.

Key words: Ion-exchange, zeolite, ammonia removal, column, chlorine regeneration

4.1 Introduction

In the mining industry, there is extensive use of ammonium nitrate explosives, which results in the generation of mining wastewaters with high concentrations of ammonia. Ammonia has several deleterious impacts on aquatic environments including a reduction in dissolved oxygen levels, eutrophication, and toxicity to fish (Environmental Canada 2010). Ammonia is present as either the ammonium ion or unionized ammonia depending on the pH and temperature, the unionized ammonia (NH_3) being responsible for the toxicity. Unfortunately, there are no analytical methods to differentiate between the two species. Thus, the ammonia concentrations can be quantified in terms of total ammonia nitrogen (TAN) concentrations, i.e., the sum of the ammonium ion (NH_4^+) and unionized ammonia (NH_3) concentrations. In accordance with Metal and Diamond Mining Effluent Regulations, under the Fisheries Act of Canada, the maximum wastewater effluent ammonia concentrations should not be acutely lethal (Minister of Fisheries and Oceans of Canada 2012). Also, to avoid any form of toxicity, Canadian Council of Ministers of the Environment (2010) advises that the NH_3 levels in freshwater bodies should be below 0.019 mg N/L. Biological nitrification is a common and effective ammonia removal method in municipal and industrial wastewater treatment. However, the biological treatment is not particularly suitable in the treatment of Canadian mining wastewaters because of its high sensitivity to low temperatures, operational complexity, and the toxicity due to heavy metals or high TAN concentrations (Stensel et al. 1976; Jorgensen & Weatherley 2003; Lin et al. 2013). To avoid the above issues one can resort to physical-chemical process alternatives, among these the following achieve substantial total ammonia removal: air stripping, breakpoint chlorination, chemical precipitation, and adsorption/ion-exchange (Dryden & Weatherley1989; Ding & Sartaj 2015; Chartrand 2018; Zhang 2022). While air stripping has the potential of being a practical method of removing ammonia, it

has some shortcomings. Air stripping becomes less efficient in cold temperatures and is impractical to use at all when the air temperature drops below freezing because icing causes operational problems. In addition, as ammonia has to be present as NH_3 to achieve high ammonia removal levels, the process has to be operated at a high pH (pH > 10-11). This results in significant scale deposition problems, and the effluent pH needs to be neutralized prior to discharge (Schoeman 1986; Zhang et al. 2017). The ammonia removal and recovery through the struvite chemical precipitation is effective but requires high chemical usage and leads to the production of sludge (Randall & Tsui 2002). In addition, transportation costs at remote Northern Canadian mines are extremely high because there are no roads, so the transportation of these chemicals to the mines and the transportation of the struvite to markets makes this option extremely expensive. Fortunately, at near neutral pHs (and lower) ammonia is in the form of NH_4^+ as opposed to NH_3, so ion-exchange (IE) technology is effective for TAN removal. It is also appropriate for the treatment of mining wastewater considering its fast-start-up times, relatively low-cost and simplicity of operation. Moreover, IE technology is of low-temperature sensitivity compared to biological treatment, thus it is suitable for Canadian mines that experience very low water temperatures (Jorgensen & Weatherly 2003; Zhang 2022).

Many IE studies conducted on TAN removal by natural and modified zeolites have reported that both zeolites are capable of TAN removal (Jama & Yücel 1984; Lin et al. 2013; Huang et al. 2018). Clinoptilolite is a natural zeolite (ion-exchange material) that can be used to remove TAN from aqueous solutions (Schoeman 1986; Koon & Kaufman 1971; Huang et al. 2015). The selectivity for the ammonium ion gives it a distinct advantage over conventional cationic IE resins (Guo et al. 2008; Chartrand 2020). Clinoptilolite has been widely researched, it has been shown to have high ammonia removals under low temperature, and it is also available at a low cost (Pommen

1983; Huang et al. 2015; Zhang et al. 2017). There has been a full-scale application in California (Svetich 1993).

While many ion-exchange studies used single solute ammonia solutions (Weatherley & Miladinovic 2004; Zhang et al. 2017), however practical applications of zeolites involve real wastewaters that contain many cations, such Ca and K, which compete for ion-exchange sites on zeolite. This competition can significantly influence NH_4^+ ion uptake (Chartrand 2018; Zhang 2022). The general order of cation selectivity for clinoptilolite was extensively studied (Ames 1960) and for equimolar concentrations it is:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{2+} > Al^{3+} > Mg^{2+} > Li^+$$

Hence, in multi-solute wastewater, clinoptilolite has a slightly higher preference for potassium than for ammonia under equal molar concentration (Chartrand 2018; Zhang 2022).

For sustainable application of ion-exchange, the media needs to be regenerated and reused. The standard alternative for zeolites regeneration are 3-14% NaCl solutions (Rahmani et al. 2004; Zhang 2022). During IE regeneration cycle, the ammonium ions get transferred to the regeneration solution so either: a) the regeneration solution must be discarded creating a secondary source of pollution, b) the ammonium needs to be removed from the regeneration solution prior to reuse; or c) the ammonium is allowed to accumulate in the regeneration solution which makes it less effective (Dryden & Weatherley 1989; Rahmani et al. 2004; Chartrand 2018). As an alternative approach, the regeneration can be conducted with NaOCl solutions. There has only been limited research on ammonia removal by zeolites followed by chlorine regeneration, most of these studies used batch tests (Huang et al. 2015; Zhang et al. 2017). These batch tests showed that zeolite regeneration by NaOCl was successful and minimized the NH_4^+ -N in the used regeneration solution (Huang et al. 2015). Most ion-exchange applications use continuous

flow column systems as opposed to batch mode. Zhang (2022) is the only reported chlorine column regeneration study with an ion-exchange column, he evaluated hypochlorite (1000 mg Cl_2/L) regeneration for an IE column system loaded with a synthetic explosives-impacted mining wastewater (EIMWW). This EIMWW contained competing cations (K and Ca) as well as ammonia, so it was a more realistic representation of field applications. Zhang (2022), as well as Huang et al. (2015) and Zhang et al. (2017), hypothesized that the ammonia nitrogen was converted to N_2 gas through breakpoint chlorination, thus ammonia was removed from the regeneration solution and prevented the above-mentioned secondary pollution and accumulation of ammonium in the regenerated solution. Zhang (2022) stated that the reaction was approximately described by the overall reaction of breakpoint chlorination:

$$2NH_4^+ + 3ClO^- \rightarrow N_2\uparrow + 3Cl^- + 3H_2O + 2H^+ \qquad \text{(eq. 4.1)}$$

As described by the above equation, H^+ ions are released, thus reducing the pH. The observed regeneration solution pH decreases from 10 to approximately 3 for a significant period of time at the beginning of the column regeneration. It should be noted that in water treatment practice the typical breakpoint chlorination occurs at Cl_2:N molar ratios of 1.6-1.7 because some more oxidized nitrogen compounds (such as NO_3^-) are also produced (Haas 2012). In addition, the chlorination reaction are very complex and they are impacted by a number of factors including pH and the Cl_2:N ratio (Black & Veatch Corp. 2010).

Zhang (2022) reported that the NaOCl regeneration was not as fast as the NaCl regeneration, and the necessary regeneration cycle duration was potentially not very practical as it was approaching the length of the loading cycles. Other operational challenges included problematic low pH

conditions and the bubble gas generation, the latter could limit the regenerant flowrates. Using batch tests Zhang et al. (2017) found that the effectiveness of the regeneration could be improved using a combined NaOCl-NaCl regenerant. Thus, there is a need to investigate NaOCl and combined NaOCl-NaCl regeneration conditions in more detail.

The main objective of this study is to assess and optimize NaOCl regeneration for a zeolite column used for EIMWW treatment. The specific objectives include:

- Evaluating less concentrated NaOCl solutions (<1000mg/L Cl_2) at different regenerant flowrates in an attempt to determine their effect on TAN uptakes, the TAN selectively, the operational problems discussed above, and the time required to accomplish the regeneration.
- Investigating the feasibility of reusing NaOCl and combined NaOCl- NaCl regeneration solutions.

4.2 Experimental Methods and Materials

To achieve the above objectives, a number of different alternative regeneration schemes were evaluated. The experiments consisted of IE column loading and regeneration cycles and were performed using the same synthetic EIMWW, the same column, the same media and the same loading conditions used by Zhang (2022). These conditions were chosen : (a) to confirne the result with Zhang Zhang (2022); and (b) to test different regeneration conditions to determine if they reduced the operational problems. Each cycle of the column tests was divided into two parts, a loading phase followed by a regeneration phase. The loading phase experiments were conducted by passing a synthetic EIMWW wastewater through a column packed with 0.7mm-1mm commercial natural zeolite (SIR-600, ResinTech Inc, Candem, NJ) particles. This zeolite was

previously found effective in the treatment of EIMWW(Chartrand 2018 ; Zhang 2022). As it is a commercial product, its source was not disclosed, but Chartrand (2018) found that it performed like a clinoptilolite. The EIMWW was prepared by disolving ammonium chloride, potassium chloride and calcium chloride hexahydrate (ACS grade, Fisher Scientific, Waltham, MA) in distilled water. This synthetic wastewater had approximately 21mg TAN as N/L (1.5 meq/L), 30 mg K/L (0.77meq/L), and 80 mg Ca/L (4 meq/L). These concentrations are realistic as they are very close to those reported by Schoeman (1986) for an underground mine wastewater (20mg TAN as N/L, 14 mg K/L, and 87 mg Ca/L). The effectiveness of the alternative regeneration schemes will be analyzed and measured in terms of the subsequent TAN loadings that can be achieved and the time required to achieve a significant degree of regeneration.

4.2.1 Column loading tests

The ion-exchange system consisted of a column and a pump. The tests used a clear glass column (ACE Glass Inc., Vineland, NJ) with a 2.2 cm inner diameter (ID) and 110 cm length. 96.1 g of SIR-600 were loaded into the column which resulted in an IE bed depth of 30.5 cm and a bed volume (BV) of 116 cm^3. A coarse sintered glass disc integrated into the column supported the IE materials. In the loading phase the flow was in the downward direction, the flowrate of the loading EIMWW solution was maintained at approximately 50mL/min (25.9 BVs/hr) by a high-pressure liquid metering pump (Optos Model3, Eldex, Napa, CA). The loading phases were 6h long. The effluent flowrate was regularly monitored by weighing the mass of effluent collected over one minute.

To determine the potassium, calcium and TAN removals, the uptakes were calculated by the integral ion mass balance equation with the trapezoidal rule integration which yields

the following equation:

$$q_{column} = \frac{1}{M}\sum_{i=2}^{n}\left(C_{feed} - \frac{C_{eff_i}+C_{eff_{i-1}}}{2}\right)\cdot(V_i - V_{i-1}) \quad \text{(eq. 4-2)}$$

where q_{column} is the uptake for a given species that has been achieved by the IE material within a column at a given time (mg or meq contaminant / g ion-exchange media);; M is the dry mass of IE material present in the column (g); C_{feed} is the influent concentration (mg or meq/L); C_{eff_i} is the effluent pollutant concentration at sample time i (mg or meq/L); $C_{eff_{i-1}}$ is the effluent pollutant concentration at sample time i-1 (mg or meq/L); and $(V_i - V_{i-1})$ is the volume of EIMWW treated during step i(L).

As discussed earlier, prior to the first experiment of this study, the system was used by Zhang (2022) to conduct column tests with the multiple loadings of a synthetic EIMWW and regeneration. The last regeneration cycle conducted by Zhang (2022) used a recycled 1000ppm Cl_2 solution as regenerant.

4.2.2. Column regeneration tests

After loading, the column was regenerated by circulating the regeneration solution in the downflow mode and collecting it for reuse, when applicable, in a later regeneration. The pH of all the regenerants solutions was adjusted to 10 before use to promote desorption, as at this pH the predominant form of TAN is NH_3. The regeneration test conditions are presented in Table 4-1, each was chosen based on the results of the previous experiments. First, a set of three loading and regeneration cycles were conducted using recycled 1000ppm Cl_2 regenerant solution, called

R1000. To better approximate field application the regenerations in this group of tests was prepared with the used regeneration solution from the previous regeneration cycle, it contained some Ca and K. The objective of the R1000 tests was to determine if the performance was similar to those reported by Zhang (2022) for the same operating conditions. The 1000 mg free Cl_2/L solution was chosen because it provides an excess quantity of chlorine required to oxidize TAN on the zeolite (i.e., Cl_2:N mass ratio >8) within the regeneration phase. All the chlorine solutions were prepared with commercial bleach (NaOCl). Once prepared, the regenerant was analyzed for free chlorine to confirm that its free chlorine concentration was 1000 mg/L. The regenerant flow rate for R1000 was approximately 16 mL/min (8.3 BVs/hr) during the 4h regeneration phases, the flow rate was chosen to minimize the problems associated with bubble generation (Zhang 2022). Second, two cycles of runs were conducted using fresh (not recycled) 250ppm Cl_2 solutions (F250), as the base for comparison with recycled 250ppm Cl_2 regenerant solutions (R250). The 250 mg free Cl_2/L solution was chosen to assess if the operational issues with gas bubble generation and low pH conditions could be avoided. For the R250 runs the flow rate was increased to approximately 50mL/min, to check if the regeneration could be accelerated using a lower chlorine concentration. Third, two sets of cycles were performed using a combination of NaCl and NaOCl prepared using recycled regenerant (R250+1.2%NaCl and R1000+1.2%NaCl). The combination of NaOCl+1.2% NaCl solutions were chosen to determine if it would result in a faster regeneration than with NaClO alone. The 1.2% NaCl regenerant was selected due to concerns about the excessive use of salt addition, this was still below the recommended 3-14% range for salt regeneration (Koon & Kaufman 1975; Chartrand 2018). Finally, for comparison a set of runs was conducted with 1.2% NaCl regenerant prepared with distilled water (1.2% NaCl). This last set of tests was conducted to quantify the benefit achieved by combining NaOCl and NaCl. It was

prepared by dissolving solid NaCl (ACS grade, Fisher Scientific, Waltham, MA) in distilled water. The ion uptake, the mass eluted during regeneration, the percentage of ion eluted of zeolite in the next cycle were calculated to evaluate the effectiveness of the regenerants. The mass of ions eluted (per g of SIR-600) was calculated using equation 4-2.

Table 4-1: Experimental set up for subsequent loadings for regeneration cycles.

TEST NAME	**Prior regeneration solution**	**Post regeneration solution**	**Regenerant flowrate [mL/min] (BVs/h)**	**Regeneration duration [h]**	**Water used to prepare regeneration solution**
R1000*	1000 ppm Cl_2	1000ppm Cl_2	16.1 (8)	4	Recycled regenerant
F250#	1000 ppm Cl_2	250ppm Cl_2	16.2 (8)	4	Distilled water
R250#	250 ppm Cl_2	250ppm Cl_2	49.9 (26)	5	Recycled regenerant
1.2% NaCl# + R250	250 ppm Cl_2	R250 +1.2% NaCl	49.3 (26)	5	Recycled regenerant
1.2% NaCl# + R1000	R250 +1.2% NaCl	R1000 + 1.2% NaCl	16.0 (8)	4	Recycled regenerant
1.2% NaCl#	R1000 + 1.2% NaCl	**1**.2% NaCl	16.0 (8)	2	Distilled water

*: 3 cycles were conducted.
#: 2 cycles were conducted

4.2.3 Analytical Methods

The TAN concentrations were quantified using the Nessler method which was adapted from Standard Method 4500-NH3 C (American Public Health Association 1992). The Ca, K and Na ion concentrations were quantified using a procedure adapted from Standard Method 3111B (American Public Health Association 2017) which uses flame atomic absorption spectrometer (AAS) (PinAAcle 500, PerkinElmer, Waltham, MA) analysis. Free and total chlorine concentrations were measured using Hach methods 8021 and 8167 (equivalent to Standard Method 4500-Cl G for drinking water) (American Public Health Association, 2017). pH values were measured with a pH meter (VER Symphony B10P, VWR, Radnor, PA) with a pH probe (VWR 89231-580, VWR, Radnor, PA).

