The Selective Ion-Exchange Removal of Ammonia from Mining Wastewater

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Abstract

The Canadian mining industry is a multi-billion-dollar effort and one of Canada's largest industrial sectors, creating jobs and security across the country. Certain practices employed within the industry have led to great developments, while increasing productivity and reducing costs. One such practice is the use of nitrogen-based explosives, which have serious environmental repercussions, namely the introduction of large quantities of ammonia into the ecosystem through means of complex blends of wastewaters also containing various metals. These explosive impacted mining wastewaters (EIMWW), must be treated before being introduced into natural waterways as ammonia pose several threats to the environment including the depletion of dissolved oxygen as well as acute toxicity for fish. Newterra, a provider of modular treatment solutions for water, wastewater and groundwater, requested an assessment of the feasibility of a brine-based ion exchange (IE) system for the removal of ammonia from EIMWW, that would be simple to operate and could be deployed in remote areas.

The following thesis consists of an evaluation of several IE materials, to determine the feasibility of an IE system for the treatment of real EIMWW. Potassium and calcium were determined to be the problematic ions present in the EIMWW, potentially leading to competitive adsorption issues. This was accomplished by comparing batch IE isotherms for five different IE materials; one natural zeolite (clinoptilolite), one modified clinoptilolite (Resintech SIR-600), and three synthetic resins (Purolite SSTC60, Amberlite IR120 Na and Bojie BC121 H) using both a synthetic single-solute ammonia wastewater and real EIMWW with a total ammonia nitrogen (TAN) concentration of 3.87 meq TAN/L (~70 mg/L). The three synthetic resins produced the largest reductions in capacities from the effects of competition and featured the following exchange capacities when treating EIMWW: 0.24±0.03, 0.25±0.01 and 0.22±0.001 meq TAN/g

for the Purolite, Amberlite and Bojie resins respectively. These were respective reductions of 87±0.96, 86±0.80 and 87±0.03 % compared to their single-solute TAN solution capacities. The two zeolites featured higher multi-component exchange capacities; 0.32±0.04 meq TAN/g for the clinoptilolite and 0.42±0.01 meq TAN/g for the SIR-600. Furthermore, calcium was found to pose minimal competitive effects and potassium was responsible for the most capacity reduction.

Batch regeneration experiments with the clinoptilolite and SIR-600 were undertaken to evaluate the long-term performance of both materials. These consisted of IE isotherms with the EIMWW followed by material regeneration with various regenerants including a 2.5 % KCl/2.5 % NaCl, a 5 % KCl, and a 2.5, 5 and 10 % NaCl solution. Ultimately, the 5 % and 10 % NaCl solutions were the only regenerants to result in an increase of capacity with the 10 % solution featuring higher capacities for both materials. After four exchange/regeneration cycles using a 10 % NaCl brine, the clinoptilolite produced the following capacities: 0.16±0.01 meq Ca^{2+}/g, 0.39±0.06 meq K^{+}/g and 0.34±0.02 meq TAN/g. For the same conditions the Resintech SIR-600 resulted in the following capacities: 0.12±0.01 meq Ca^{2+}/g, 0.52±0.01 meq K^{+}/g and 0.46±0.00 meq TAN/g.

Based on the higher TAN exchange performance, column studies were performed with the Resintech SIR-600 to validate the material’s performance using a more realistic mode of operation similar to real world applications. This was accomplished by comparing the capacities of the material using both a single solute TAN wastewater as well as the EIMWW and a breakthrough concentration criterion of 0.55 meq TAN/L (~10 mg/L). The EIMWW featured breakthrough after only 50 bed volumes, comparatively to the synthetic TAN solution where breakthrough occurred after 274 bed volumes, indicating that competition played a significant role in the performance of the system.