4.3 Results and Discussions

4.3.1 Loading of the column that was regenerated with a recycled 1000ppm (R1000)

Three R1000 cycles (R1000-1, R1000-2 and R1000-3) were performed to establish that the column performance was stabilized. Figure 4-1 presents the breakthrough curves for the three key ions during the three R1000 loading tests, the main observations are as follows. First, the Ca breakthrough of each subsequent cycles started slightly later than the previous cycle. Second, the K breakthrough curves for the three cycles R1000 shows that each successive K breakthrough occurred earlier. Finally, the first TAN breakthrough starts slightly later, however later parts of the breakthroughs are fairly similar. The changes in the breakthrough curves occurred because the media was re-equilibrating to the regeneration conditions. The most direct comparison with the literature is the initial R1000 run with the final run by Zhang (2022) who used the same operating

conditions (6h loading + 4h regeneration) and the same media. The breakthrough curves for R1000 (Figure 4-1) are similar to those obtained by Zhang (2022), however the K and TAN breakthroughs occur slightly earlier while the Ca breakthrough occurs slightly later. The slight differences are not surprising given that the column is still stabilizing to these regeneration conditions as indicated by the changes observed in the R1000 cycles. Thus, these experiments serve to confirm the results of Zhang (2022).

Eq. 4-2 and the breakthrough curves were used to calculate the ion uptakes for the three R1000 loading cycles, as well as the last loading cycle performed by Zhang (2022), and these loadings are presented in Figure 4-2. Note that this study used the same column and media that was used by Zhang (2022), and the R1000-1 cycle was the next loading cycle performed after Zhang's last cycle. Thus, the R1000-1 ion uptakes should be similar to those obtained by Zhang (2022). Since the Ca breakthrough of each subsequent cycle occurred slightly later this led to a slight increase in the Ca uptakes with each cycle. The increasing Ca uptakes were rather surprising, however it follows the pattern observed by Zhang (2022). It appears this is the result of the column still re-equilibrating in conjunction with the fact that the Ca concentration is several folds higher than that of the other ions. On the other hand, the K uptakes remain fairly constant, the TAN uptakes decrease somewhat (0.25 to 0.18 meq/g) while the total ion uptakes slightly increased (0.60 to 0.66 meq/g). Thus, the ion uptakes in the current study confirm the work of Zhang (2022).

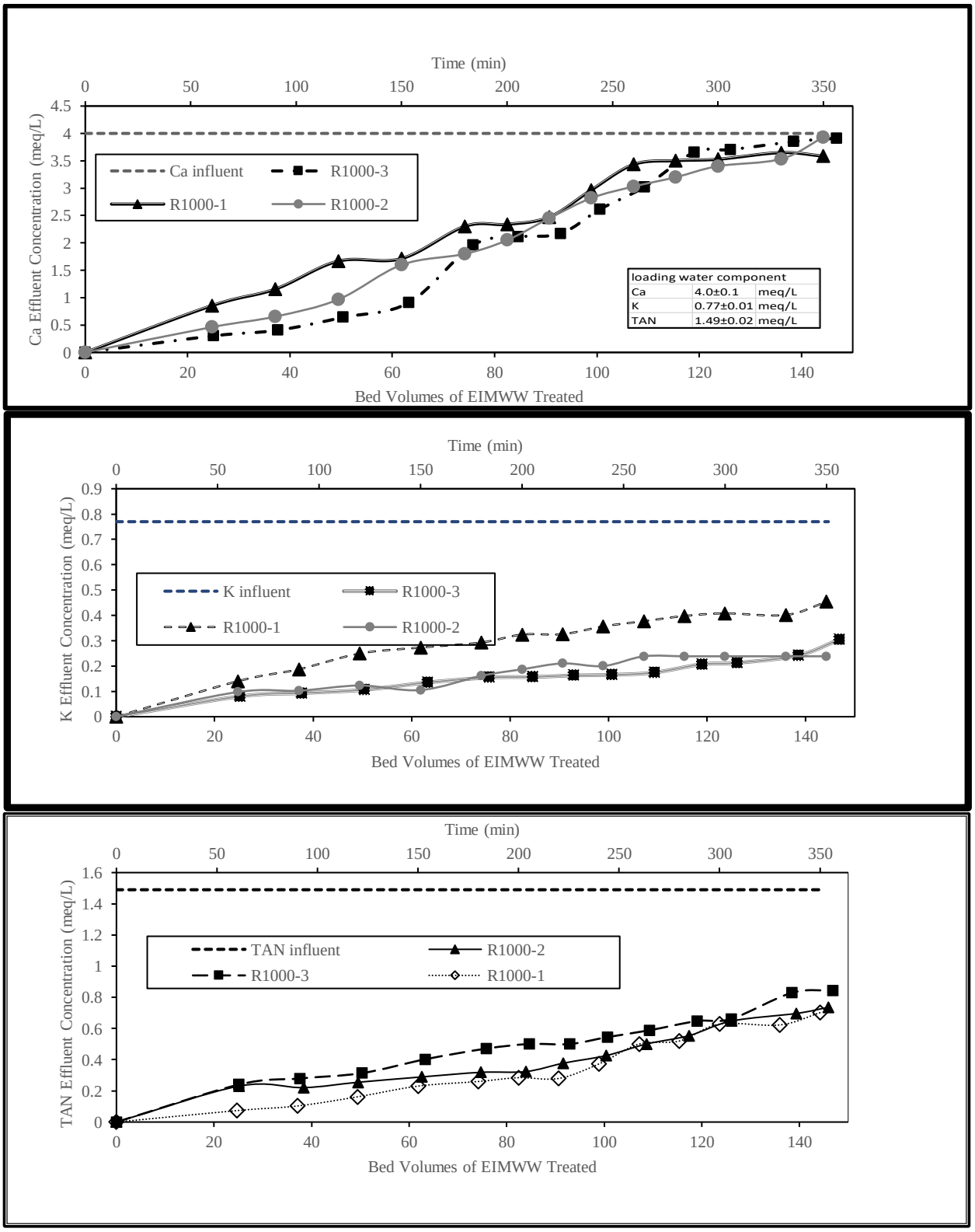


Figure 4-1 Breakthrough curves of Ca(top), K(middle), TAN (bottom) for the R1000 cycles.

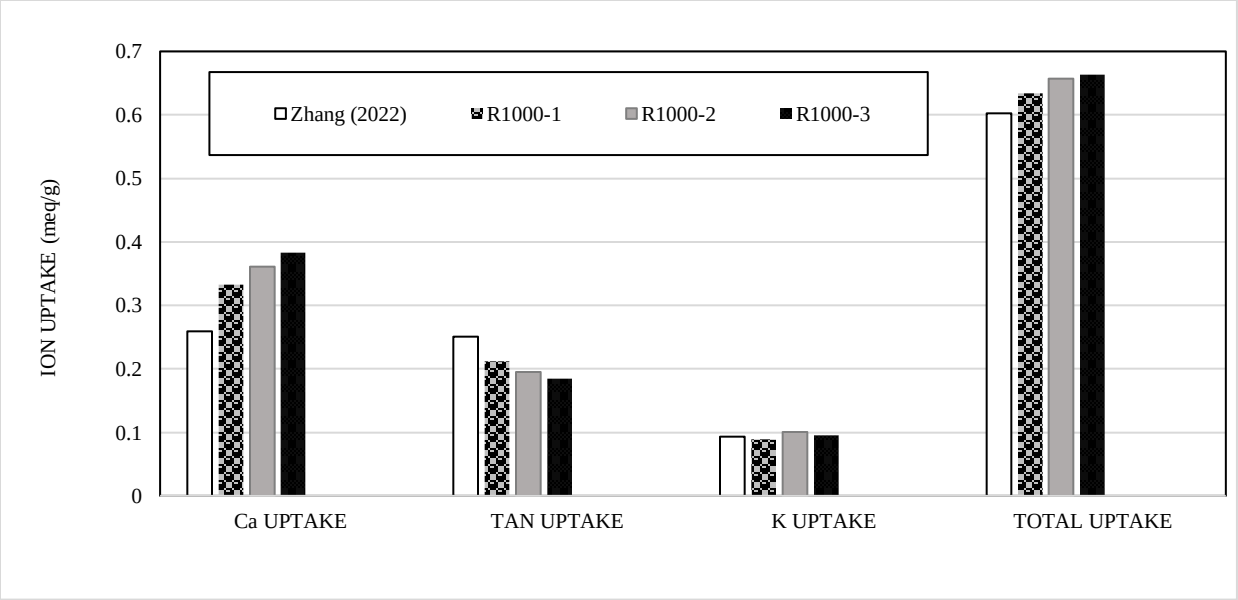


Figure 4-2 Comparison of the ion uptakes for the SIR-600 column's R1000-1,-2,-3 loading runs and Zhang (2022).

Schoeman (1986) conducted bench-scale column loading tests for clinoptilolite with an underground mine water of similar composition using salt regeneration. For the 2 mg NH_4/L breakthrough level the current study yielded less volume of water treated than Schoeman (1986) (15 vs. ~68 BVs) and lower TAN uptakes (0.025 vs. 0.086 meq/g). The lower performance may be explained by the higher flow rate (26 BVs/h vs. 10 BVs/h) used in this study, the zeolite type and larger zeolite particle size, and the different zeolite regeneration method.

Based on Ames (1960) clinoptilolite's selectivity rating for equimolar solutions, Ca has the lowest selectivity of the three ions studied, and K has a slightly higher selectivity than TAN, yet the column loadings in Figure 4-2 show a reverse trend. The fact that the column's ion uptake was highest for calcium is likely due to the much higher calcium concentration in the feed (Ca=4.0 meq/L; K=0.77 meq/L; TAN =1.49meq/L). This may also explain why the column had a higher

TAN uptake than K uptake. The latter may have also been influenced by the dynamics of the column system as suggested by Chatrand et al. (2020)

4.3.2 Regenerations of the column with recycled 1000ppm Cl_2 (R1000) solutions

The chlorine-ammonia reactions are complex and they are impacted by pH and the Cl_2:N ratio. When the Cl_2:N molar ratios is less than 1.5, the sequential classical reactions that occur indicate that NH_3/NH_4^+ is oxidized to NH_2Cl, $NHCl_2$, and then to NCl_3 (Black & Veatch Corp. 2010). As the Cl_2:TAN ratio increases to 1, the main product is monochloramine (NH_2Cl). With further increases from 1 to 1.5, dichloramine and trichloramine are formed and they are mostly converted to N_2 gas, which is lost to the atmosphere. Addition of chlorine beyond the above level results in increasing free chlorine concentration in the solution. The critical 1.5 level is often referred to as the breakpoint chlorination (Haas 2012).

During the Cl_2 regeneration of the TAN loaded SIR-600 column the same breakpoint chlorination reactions appears to take place (Zhang 2022). To investigate the mechanisms of the chlorine regeneration process, the pH, regeneration effluent's free chlorine, and total chlorine concentrations were measured at different times during the regeneration phase (Figure 4-3). This figure shows that for the initial 13 bed volumes of regenerant processed the free chlorine concentrations were much lower (below 18 mg/L) than the feed concentration and then increased to 980ppm and dropped to approximately 830 mg/L at the end of the regeneration process. The total chlorine concentrations were very close to the free chlorine concentrations throughout the regenerations. Thus, the combined chlorine concentration, i.e., the difference between free chlorine and total chlorine curves, was small during the regeneration (avg= 15 mg/L). This suggests that only a limited amount of chloramines remained.

Figure 4-3 also shows that the pH dropped almost immediately from 10 to approximately 3 and remained at such low levels for about the first 16BVs of regenerant processed. The initial sharp decrease was caused by the regenerant replacing the distilled water, i.e., present within the column's voids prior to introduction of the NaOCl solution. From 16 to 20 BV of regenerant processed, the pH increased sharply to approximately 7.5 and increased gradually thereafter reaching a final value of approximately 9. The similar patterns in the pH, total and free chlorine in the effluent regenerant (Figure 4-3) suggest the pH is related to the free chlorine. This is presumably because of the reactions described by Eq. 4.1. Note that as was the case with Zhang (2022) the pH decreased to a value of 3 as opposed to a value of 2 as predicted by Eq. 4-1.

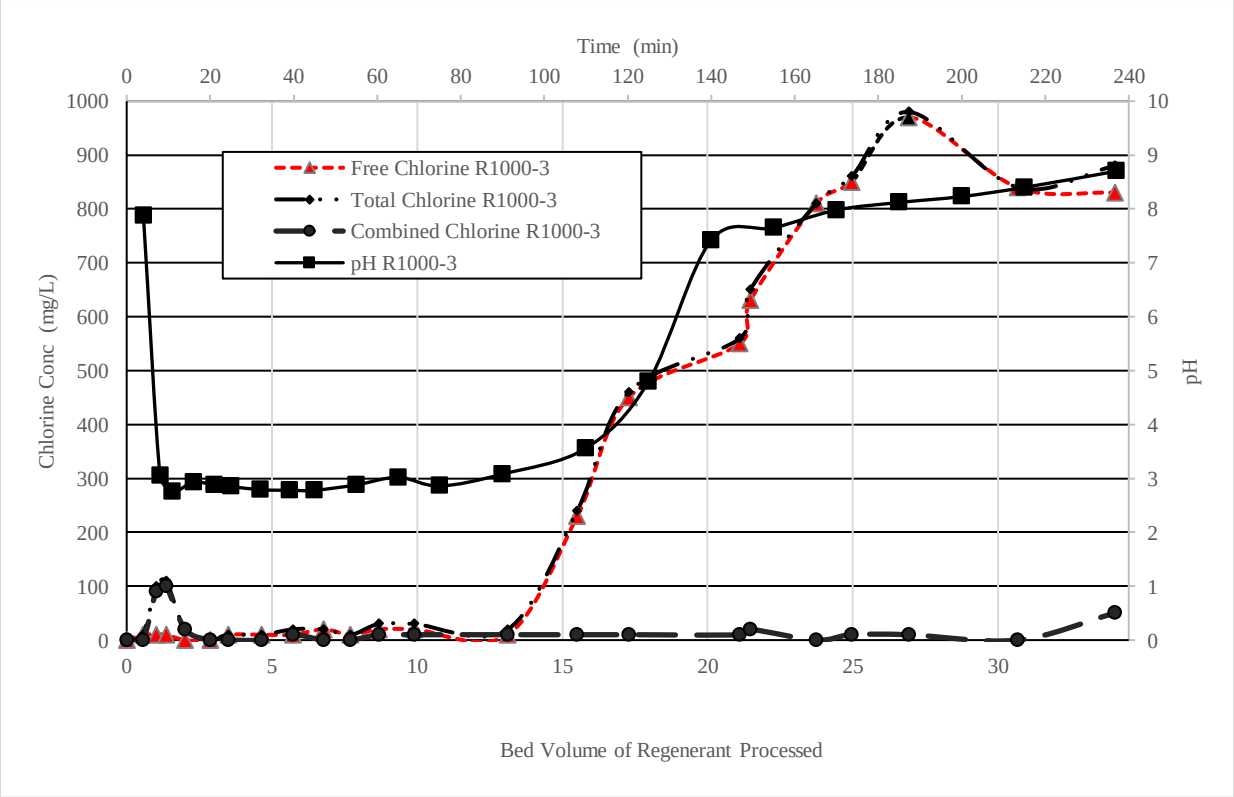


Figure 4-3 Effluent regenerant water quality during the 4h-regeneration in R1000-3: pH, combined chlorine, total chlorine, and free chlorine.

Figure 4-4 presents the key ion effluent concentrations profiles during the R1000-3 regeneration cycle, the other regeneration cycles yielded similar results and only the last cycle is presented as it should be the most stable. As expected, initially there were sharp peaks, then the effluent Ca and K concentrations decreased with time. The Ca effluent concentration was significantly higher than those the K effluent concentration, particularly during the initial peak period. This was expected as the Ca uptake was almost four times higher than the K uptake. It should be noted that because some of the TAN is oxidized to N_2 gas and escapes, the TAN concentration profile of the efffluent regenerant does not fully account for TAN removed from the zeolite by the regeneration. This is the apparent reason for the lack of an initial peak in the TAN profile. As the nitrogen content of the gas was not quantified, it is impossible to perform a complete nitrogen mass balance.

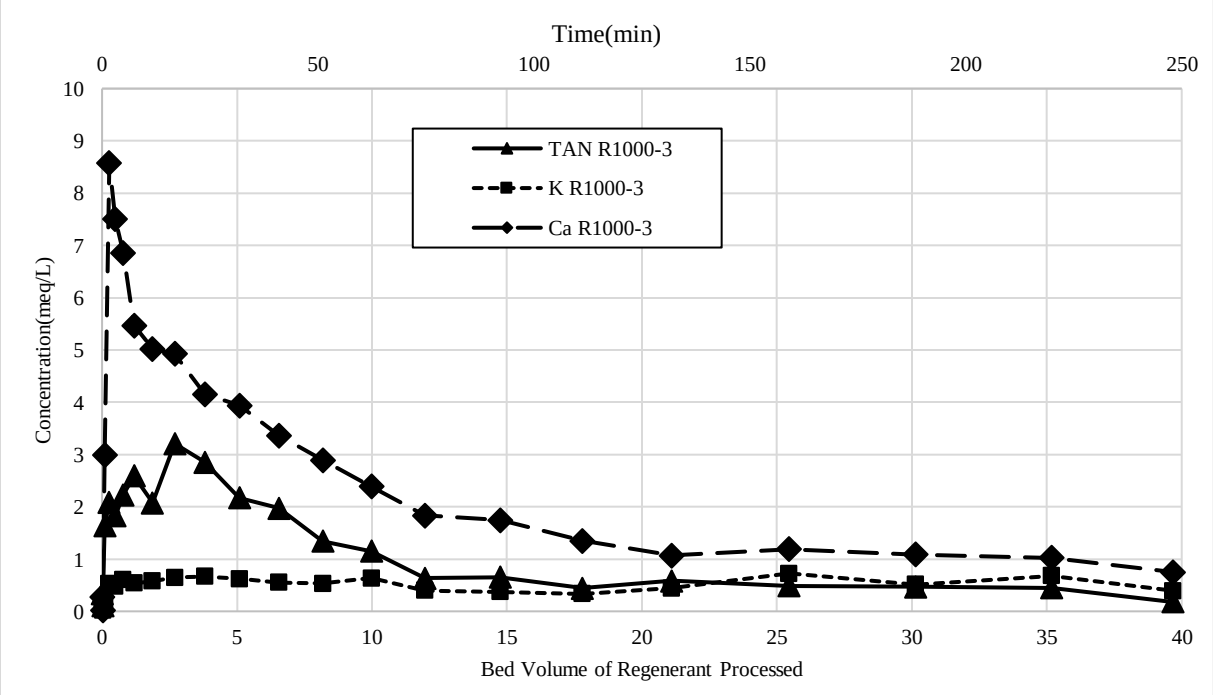


Figure 4-4 Comparison of the ions effluent concentration during the regeneration of R1000-3.

The major concerns arising from the R1000 cycles were the low pH and gas bubble generation during the regeneration. Accordingly, for the next sets of loading/regeneration cycles the concentration of the chlorine regenerant was reduced to 250 ppm Cl_2.

4.3.4 Comparison of the regeneration/loading cycles with fresh (F250) and recycled 250 (R250) chlorine solution at different regeneration flowrate.

These set of tests used 250 mg/L chlorine regeneration solutions to determine if reducing the chlorine concentration would minimize the problems encountered in the R1000 cycles (i.e., slow rate and temporary low pHs) and determine its effect on TAN uptakes/TAN selectivity. As discussed earlier the only other chlorine regeneration of zeolite columns loaded with TAN used 1000 mg/L chlorine (Zhang, 2022), thus the 250 mg/L chlorine regeneration solutions represent new knowledge. Firstly, the F250 tests were conducted followed by the R250 tests. The F250 cycles [(6h loading phase + 4h regeneration phase (@16mL/min)] was conducted with a fresh 250 mg free Cl_2/L regeneration solution, prepared with distilled water. Figure 4-5 shows the comparison of the free chlorine, combined chlorine during the regeneration of the second F250 cycle (i.e., F250-2). The effluent combined chlorine concentration approaches the feed free chlorine levels (250 mg free Cl_2/L) at 5BVs of operation, remains over 200 mg Cl_2 /L for until about 12 BVs and then decreases gradually reaching 40 mg Cl_2 /L at the end of the regeneration. This is in contrast to the result for R1000-3 (Figure 4-3) in which the average combined chlorine concentration was only 15mg/L. During the F250-2 regeneration, the free chlorine gets converted into combined chlorine and implies that the 250 mg Cl_2 /L solution provides insufficient chlorine

to drive the TAN conversion to N_2 gas and instead the N remains as chloramines. The effluent regenerant pH decreases much more gradually than in the R1000 regeneration, but it plateaus at a value of approximately 3.25 after 25BVs. It is suggested that the pH of the effluent regenerant is related to the free chlorine level, since most of the influent free chlorine is consumed producing combined chlorine instead of fully oxidizing the TAN to N_2 and H^+.

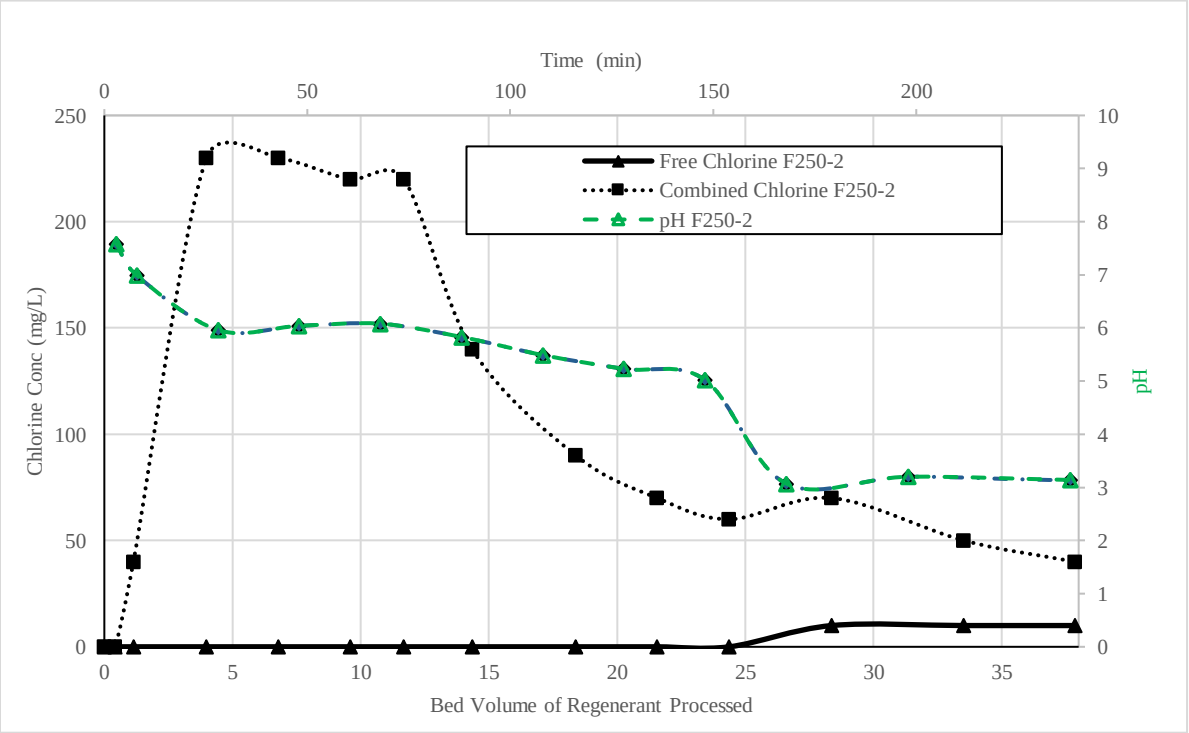


Figure 4-5 Effluent regenerant water quality during the 4h-regeneration in F250-2: pH, combined chlorine, and free chlorine.

The insufficient chlorine for full ammonia oxidation can be determined using eqn 4.1, which shows that the oxidation of ammonia nitrogen by chlorine to gaseous nitrogen at the breakpoint would theoretically require 1.5 mole of chlorine (Cl_2) per mole of ammonia oxidized (Black and Veatch Corp. 2010). Based on the TAN on the column prior to regeneration and the 16 mL/min of 250

mg/L free chlorine in the regenerant, the 1.5 Cl_2: TAN ratio for breakpoint chlorination would be theoretically achieved in 358 minutes. As this is substantially higher than 240 minutes (4 hours), it is evident there was not enough Cl_2 delivered to achieve breakpoint chlorination. This suggests that the F250 regeneration needs a greater throughput of free chlorine. This could be achieved through using a larger chlorine concentration (which was already analyzed earlier with R1000) or a larger regenerant flowrate. Thus, the next regeneration tests (R250) were conducted with a larger regenerant flow rate (50mL/min) and had a longer regeneration phase (5h). The R250-1 [(6h loading +5 h regeneration) regenerant Cl_2 regeneration solution was prepared with the used regeneration solution from the previous regeneration cycle (F250-2) while the R250-2 was prepared from the previous used regeneration cycle (R250-1).

The regeneration phase of R250-2 (i.e., the second R250 cycle) using 50mL/min of regenerant yielded a very different free chlorine profile (Figure 4-6) from that 16mL/min for F250-2 (Figure 4-5). For the R250-2 regeneration, the effluent regerant free chlorine concentration rises to much higher levels because there was more free chlorine present within the column which drove the reaction further as evident from the higher effluent free chlorine concentration than for the than for F-250 (30 to 180 mg/L versus <10 mg/L).

As discussed earlier, the pH of the regenerant effluents is related to the chlorine level in the effluents. During the recycled 250 Cl_2 /L regenerations the effluent pH decreased very rapidly to approximately 3.8, increases starting at 33BVs and plateaus at about 44BVs of operation and then gradually increases to approximately pH= 8.

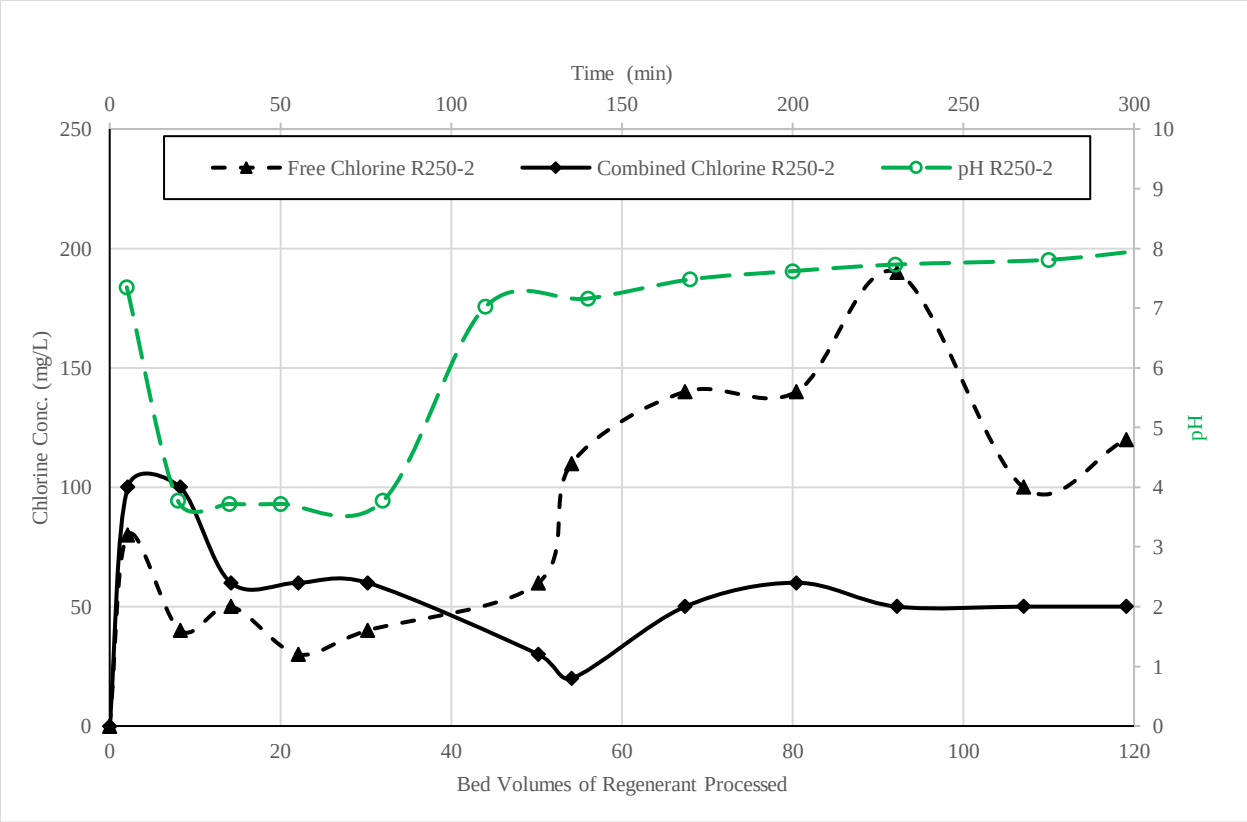


Figure 4-6 Effluent regenerant water quality during the 5h-regeneration in R250-2: pH, Combined chlorine, and Free Chlorine.

It is important to compare the combined chlorine effluent profile of the regeneration using 250 mg Cl_2/L solutions. The presence of significant concentrations (50 mg/L) in the effluent shows that there was insufficient chlorine to convert the ammonia to N_2 gas. The effectiveness of the F250 and R250 was determined by considering the time required to provide the necessary mass of chlorine for breakpoint chlorination. F250 needed 358 minutes to provide the necessary chlorine, then because of the higher flowrate the time necessary for R250 to deliver the same chlorine would be about 114 min or ~ 50 BV. Given that the effluent regenerant free chlorine concentration does not continue increasing (drops towards the end) and there is substantial combined chlorine, this

means sufficient chlorine does not reach all the media at this flowrate possible channeling. Thus, the increase in the combined chlorine (50mL/min) after 54 BVs in the R250 regenerations was not effective. To reduce the amount of combined chlorine produced (to yield a more effective regeneration) a lower flowrate of regenerant containing a higher concentration of chlorine is necessary. Initially the Na concentration of the used regenerant were not measured, when this information became available for the R250 used regenerant, it became evident that the Na concentration of the effluent regenerant solution decreased significantly, 80% of the Na was consumed during the regeneration. This confirms that part of the regeneration was due to the (14 meq Na/L) in the NaOCl regenerant. The speed of the regeneration can be determined in terms of the BV required compared to standard salt regeneration from the literature. The column studies (with salt regeneration) in the literatures seem to regenerate the columns in about 30 BV(Schoeman 1986; Koon & Kaufman1971). As it was not possible to conduct a nitrogen mass balance for the NaOCl regeneration, it is impossible to determine when the regeneration is complete. Instead one needs to use indirect measures such as the effluent regenerant pH reaching a high level. For the chlorine regeneration (Figure 4-6), the effluent pH reaches a plateau stage at approximately 60 BV, thus the NaOCl regeneration takes significantly longer to complete than NaCl regeneration. One can estimate the extent of the regeneration of the zeolite in terms of TAN using the free chlorine concentration of the effluent regenerant. If one ignores the last two points in the free chlorine profile (Fig. 4.6), which have lower free chlorine concentrations, one would assume that the regeneration is substantially complete in 230 minutes. This is longer than the approximate 180 minutes suggested by the analogous figure (Fig. 4.3) for the 1000 mg/L free chlorine regeneration. And thus, the R-250 regeneration is even slower than the R-1000 regenerations.

The different regeneration flowrate for F250 (16 mL/min) and R250 (50 mL/min) also resulted in different breakthrough curves despite both loading operations for R250 and F250 were the same. The Ca, TAN, and K breakthrough curves of cycles F250 and R250 were analyzed, and their main characteristics were as follows. The Ca breakthrough occurred significantly later for the R250 than F250 loadings run resulting in a higher Ca uptake. The reason may be that there was that more Ca eluted during the early part of the regeneration and part of the initial peak was missed because of the low frequency of the sampling. In the next set of experiments more effluent samples were collected during the early part of the regeneration. The K breakthrough for R250 loading occurs slightly later than for F250. Accordingly, the K for the R250 loading cycle achieved slightly high K uptakes than F250. The R250 TAN breakthrough curves were delayed compared to those for the F250 cycles. Thus, the after each loadings of the R250 regeneration the TAN uptakes increases. The calculated Ca, TAN and K uptakes for the loading run are presented in Figure 4-7, the TAN and K uptakes increased slightly, while the Ca uptake increased significantly. The near doubling of the calcium ion uptake was presumably due to the 3.1 times higher mass of free chlorine and Na applied in the R250 regeneration. Furthermore, the switch to a fresh 250 mg Cl_2 /L solution (F250-2) (from a 1000 mg Cl_2 /L solution, i.e., R1000) resulted in a reduction in the Ca, TAN, and K uptake of 18.3, 2.5, and 5 %, respectively. These results are reasonable because the lower chlorine concentration leads to a less effective regeneration.

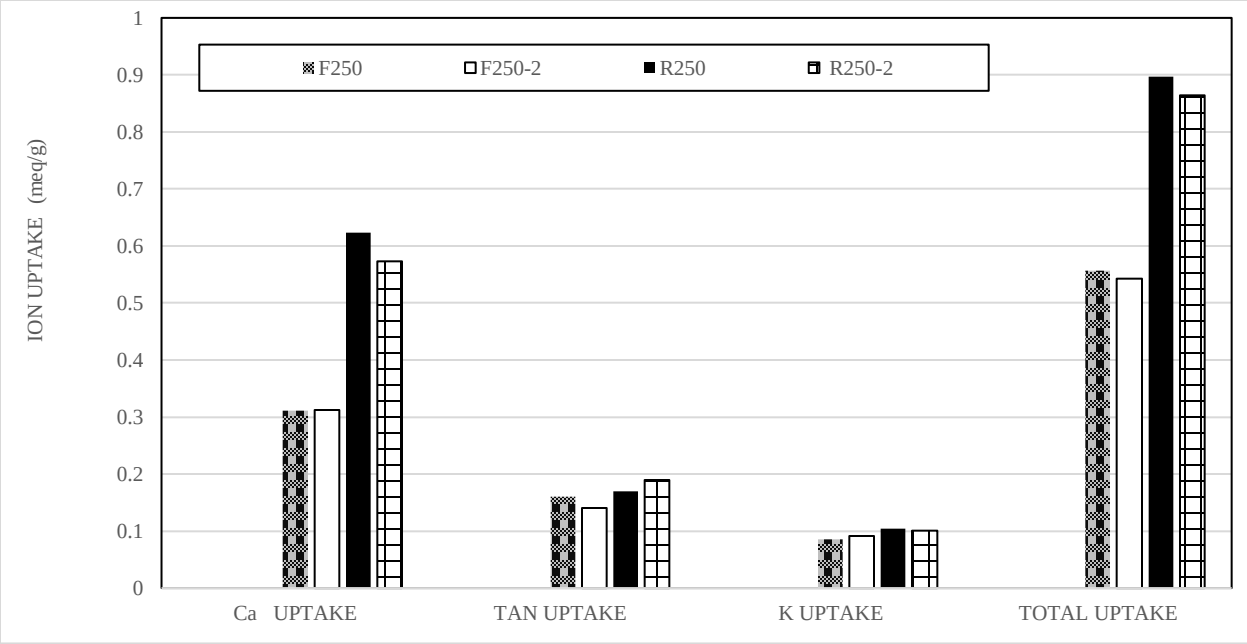


Figure 4-7 Ion uptakes for the SIR-600 column's all F250s'and R250s' loading phases.

As mentioned above the regeneration of ammonia-loaded zeolite columns with 250 mg/L Cl_2 solution represents new information. The 250 ppm Cl_2 solution improved the low pH conditions (3.2 for F250 and 3.6 for R250 vs. 2.8 for R1000), however the pH levels are still very low. The F250 and R250 regenerations avoided the gas bubble generation problem which was a concern for the R1000 regeneration. Given the results of the R250 cycles, it is clear that the 50 mL/min flowrate is too high due to the greater combined chlorine formed than in the R1000 regeneration (avg. 50 mg/L versus avg. 6.5 mg/L) over the entire cycles. And as discussed above the R-250 regenerations proved to be slower than the R-1000 regenerations.

Alternative chlorine regeneration schemes may prove superior, for example a 500 mg/L free chlorine solution processed at 25 mL/min. However, there are many potential concentration-flowrate combinations that may work better and this will require a lot experiments to identify if faster chlorine regenerations are possible. Due to our industrial partner's desire to identify more

rapid regenerations it was decided to forego the above experiments and to investigate the use of regeneration solutions with NaOCl and a small amount of NaCl. The next set of loading/regeneration cycle included the addition of NaCl to the recycled regenerant for a lower chlorine concentration (250 mg free Cl_2/L) and a higher chlorine concentration (1000 mg free Cl_2/L) to determine the influence of NaCl to a hypochlorite solution.

4.3.5 Cycles using combined NaOCl-NaCl regeneration solutions

The objective of this section is to assess if the addition of salt to the regeneration solution would result in faster regenerations and higher uptake capacities. Conventional NaCl regeneration solutions range from 3 to 14%, given that NaCl is used in conjunction with NaOCl, it was decided to use 1.2%NaCl for these tests. Two cycles were performed for the 1.2% NaCl+ R250 regenerations at 50mL/min (6h loading +5h regeneration) to obtain relatively stable results because the media in the first loading phase was actually regenerated using the previous regeneration conditions. Figure 4-8 shows that during the regeneration of 1.2% NaCl+R250-2 cycle, the effluent ion concentrations at the initial peak (0-10BV of regenerant processed) were significantly larger than those for the R250-2. During the regeneration with 1.2% NaCl+R250-2, the effluent Ca (top), K (middle) and TAN concentration increased rapidly reaching a peak and then gradually decreased from till the end of the run. The higher sodium concentrations (205 meq Na/L +14 meq Na/L) in the 1.2% NaCl + R250 regeneration solution was able to displace the previously sorbed ions therefore more Ca, K and TAN came out of the system. Again, the chlorine in the regenerant leads to the partial regeneration via the ammonium-chlorine reaction yielding nitrogen gas, thus the TAN elution does not provide a complete picture of the TAN removed from the media during the

regeneration. After 20 BV of regenerant processed the effluent TAN (bottom) concentration profiles TAN for 1.2% NaCl+R250-2 cycles are very similar to that for the R250 cycle. They differ during the first 20 BV of regenerant processed, the 1.2% NaCl+R250-2 regeneration shows a TAN peak while the R-250 regeneration does not, presumbaly because of TAN elusion due to the higher sodium concentration (205 meq Na/L vs 14 meq Na/L).

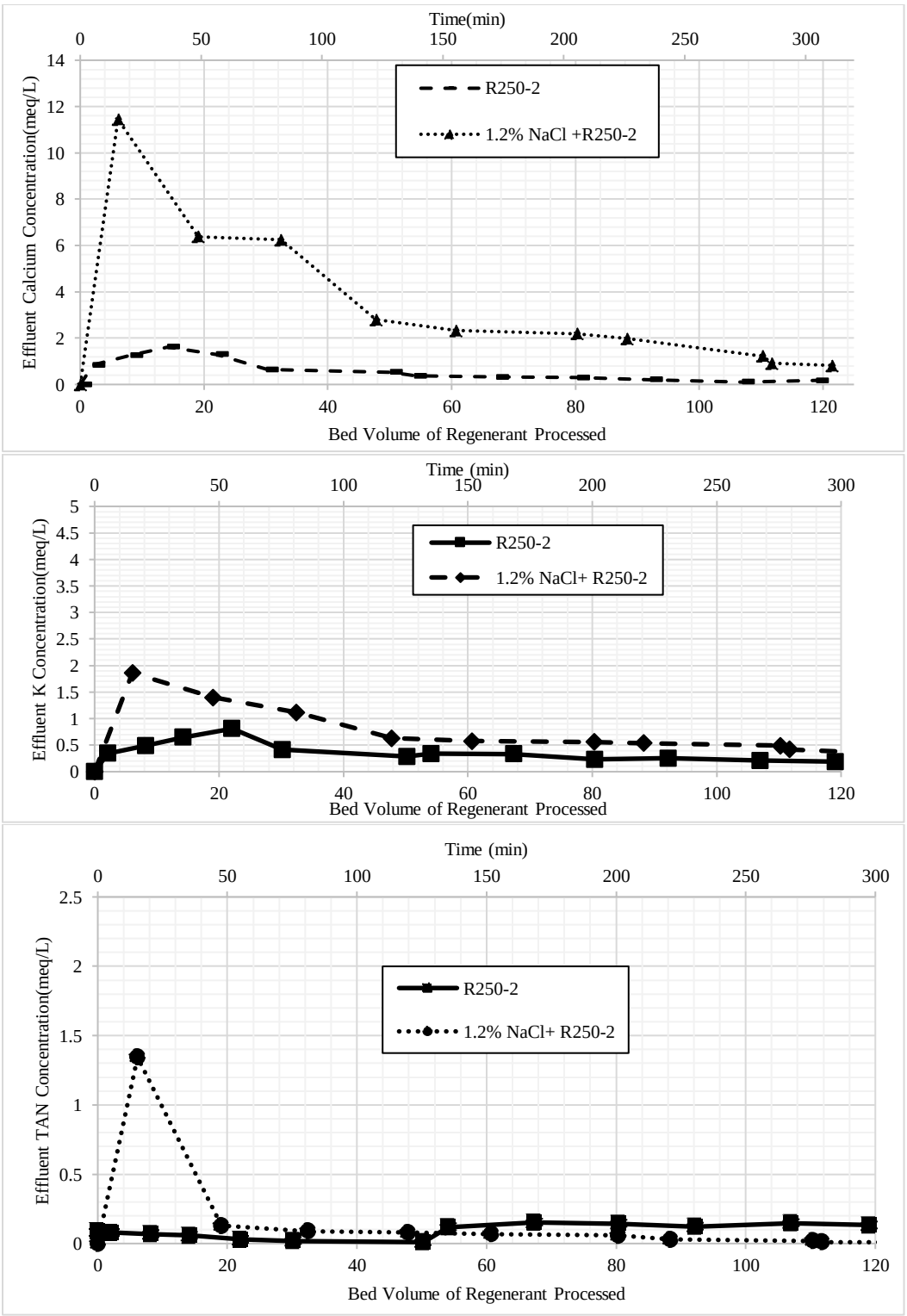


Figure 4-8 The comparison of effluent ion concentration profiles Ca(top), K(middle), TAN (bottom) during the R250 and 1.2% NaCl +R250-2

The free chlorine concentrations and pH were measured in the regeneration effluent samples taken at different times during the regeneration phase (Figure 4-9). Figure 4-9 (top graph) shows effluent regenerant free chlorine concentrations 1.2% NaCl+R250-2 was significantly lower for the first 20BVs of operation than R250-2. Thereafter, the 1.2% NaCl+R250-2 had higher free chlorine concentrations. Figure 4-9 bottom shows that more TAN was eluted during this period of the 1.2% NaCl+R250-2 regeneration, so the lower initial free chlorine concentrations suggests that more TAN was being eluted and significant quantities of it were being oxidized by the chlorine. Thus, there appears that there was subtantial regeneration during this period. Thereafter, the free chlorine concentrations increased gradually to the 170-180 mg free Cl_2/L level and remained so for most the regeneration, note that during this time these concentrations were significantly higher than those for the R250-2 regeneration. These higher free chlorine levels for the 1.2% NaCl + R250-2 than in the R250-2 regeneration (Figure 4-9) likely occurred because there was less TAN remaining to be oxidized. This indicates that the 1.2% NaCl+R250-2 regeneration proceeds more rapidly.

In turn, this suggests that for the chlorine alone regeneration (e.g., R-250) the chlorine needs to diffuse to the TAN sites on the SIR-600 in order regenerate the media. The pH of the effluent R250-2 regeneration achieved a similar pattern as 1.2%NaCl+R250-2 regeneration. It seems that if pH is nearly the same, the H^+ generation should be very similar, and the amount of TAN oxidized by chlorine is nearly the same. This suggest that elution prior to oxidation is not so important to TAN oxidation. However, as mentioned above, the effluent free chlorine concentrations suggest the media is regenerated more rapidly by the 1.2% NaCl + R250 solutions. The uptakes of these set of experiments, which are indicative of the extent of the regeneration at the completion of the regeneration cycle, will be discussed in conjunction with those of the next set of experiments.

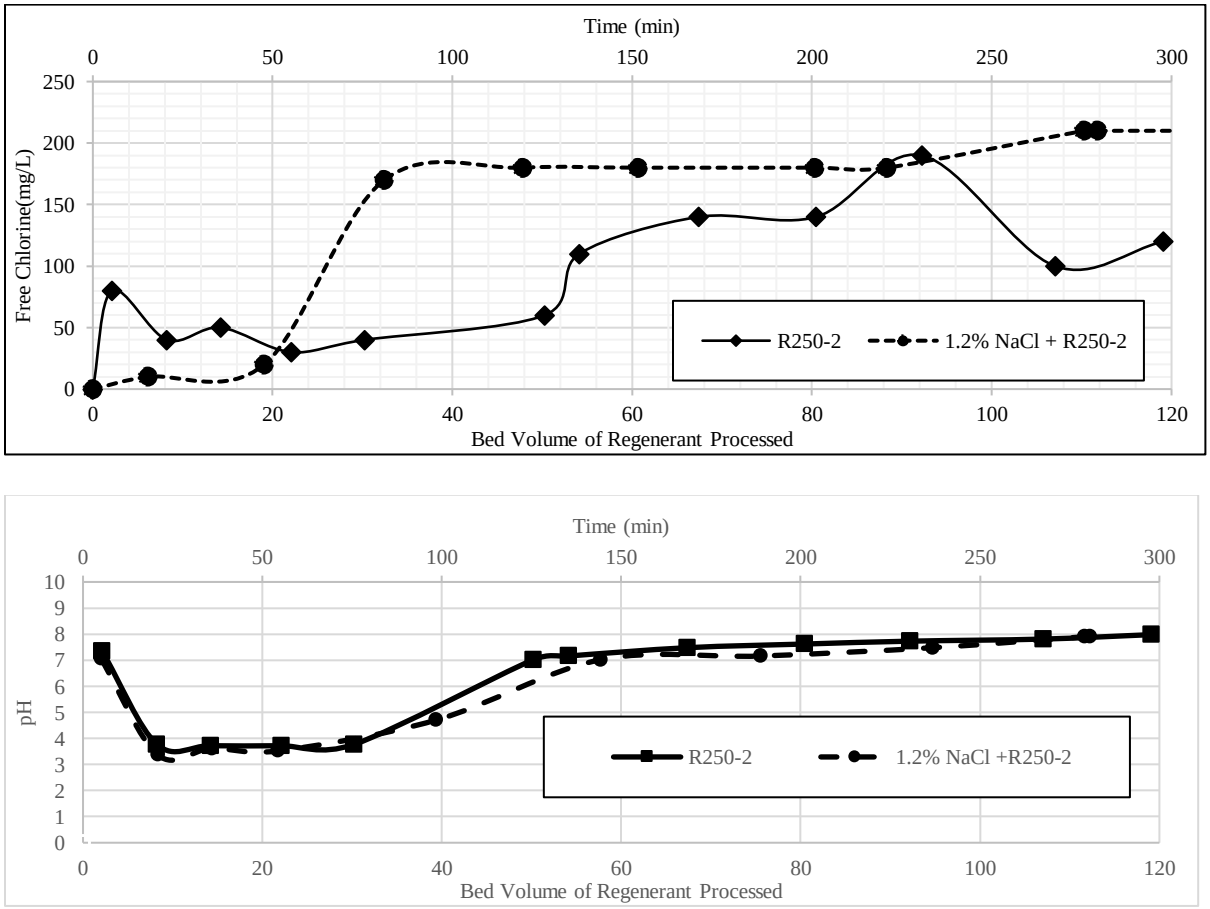
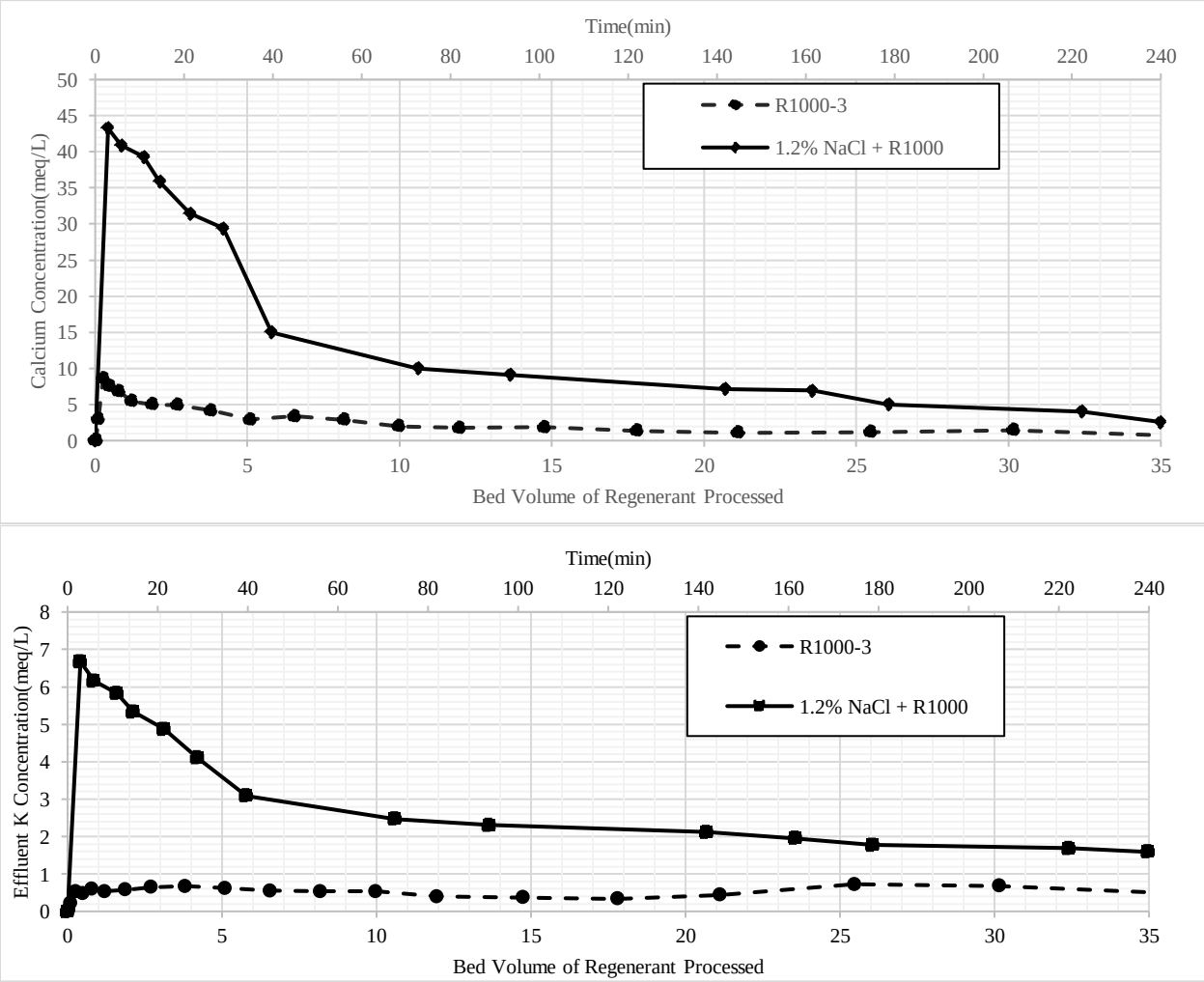


Figure 4-9 The comparison of Free chlorine(top) and pH(bottom) for the SIR-600 column's during and 1.2% NaCl+ R250-2

To evaluate if regeneration can be accelerated, the next set of experiments used regeneratoions with recycled 1.2% NaCl plus a higher chlorine concentration (1000 mg free Cl_2 /L) solution (1.2% NaCl + R1000). One of the considerations of combined NaClO-NaCl regeneration (1.2% NaCl + R1000) is a higher chlorine concentration should lead to a lower pH and possibly more bubbles. Accordingly, the regenerant flowrate was reduced from 50 mL/min to 16 mL/min (8.3 BVs/h), which helped avoid this problem during the R1000 regenerations. This part of the section compares

its results to those of NaCl + R1000 the R1000 cycles presented in section 4.3.1 to 4.3.3. Figure 4-10 describes the effluent regenerant Ca, K and TAN elusion during the 1.2% NaCl +R-1000 and R1000-3 regenerations. The Ca(top) and K (middle) profiles show that during these regenerations, both the Ca & K concentrations for the 1.2% NaCl + R1000 peaked to significantly larger values than for the R1000-3 regeneration and concentrations of these ions remained remained higher for the length of the regeneration phases.



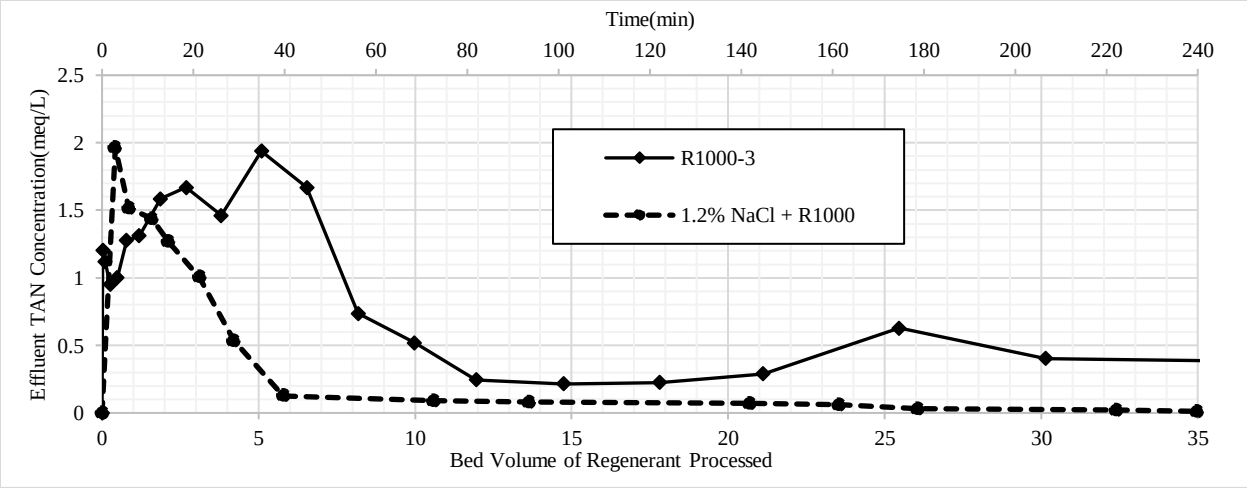


Figure 4-10 The comparison of effluent ion concentration profiles Ca(top), K(middle), TAN (bottom) during the R1000-3 and 1.2% NaCl + R1000.

It appears the higher amount of sodium in the 1.2% NaCl + R1000 regeneration solution was able to displace the previously sorbed ions, therefore more calcium and potassium came out of the system.

Figure 4-11 shows the free chlorine and pH of the effluent regenerant during the last 1000 mg Cl_2 /L solution (R1000-3) and the 1.2% NaCl + R1000 regenerations. The free chlorine concentration for the 1.2% NaCl + R1000 were very low for the first 6BV, then increased sharply till about 12 BVs and then gradually levelling off at approximately 980 mg Cl_2/L. The free chlorine concentrations for the R1000-3 regeneration were very low for the first 12 BVs, then increased gradually and levelled off at approximately 820 mg Cl_2/L. The effluent regenerant pH for the 1.2% NaCl + R1000-2 did not decrease quite as much as for the R100-3 regeneration, and it did so for a much shorter time. After 120 minutes the 1.2% NaCl + R1000-2 effluent pH had already a value of 9.

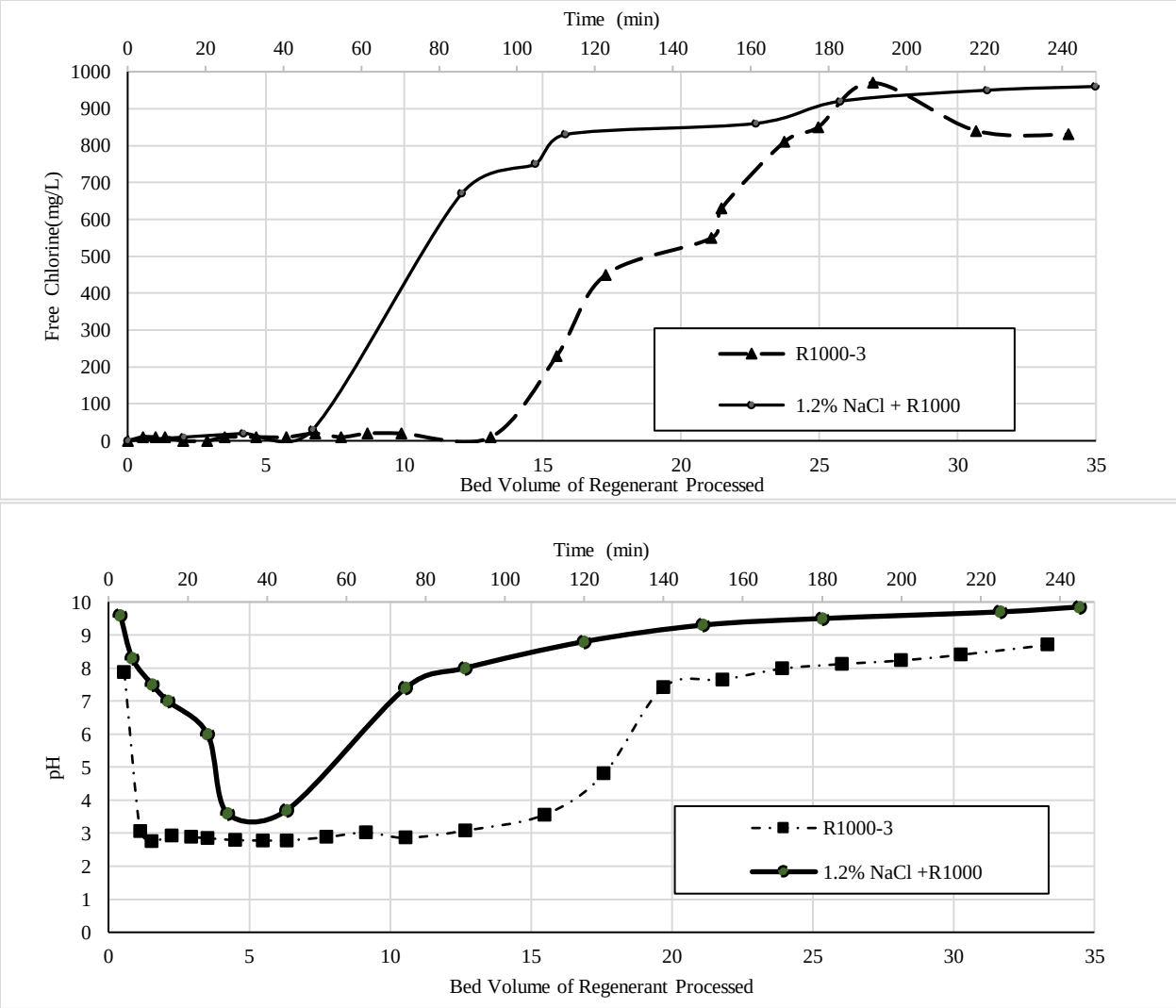


Figure 4-11 The comparison of free chlorine(top) and pH(bottom) for the SIR-600 column's during the R100-3 and both 1.2% NaCl+R1000.

The breakthrough curves of Ca, K and TAN for the SIR-600 regenerated with 1.2% NaCl+R250-22 and 1.2% NaCl+R1000 were delayed compared to those without salt. This was probably because the addition 1.2% NaCl to the NaOCl achieved more elution creating more available sites. The breakthrough curves for the key ions (Ca, K and TAN) led to greater ion uptakes for the combined NaCl-NaOCl than NaCl.

The total ion uptake results for the regeneration with 1.2%NaCl (2hrs) was 11% higher than reported by Zhang for his 1 hr long 5%NaCl (shown as SSL3 in Figure 4.12). The uptakes would had been presumably closer had Zhang's regeneration had the same duration. Also, the total ion uptake for the 1.2%NaCl regeneration was 1% higher than the 1.2% NaCl+R250-2 regeneration cycles.

Accordingly, there was limited change in the TAN uptakes, based on Figure 4-12 for R1000-3 (q_{TAN}/q_{Ca} =0.483); 1.2% NaCl regeneration (q_{TAN}/q_{Ca} = 0.404); R250-2 (q_{TAN}/q_{Ca} = 0.33); 1.2% NaCl +R250-2 (q_{TAN}/q_{Ca} =0.317); 1.2% NaCl +R1000 (q_{TAN}/q_{Ca} = 0.36) and 1.2% NaCl regeneration (q_{TAN}/q_{Ca} = 0.404). The fact that the column's ion uptake was highest for calcium is likely due to the much higher calcium concentration in the feed (Ca=4.0 meq/L; K=0.77 meq/L; TAN =1.49meq/L). This may also explain why the column had a higher TAN uptake than K uptake. This may have also been influenced by the dynamics of the column system as suggested by Chartrand et al. (2020).

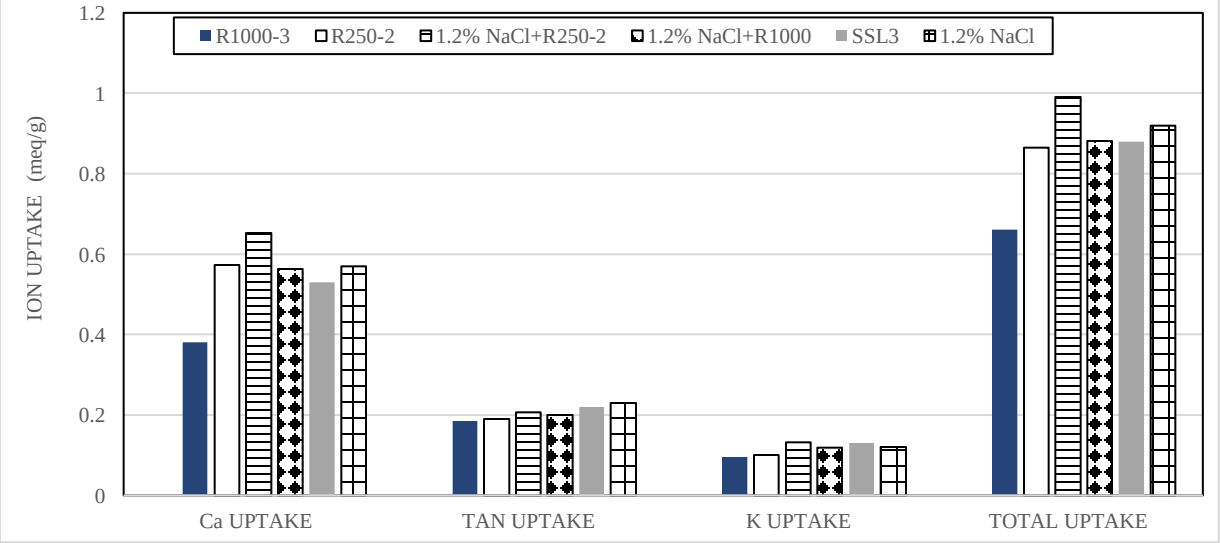


Figure 4-12 Comparison of the ion uptakes for the SIR-600 column's previous run R1000-3, R250-2 with 1.2% NaCl+ R250-2, 1.2% NaCl +R1000 and 1.2% NaCl loading runs

Furthermore, these various regeneration schemes do not significantly impact the TAN:K ratios (Figure 4-13), and TAN uptake in Figure 4-12. The column had qTAN/qK values of approximately 2 for all the regeneration conditions and the ratio did not change much with bed volumes of water treated. Thus, the SIR-600 column had a much higher selectivity for TAN over K.

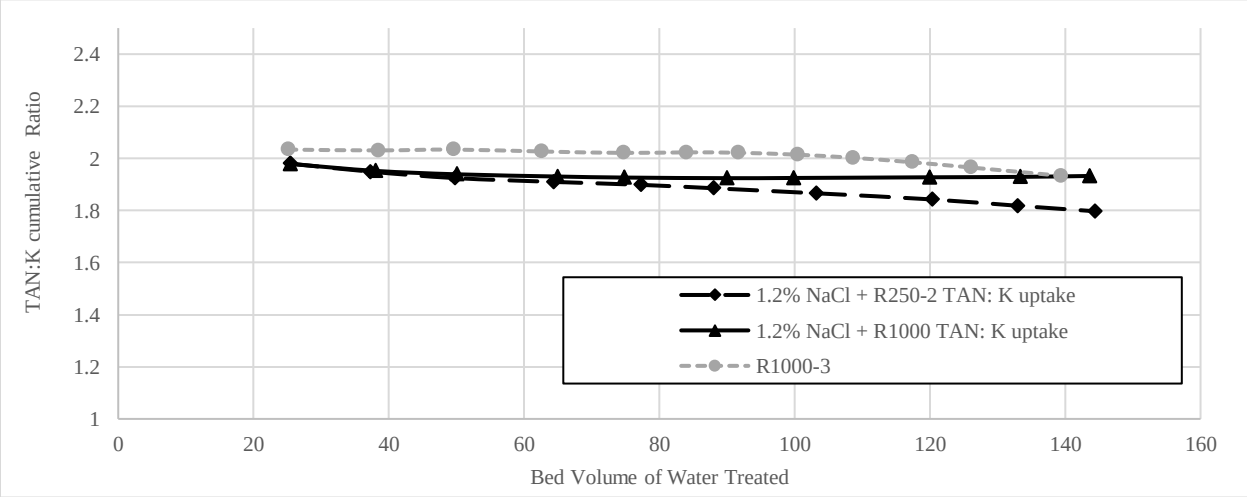


Figure 4-13 Comparison of the TAN: K cumulative ion ratios for the SIR-600 column's previous run R1000-3, 1.2% NaCl+ R250-2, 1.2% NaCl +R1000 loading runs

4.4 Conclusions

The chlorine regenerations of the ammonia-loaded zeolite column were effective, confirming the work of Zhang (2022), the only other same type of column regeneration. As pointed out by Zhang (2022) the column loading/regeneration/tests with SIR-600 media/regeneration solutions combinations showed significant lower preference for K than TAN in the synthetic EIMWW. The column's ion uptake was the highest for calcium is likely due to the much higher calcium concentration in the feed (Ca=4.0 meq/L; K=0.77 meq/L; TAN =1.49 meq/L). Also as found by Zhang (2022) the chlorine regenerations were slower than the salt regenerations in the literature

and they resulted in low pH conditions. The main contribution of this study was that it investigated the regeneration of ammonia-loaded zeolite columns using lower concentration chlorine solutions and chlorine-NaCl solutions in attempt to accelerate the regeneration and avoid the low pH conditions. The 250 mg/L chlorine concentration regeneration solutions reduced but did not eliminate the low conditions and the regeneration seemed to be somewhat slower than those using 1000 mg/L free chlorine solutions. Although the NaOCl regeneration cycles were relatively long they were shorter than the loading cycles, so they are practical. There may be other chlorine regeneration concentration and flowrate combinations solutions that may yield somewhat faster regenerations, but this study then focused on accelerating the regenerations by incorporating NaCl into the NaOCl regeneration solutions. The NaCl-NaOCl solutions were considerably faster than the NaOCl regenerations, however, possibly based on the length of the regeneration cycles used, the TAN uptakes did not change significantly. In addition, the inclusion of such concentrations NaCl, will result in an additional waste stream when eventually the used regeneration solution needs to be discarded. So NaOCl generation seems to be preferable to NaOCl+NaCl regeneration.

Acknowledgements

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Chapter 5: Impacts of Long-Term Low-pH Exposure on Ion-Exchange Material Performance and Durability

Abstract

Chlorine regeneration of a zeolite column loaded with ammonium, calcium and potassium resulted in used regenerant with pHs around 3, this raised concerns about the durability and integrity of the zeolite. The objective of this study was to assess the impact of long-term (3 months) batch exposure to low pH solutions (pH=2, 3, and 4) on the characteristics of the zeolite. Thermal gravimetric analysis (TGA) and powder x-ray diffraction (PXRD) indicated the low pH exposure did not significantly impact the physio-chemical characteristics of the zeolitic material. Scanning electron microscope images, however, showed that for all conditions there was a wearing down of the outer surface of the zeolite particles. This was confirmed by the particle size analysis, which showed that the lower the pH, the greater mass of fines generated. The particle size reduction was also accompanied by a decrease in the BET surface area which resulted in a proportional decrease in the TAN uptake (by 58% and from pH=4 to pH=2). Accordingly, using chlorine regeneration of pH<4 will result in a reduction in the lifetime of the zeolite and a gradual decrease in it TAN uptake.

Key words: ion-exchange, zeolite, low pH, ammonia, chlorine regeneration, competitive ion uptake

5.1 Introduction

Explosives impacted mining wastewater (EIMWW) are a concern because of their high ammonia concentrations. Ion-exchange (IE) technology using zeolites is a viable option to treat mining wastewater for the removal of ammonia because of its requirement for minimal supervision, and it is not impacted by low temperatures and toxicity (Clifford et al. 2012). IE operation requires frequent regeneration of the media to maintain its uptake capacity. The standard approach to regenerate zeolites is to use salt (NaCl) solutions, but the used regenerant solution containing high concentrations of ammonia and very high salt concentrations are a challenge as it represents a secondary source of pollution. They could be reused if the ammonia is removed. Air stripping under high pH conditions is one technique used for this purpose (Chartrand 2018). However, because of the cold weather this approach is not feasible in Northern Canadian mines. Regeneration using a hypochlorite solution seems a promising method, the chlorine oxidizes the ammonia into nitrogen gas without generating serious secondary pollution (Huang et al. 2015; Zhang et al. 2017).

Zhang (2022) studied the regeneration of a synthetic (EIMWW) loaded zeolite (SIR-600) column using a 1000 mg/L free chlorine solution. The EIMWW contained approximately 21 mg ammonia as N/L, 30 mg K/L, and 80 mg Ca/L (1.5 meq/L, 0.77meq/L, and 4 meq/L, respectively). During the first two hours of the chlorine regeneration the IE media was exposed to low pHs (i.e., ~3) due to the reactions between the chlorine and the ammonium on the IE material or eluting from it. Hence, there are concerns about the impact of low pH on the integrity of the IE material. And thus, the objective of this study is to assess if the low pH exposure is a significant long-term concern. Low-pH batch exposure experiments were conducted to assess its impact (i.e., change) on the IE materials' physio-chemical characteristics and ammonium uptake.

5.2 Experimental Materials and Methods

5.2.1 Experimental Materials

This study was undertaken using a commercial zeolite (SIR-600, ResinTech Inc., Candem, NJ) since it was used in by Zhang (2022) who reported the existence of the low pH conditions during chlorine regeneration. Although the supplier does not divulge what type of zeolite SIR-600 is, it performs similarly to clinoptilolite (Chartrand 2018). Previous studies showed SIR-600 performed well in terms of ammonium uptake and a slightly higher selectivity for ammonium over potassium in column tests (Chartrand et al. 2020; Zhang 2022). In this study the ammonium uptake capacity was quantified by batch loading experiments conducted using the same synthetic EIMWW wastewater used by Zhang (2022). It was prepared with ammonium chloride, potassium chloride and calcium chloride hexahydrate (ACS grade, Fisher Scientific, Waltham, MA). The synthetic wastewater had approximately 21 mg ammonia as N/L, 30 mg K/L, and 80 mg Ca/L (1.5 meq/L, 0.77meq/L, and 4 meq/L, respectively). The low pH exposure was achieved using solutions with pH = 2, 3 and 4. The acidic solution with a pH=2 was prepared by adding 2.04 mL of 0.1 M solution of sulfuric acid (ACS grade**,** Fisher Scientific, Waltham, MA) using an automatic pipette (Labnet Biopette, Brockville, Canada). The pH=3 and pH=4 solutions were prepared using universal buffer mixtures, i.e., combinations of sulfuric acid with citric acid (ACS grade**,** Fisher Scientific, Waltham, MA).

5.2.2. Low-pH Batch Exposure Experiments

The exposure tests consisted of adding 50 g of SIR-600 to a 1 L glass bottle, filling it with water of the selected pH, sealing it and then rotated it an end-over-end bottle tumbler for an exposure time of three months. The mixing provided by the tumbler was gentle as it only rotated at

approximately 10 rpm. In Zhang's IE column experiments, the media is in contact with low pH conditions for nearly 2 hours per regeneration cycle and four regeneration cycles were performed per day (Zhang 2022). That is 8 h of exposure per day. Thus, the 90 days low pH batch exposure tests is equivalent to that of 270 days of column operation. After the three months, the SIR-600 was recovered using vacuum filtration through 0.45 μm membrane filters (GN-6, Pall, Port Washington, NY), and then dried in an oven (~ 105^{o}C) for 24 hours. Then, the cooled samples were characterized. In addition, another set of bottles with 50g of SIR-600 and 1L of distilled water were subjected to the 90 days of mixing to act as controls, they helped determine if changes arose from the contact period with water and if there was particle attrition through the mixing.

5.2.3 Material Characterization Methods.

The SIR-600 physio-chemical characteristics investigated were the particle size distribution analysis, scanning electron microscope (SEM) images, BET surface area analysis, thermal gravimetric analysis (TGA) and powder x-ray diffraction (PXRD). The BET surface area analysis was performed in the Chemistry and Biomolecular Science Department of the University of Ottawa using N_2 adsorption-based surface area analyzer (ASAP 2020, Micromeritics, Norcross, GA). The BET samples were analyzed at 77K. The surface gravimetric analysis (TGA) tests were performed in the Civil Engineering Department of the University of Sherbrooke using a differential scanning calorimetry analyzer (Q10, Q Series™, Newcastle, DE), at temperature rise rate of 10^{o} C/min, the measurements included a baseline correction. The SEM images of the SIR-600 was performed at the Advanced Research Center of the University of Ottawa. The SEM were captured with a field emission SEM (JMS7500F, JEOL Ltd, Tokyo, JP). Powder x-ray diffraction was conducted at the Science, Technology, Engineering and Mathematics (STEM) complex of the

University of Ottawa. The PXRD tests were performed with the Rigaku Ultima IV Diffractometer (I R Technology Services Pvt. Ltd, Mumbai, India).

The particle size distribution tests were conducted following a sieve test procedure adapted from ASTM method D6913/D6913M-17 (ASTM 2017). After the three months low pH exposure, approximately 50g of dried SIR-600 were loaded on top of a stacked series of pre-weighed sieves (12, 16, 20, 40 and 50 US mesh). The sieves were shaken with a sieve shaker (SS-8R, Gilson Co, Lewis Center, OH) for about 10 minutes. Then each sieve was re-weighed to obtain the mass of SIR-600 retained in them. The "control" was a true control in that it pertains to a SIR-600 placed in a bottle filled with distilled water (pH=7) for all material characterization methods and mixed in the end-over-end tumbler along with the other pH = 2, 3 and 4 bottles.

5.2.4 EIMWW Batch Loading Experiment.

The EIMWW batch loading tests were performed as part of the impact of long-pH exposure tests to determine their impact on the ammonium uptake capacity. 0.2 g of SIR-600 was placed in a 100 mL glass bottle and filled with the synthetic EIMWW. The synthetic EIMWW had a *pH* of approximately 4.1. Then 0.2g samples of SIR-600 that had been exposed to pH=2, pH=3 and pH=4 were added to 100 mL bottles. These bottles were then filled with the EIMWW to the top, without headspace, to prevent the loss of ammonia due to its volatility. Teflon tape was entwined on the threaded neck of the bottles to ensure the screw-on cap provided a good seal. The sealed bottles were rotated in an end-over-end tumbler at a speed of approximately 10 rpm for 48 hrs to make sure that there was efficient solid/ liquid contact and equilibrium was reached. Then, the

bottles were taken out from the tumbler, and the liquid was separated by vacuum filtration through a 0.45 μm membrane filter (GN-6, Pall, Port Washington, NY).

The filtrate ion concentrations are the equilibrium liquid phase concentrations (C_{eq}). The equilibrium solid phase concentration (Q_{eq}) of the ions can be obtained using the following equation (eq. 3.3) based on the mass balance of the initial and final solid-phase and liquid-phase concentrations of the particular ion.

$$Q_{eq} = \frac{(C_{\text{in}} - C_{\text{eq}})\,\text{V}}{M} \qquad \text{(eq. 5.1)}$$

Where Q_{eq} is the ion uptake of the SIR-600 (meq/g, SIR 600), V is the volume of liquid in the bottle (L); C_{in} is the ion concentration in the control bottles, i.e., bottles without SIR-600 (meq/L); C_{eq} is the equilibrium ion concentration (meq/L); and M is the mass of SIR-600 (g). The ammonium, K^+ and Ca^{2+} concentrations of the liquid were then analyzed. The experiments were conducted in duplicate at room temperature (~22^0C), and the average results were reported.

5.2.5 Analytical Methods

The TAN concentrations were quantified using the Nessler method which was adapted from Standard Method 4500-NH3 C (American Public Health Association, 1992). The Ca, K and Na ion concentrations were quantified using a procedure adapted from Standard Method 3111B (American Public Health Association, 2017) which uses flame atomic absorption spectrometer (AAS) (PinAAcle 500, PerkinElmer, Waltham, MA) analysis. pH values were measured with a pH meter (VER Symphony B10P, VWR, Radnor, PA) with a pH probe (VWR 89231-580, VWR, Radnor, PA).

5.3 Results and Discussion

5.3.1 TGA Analysis

The TGA examination of the SIR-600 samples are shown in Figure 5-1. As seen at TGA curves, weight loss was continuous during the heating up to 750 °C. Rapid weight loss was observed in the temperature range from 38 to 400°C, a moderate one was recorded from 400 to 700°C. Korkuna et al. (2006) reported zeolites with aluminosilicate functional groups have two forms of water – intact molecules and OH groups existing in the structure of silicate minerals. During the TGA analysis the intact water is eliminated at below 100 °C, whereas hydroxyl groups are removed at T > 400 °C. Thus, the structural water (OH groups) from aluminosilicates materials clinoptilolite is eliminated after exceeding 360 °C (Kithome et al. 1998; Mihlay et al. 2012). The TGA for the control and low-pH exposed samples were similar. Thus, there is no significant difference between the treated and the control samples.

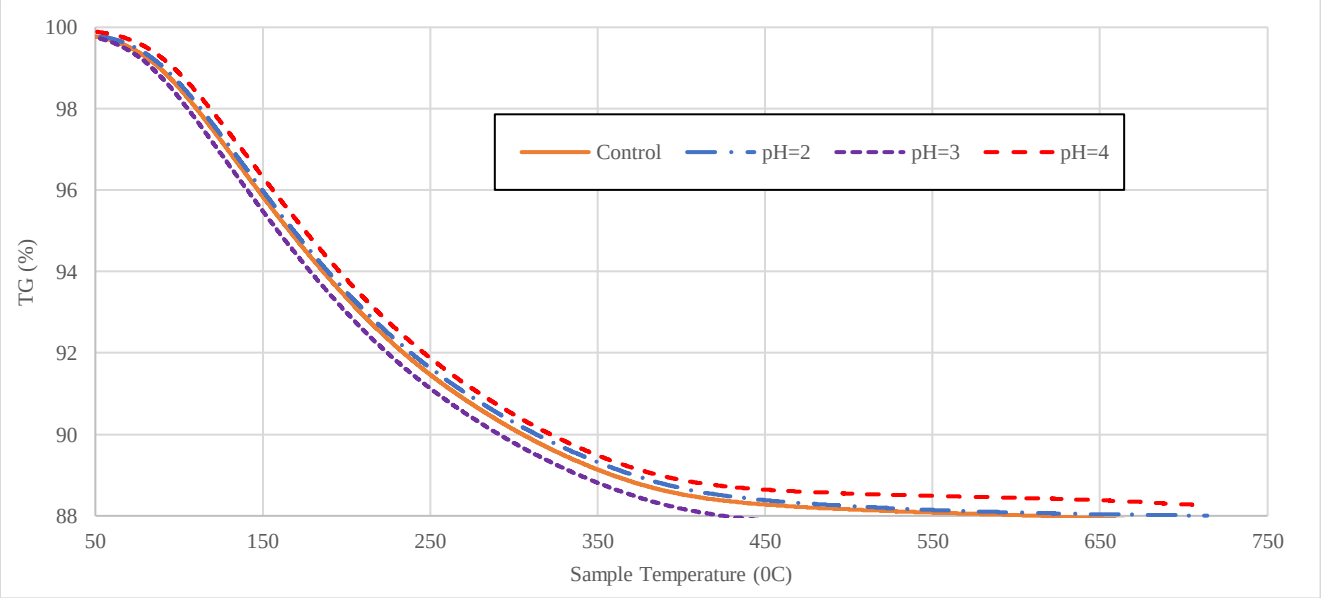


Figure 5-1 TGA analysis of the SIR-600 samples exposed to distilled water (control) and with pH 2, 3, and 4 solutions.

5.3.2 PXRD Analysis.

The major observation from the PXRD analysis of SIR-600 samples exposed to distilled water (control) and the pH 2, 3, and 4 solutions (Figure 5-2) was the exposure to low pHs did not change the diffraction pattern. The crystalline characteristics of SIR-600 was unchanged before and after exposure to low pHs. Also, from the PXRD analysis of the SIR-600 samples were that each sample had the highest peak at approximately 900 counts at 2 Theta values of approximately 22 degrees. In addition, the difference in the peak heights among SIR-600 before exposure and the ones exposed to the low pHs were quite small. The peak intensities in the XRD cannot identify the Al peak, the Si peak and the O peak. To directly compare the Al:Si ratio, the technique is XRF (X-Ray Fluorescence), which would directly output the mass percent of Si and Al (and most other heavy elements) in the overall sample. Unfortunately, there was no samples left, so it was impossible to perform XRF analysis.

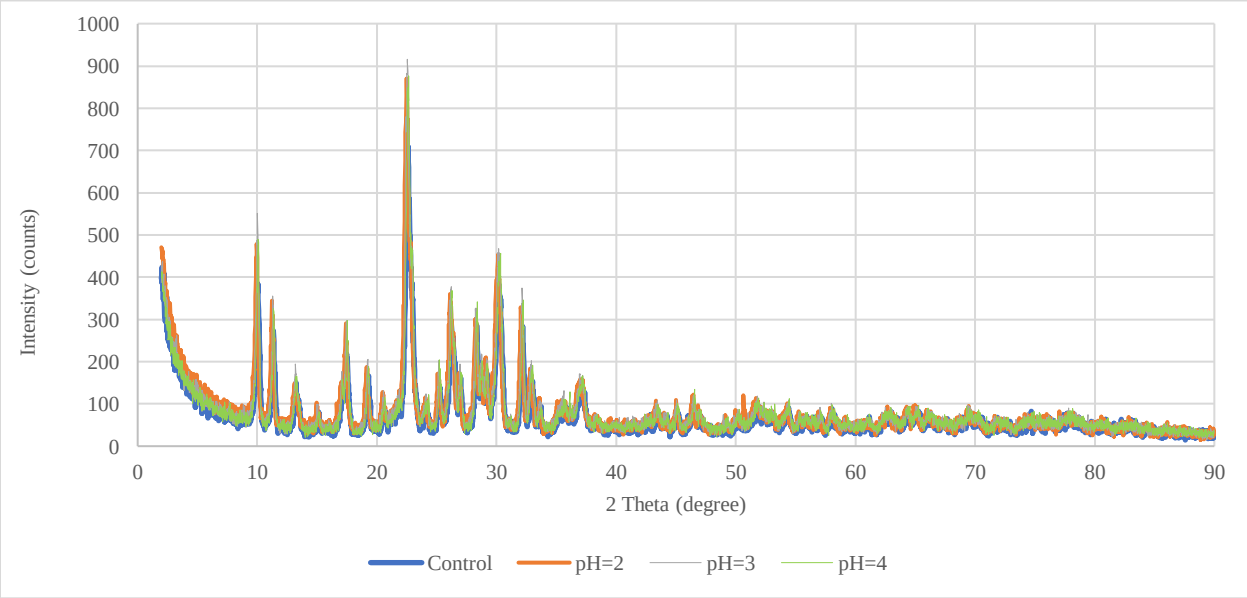
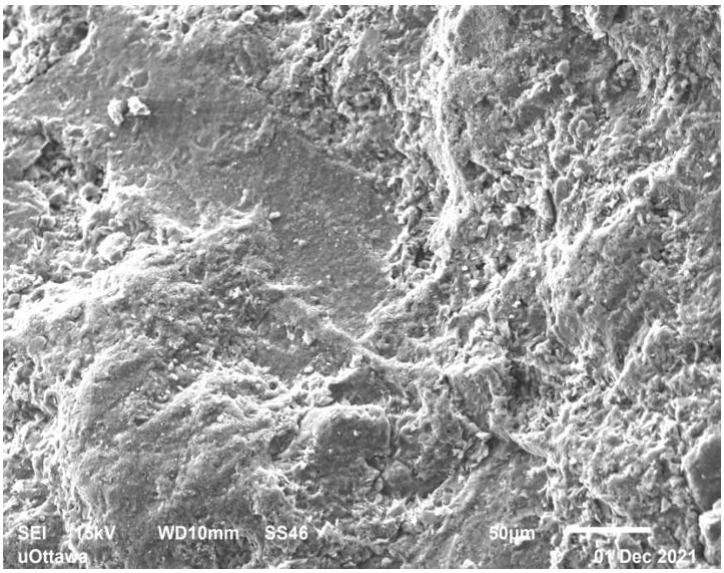


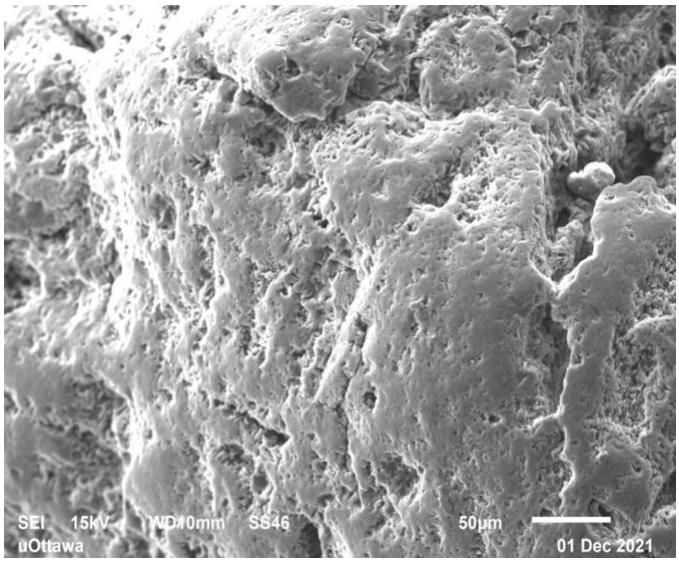
Figure 5-2 PXRD analysis of SIR-600 samples exposed to distilled water (control) and with pH 2, 3, and 4 solutions.

5.3.3 SEM Analysis

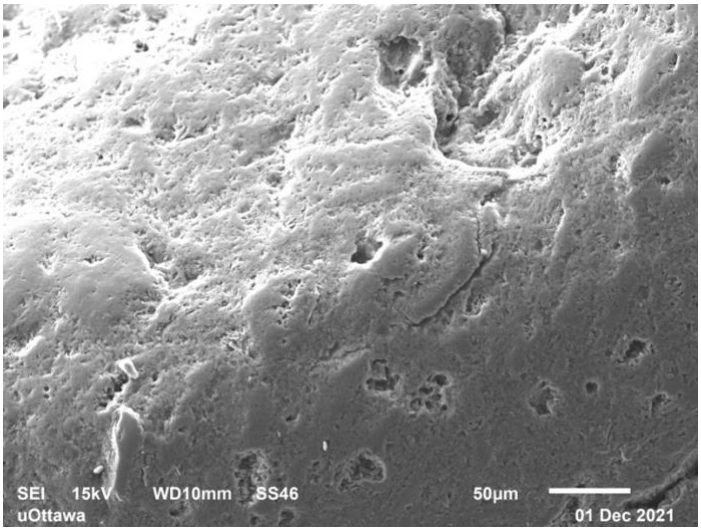
Comparing the SEM-based images for the morphology of the four samples (Figure 5-3) shows that there were differences observed between the control SIR-600 and that exposed to low pHs for 3 months. The SEM images (Figure 5-3) show that the control SIR-600 has a rougher surface which is a typical feature of clinoptilolite (Wang et al. 2007; Mihaly et al. 2012; Zhang 2022). The effect of the low pH exposure combined with mixing in the tumbler, appear to have changed the external part of the IE materials. The sharp edges seemed to have been worn down for all low pH exposure samples, resulting in smoother surfaces. The smoothening of the particle surfaces of the low pH exposures seems to indicate that there some grinding action that may lead to the formation of fines. The pH=2 and pH=3 results are consistent with this hypothesis, however the pH=4 results are not. Similarly, it may be hypothesized that the smoothening is accompanied by the loss of ion exchange sites. SEM images cover a very small area and selecting representative areas to photograph is difficult. Possibly more images may have led to somewhat different conclusions. It should be noted that these are images of the surface and provide no indication as to how deep into the particles was the impact of the low pH solutions.



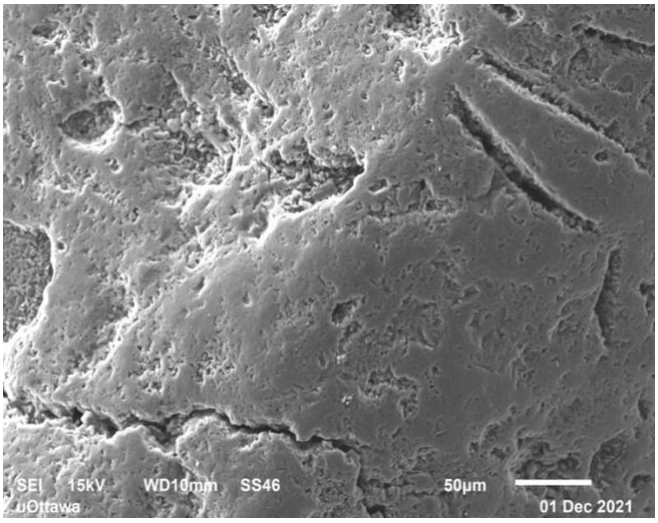
(a) Control



(b) pH=2



(c) pH=3



(d) pH=4

Figure 5-3 SEM image of SIR-600 control (a); and SEM images after 3- months of pH=2 (b); of pH3=(c) and pH=4 (d) solutions.

5.3.3 Particle size distribution

The particle size distribution analysis are presented in Figure 5-4, the bars represent the average of duplicate tests. For the control and pH=4 the average percent retained in the three largest size fractions were very similar, somewhat lower (7%) for pH=3 and even lower (12%) for pH=2. Because of the overlapping confidence intervals the changes were not statistically significant for all the fractions except for the fines collected in the pan, however the average mass fraction for the largest three fractions decrease with decreasing pH. So, the fines data indicates that the exposure to pH 2 and 3 results in some particle degradation resulting in the formation of fines (<200 microns) and the mass of the fines is a function of the pH. Thus, it appears the exposure to very low pHs led to a change in the zeolite particles.

The particle size of control SIR-600 samples fell mainly into the 400 microns to 1680 microns range, this is consistent with the manufacturer's specification (ResinTech Inc, 2020). The particle size distribution in this study was very similar to that reported by Zhang (2022) for a SIR-600 sample. The small differences may have been caused by: a) friction from the mixing in the tumbler over the long exposure period; and/or b) that samples originated from different batches of SIR-600.

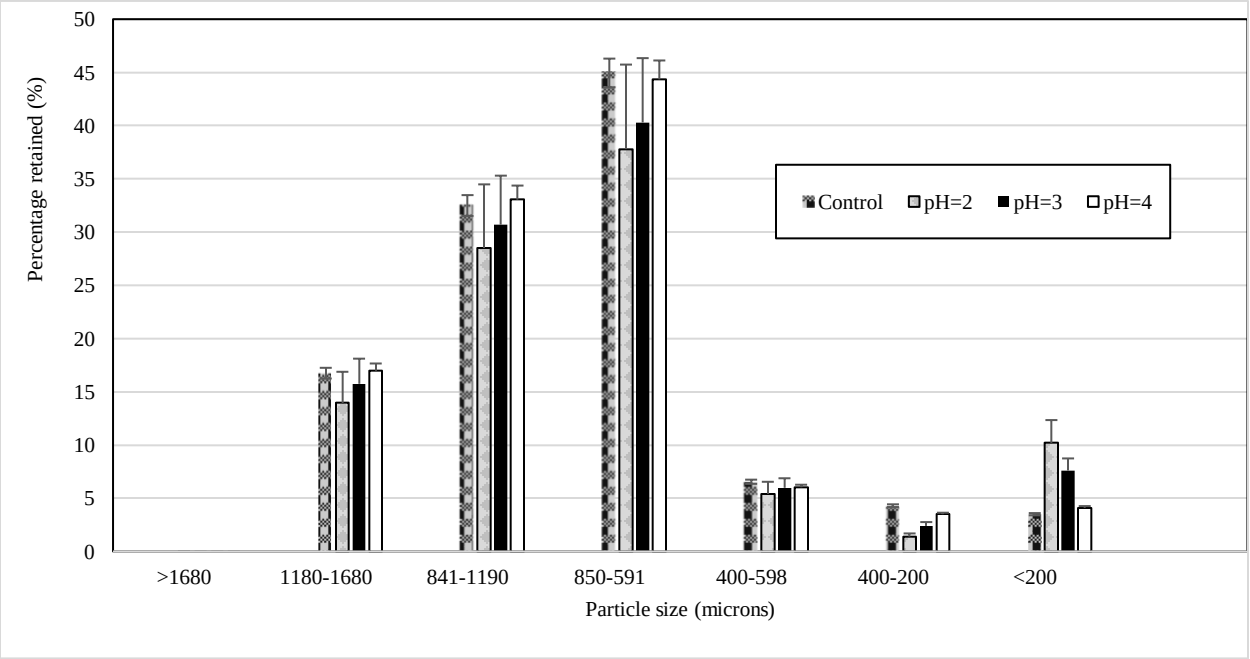


Figure 5-4 Particle size distributions of SIR-600 exposed to distilled water(control) and pH 2,3, and 4 solutions

Again, the fines in the pH=2 and pH=3 results are consistent abrasion losses that led to surface smoothening observed in the SEM images, but the surface smoothening of the particles exposed pH=4 do not result in the generation of significant additional fines. It appears that surface smoothening observed for pH=4 samples was not as deep resulting in minimum fines.

5.3.5 BET Analysis

BET surface area measurements for the control and low pH exposed samples are presented in Figure 5-5. The BET surface area of the control samples is similar to those reported by Zhang (2022) for SIR-600($16 m^2/g$), and it should be noted that samples used in this study originated from a different batch of SIR-600. The decreasing BET surface area with decreasing pH is consistent

with decreasing particle size. The BET surface decreased by 8.33% from pH=4 to pH=3 and it decreased by a factor of 9.09%. from pH=3 to pH=2. According to the SEM images (Figure 5-3) there appears to change to the exterior of the SIR-600 particles, the limited changes in the BET surface areas suggests the interior did not change much.

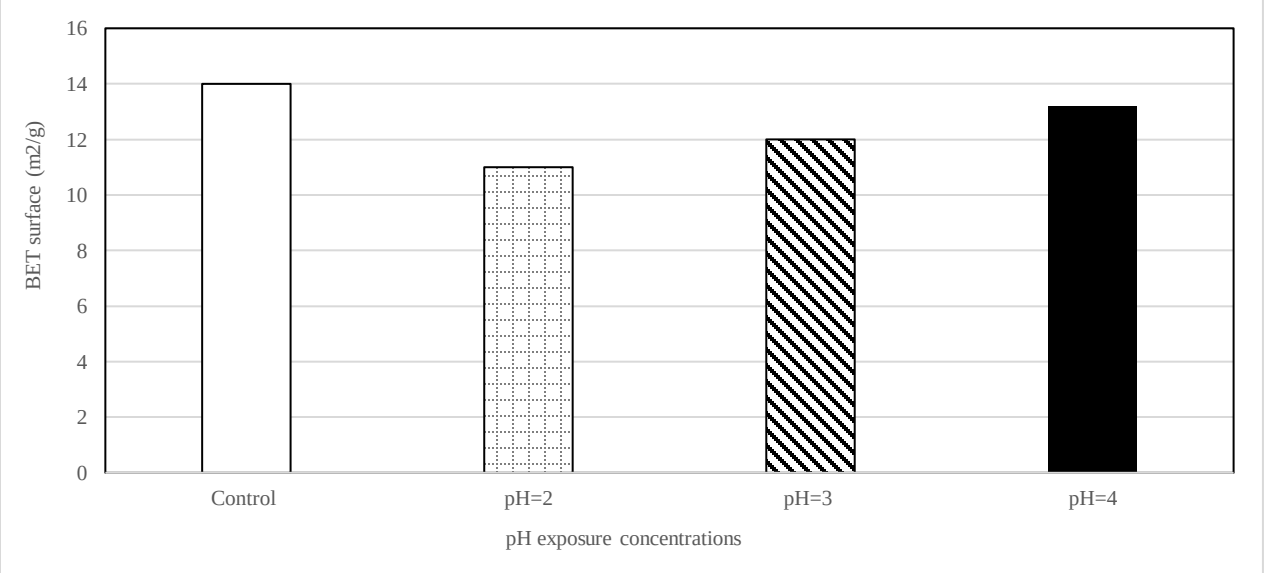


Figure 5-5 BET analysis of SIR-600 without (control) and with pH (2,3,4) solutions.

5.3.6 TAN uptake

Figure 5-6 shows the TAN uptakes of the SIR-600 from EIMWW after the 3-month exposure to the pH=2, pH=3, and pH=4 solutions and the pH=7 solution (control). The control yielded a TAN uptake of 0.19meq/g, this was somewhat smaller than the 0.25meq/g value reported by Zhang (2022), however, his SIR-600 originated from a different batch and were not subjected to long term exposure to solutions with mixing. The SIR-600 exposed to a pH=4 solution had similar TAN uptake capacities to those of the control, and the capacities decreased with decreasing pH. From

pH=4 to pH=3 the TAN uptake decreased by 36% and from pH=3 to pH=2 it decreased by a factor of 34%. Finally, given that pH=2 has an H^+ concentration 10 times larger than at pH=3, it was expected the impacts would be more severe for pH=2. Accordingly, exposure to pH=2 and pH=3 should result in some of the properties change in this zeolite. As shown in Figure 5-7, the decreases in TAN uptake are consistent with the reduction in BET surface area.

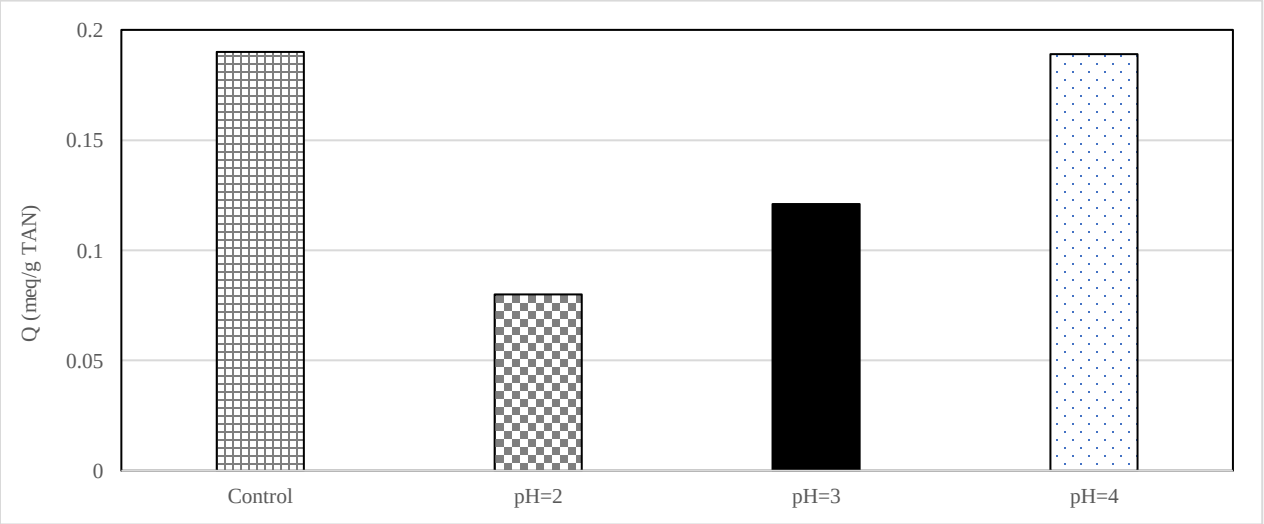


Figure 5-6 TAN ion uptakes of SIR-600 with the control and the pH (2,3,4) exposed SIR-600.

5.4 Discussion

The characterization of the zeolite samples exposed to methods low pH solutions for three months yielded the following key results. First, the TGA and PXRD analysis showed that there was no significant change in the chemical characteristics of the SIR-600 material. Second, the SEM images showed that long-term exposure to solutions with pH 2, 3 and 4 resulted in smoothening the surface of the zeolite particles, however the images do not provide information as to what depth

the particles were impacted by the low pHs. Third, the particle size distribution of the pH=2 and pH=3 exposed zeolite showed that exposure the lower pH of the exposure solution created more fines (12.7% of the total mass at pH=2 and 7.7% at pH=3). Based on this one change on would expect the larger size particles would have decreased somewhat in size and that some of the outer layers of the larger particles would had been lost. Fourth, the decrease in BET surface area is consistent with the above interpretation of decreasing of the particles within the largest size fractions. Finally, with the decrease in BET surface one would reasonably expect that there would be a decrease in the TAN uptake that was observed. This is further illustrated in Figure 5-7 which shows such a decreasing pattern, there is an extremely high correlation (R^2 >0.99) between the TAN uptakes and both the BET surface area and the % fines. The very small decrease in the TAN uptake of the SIR-600 exposed to pH=4 w.r.t. the control suggests that at pH=4 the ion exchange sites were not significantly impacted.

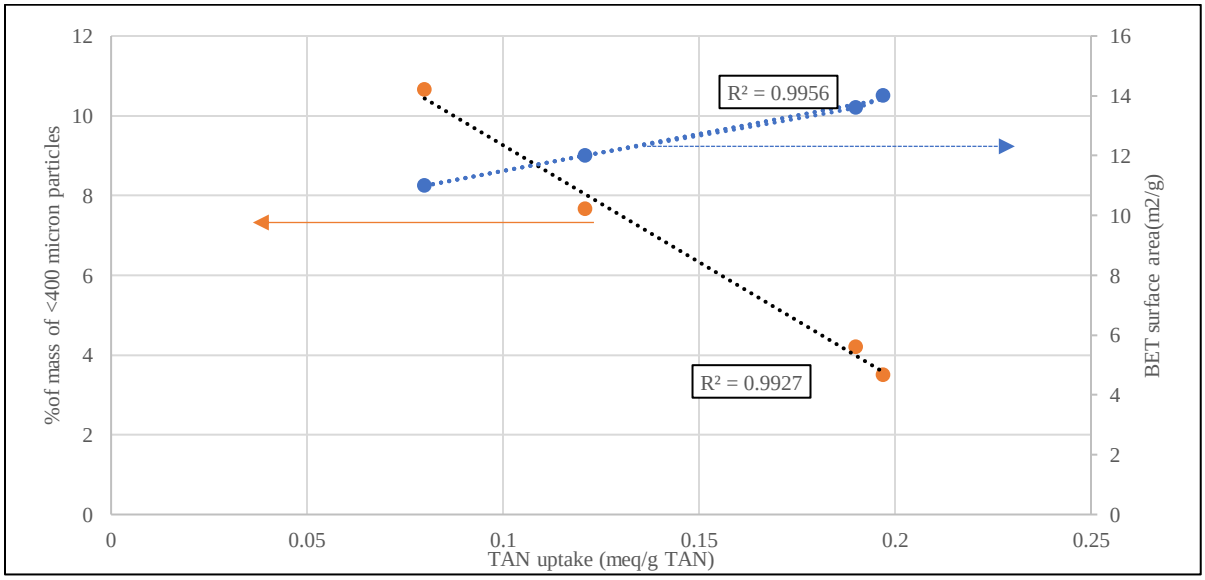


Figure 5-7 The trendline with the R^2 value between the TAN uptake and both the BET surface area and the % fines

5.4 Conclusions

The main conclusions of this study are as follows:

1. Long-term exposure pH=4 solutions did not significantly alter the zeolite particles and their capacity to TAN uptake.
2. Exposure to pH=2 and pH=3 solutions did not significantly impact the overall chemical characteristics of the zeolite as characterized by TGA and PXRD, however it seems to have led to the destruction of the outer layers of the zeolite particles decreasing their BET surface area and TAN uptake capacity. The lower the pH, the greater the impact.

Thus, it is recommended that, if possible, SIR-600 should not be exposed to pHs below 4. Regeneration using lower chlorine concentrations, which would result in less of pH decrease, should be investigated. Planning of zeolite systems using chlorine regeneration should recognize that the long-term TAN uptakes will be lower and the media may have to replaced more frequently.

Acknowledgements

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Chapter 6: Conclusions

The TAN uptakes for NaOCl regeneration was comparing with those of NaCl regeneration. The focus of the thesis was comparing the performance of the IE systems regenerated with NaCl, NaOCl+NaCl with those that uses a chlorine regeneration solution for TAN removal. Also, investigating the long-term exposure to low pH conditions on the characteristics of the IE material used in this study (SIR-600).

The main competing cations were potassium and calcium. The main conclusions are as follows:

1. In the column loading/regeneration/tests with SIR-600 media/regeneration solutions combinations showed significant lower preference for K than TAN in the synthetic EIMWW. This confirmed the findings of Zhang (2022).

2. The TAN loadings achieved using NaOCl regeneration were almost identical to those achieved with NaCl regeneration, NaCl + NaOCl regeneration after multiple operational cycles, although NaOCl regeneration needed a longer duration.

3. Although NaOCl regeneration was slower than NaCl and NaCl+ NaOCl regeneration, NaOCl regeneration is still promising because it achieves similar TAN uptakes while not eventually producing a secondary waste stream.

4. The long-term low-pH batch exposure tests showed that long-term exposure pH=4 solutions did not significantly alter the zeolite particles and their capacity to TAN uptake.
5. The same tests showed that exposure to pH=2 and pH=3 solutions did not significantly impact the overall chemical characteristics of the zeolite as characterized by TGA and

PXRD, however it seems to have led to the destruction of the outer layers of the zeolite particles decreasing their BET surface area and TAN uptake capacity. The lower the pH, the greater the impact. Thus, chlorine regeneration appears to shorter the durability of the zeolite.

6.2 Recommendations

1. The gas collected from the column chlorine regeneration could be characterized to verify the reaction mechanism behind the chlorination.

2. Future experiments should consider upflow mode continuous column operating conditions for the regeneration cycles. They should be compared with downflow flow mode regenerations applied for this thesis to determine the impacts of TAN uptake.

3. It is recommended that future study to perform XRF analyzes the peak intensities for the Al peak, the Si peak and the O peak, and to directly compare the Al:Si ratio which would directly output the mass percent of Si and Al (and most other heavy elements) in the overall sample.

Appendices

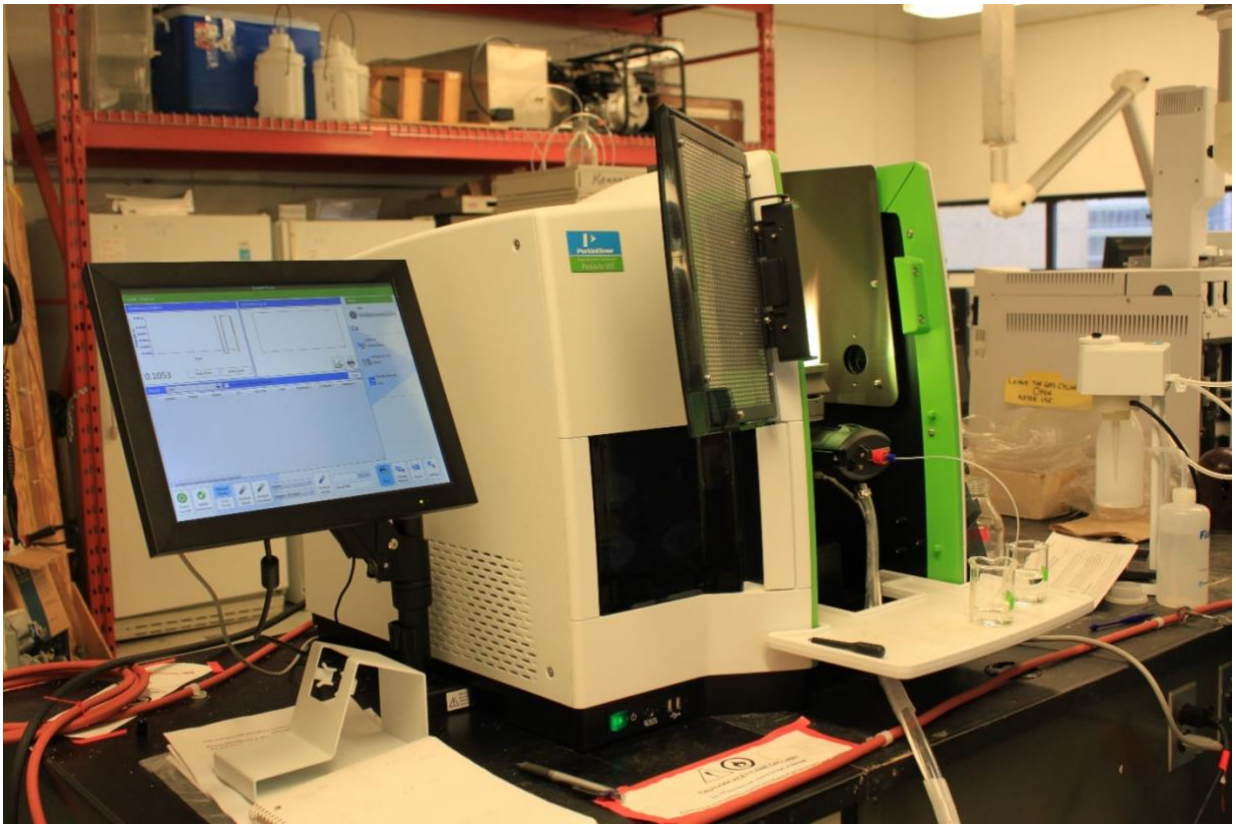

Figure A-1 PerkinElmer PinAAcle 500 Flame Atomic Adsorption Spectroscopy Metal Analysis Unit