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List of Abbreviations

AA: Atomic Absorption

ASC: American Chemical Society

BV: Bed volumes

BET: Brunauer-Emmet-Teller

CCME: Canadian Council of Ministers of the Environment

DIV/0: Division by zero

DVB: Divinylbenzene

EIMWW: Explosive impacted mining wastewater

ICP: Ion coupled-plasma

I.D.: Internal Diameter

IE: Ion exchange

LOI : Loss on ignition

M: Molar

min: Minutes

MTZ: Mass transfer zone

rpm: Rotations per minute

SAC: Strong-acid cation

SBA: Strong-base anion

SD: Standard deviation

SST: Shallow Shell Technology

TAN: Total ammonia nitrogen

VOC: Volatile organic compounds

WAC: Weak-acid cation

WBA: Weak-base anion

w/w: Weight by weight

List of nomenclature

$\propto_j^i$: Separation factor for ions i and j

A^+: Ion A

B^+: Ion B

b: Langmuir adsorption model constant

^oC: Degrees Celsius

C_i: Initial aqueous phase contaminant concentration

C_{eff}: Contaminant concentration in the effluent of column

C_{eq}: Equilibrium aqueous phase contaminant concentration

C_{feed}: Contaminant concentration in the initial column feed

C_L^*: Gas-liquid equilibrium concentration

C_g: Gas phase concentration

dt: Delta t, given time step

eq: Equivalent units

g: Grams

H_c: Henry's law constant

K_A^B: Selectivity of resin for ion B over ion A

K_f: Freundlich model constant

L: Liters

f: Fraction of ammonia in unionised form m: Meters

M: Mass of ion exchange material

M_{Liquid}^{X}: Mass of contaminant X in the liquid (aqueous) phase

M_{Solid}^{X}: Mass of contaminant X in the solid phase

$1/n$: Freundlich model constant

n: Electrical charge of ion in question

pKa: Acid disassociation constant

q_{eq}: equilibrium ion exchange capacity for contaminant in questions

q_i: initial solid phase contaminant concentration

Q: Flow rate passing through column

Q_m: Langmuir monolayer constant

R: indicates resin phase ion

R^2: R-squared value

S: Semmens

T: Temperature of solutions

V: Volume of the System

X: Solid (resin) phase concentration

Y: Liquid (aqueous) phase concentration

%: Percentage

Chapter 1: Introduction

1.1 Mining Industry and Environmental Consequences

The Canadian mining industry is one of the largest in the world and was at the time of writing the first in exportation of Potash, second for Uranium, Nickel and Nobium and third for Cobalt, Aluminium and Platinum group metals. In 2015 Canada produced a gross domestic product of $24.6 billion in mineral extraction and $30.9 billion in mineral processing and manufacturing (Marshall 2016). This multi-billion-dollar industry is crucial to the Canadian economy and is a large provider of employment within Canada.

Mining activities have the potential to release toxic materials into the environment. Some of these negative impacts that require proper management include the generation of extremely polluted wastewaters due to ore contact and the release of heavy metals from mine tailings that need to be properly managed. Among the mining related sources of contaminants are the ammonia-laden explosives impacted mining wastewaters (EIMWW). The main concerns about the discharge of ammonia into the environment are the biological oxidation of ammonia (nitrification) resulting in a significant decrease in the dissolved oxygen available to aquatic life in the receiving water, the introduction of nitrates into groundwater sources, acute toxicity to aquatic life posed by unionized ammonia and contributing to the eutrophication of waterways due to excess nutrients (Nehring et al. 1990; Halling-Sørensen and Jorgensen 1993; Burow et al. 2010; United States Environmental Protection Agency 2013).

Treatment methods for the reduction of ammonia concentrations traditionally revolve around the nitrification/denitrification process, which relies on biological processes to transform ammonia into nitrogen gas. Other methods include the use of elevated pH (pH > 10) and temperature to convert the ammonia to ammonia gas with subsequent air-liquid contact to strip off the ammonia from solution, adsorption and ion exchange, chemical precipitation, application of microwave, application of ultra-sound, and breakpoint chlorination (Li et al. 2011; Dong and Sartaj 2016; Montégut et al. 2016).

Most mining projects are in very isolated areas that have neither the accessibility nor the manpower to support large scale treatment plants. Therefore, there is a need for a simple, efficient and compact treatment method for any resulting wastewater in order to minimize environmental impacts. Ion exchange (IE) technology because of its capability for treatment, and its ease of operation, could potentially be a viable process to treat such specific blends of wastewaters. Due to high transportation costs of wastewater and the risks involved in the transportation of highly acidic regenerants, the exhausted ion exchanger could be regenerated using a brine solution that could be prepared on-site.

1.2 Objectives

The principal goal of this research was to evaluate the feasibility of an IE system for the removal of ammonia from a real blend of EIMWW, as well as to establish the theoretical foundation that would allow for the future design of such a treatment system. This was achieved by assessing the suitability of five different IE media for the removal of ammonia from a real EIMWW which also contained potassium and calcium. These other ions are also removed by IE media and have the potential of significantly impacting the removal of ammonia due to competition. The specific objectives of this thesis are as follow. First, to use batch adsorption isotherms to evaluate five different IE media for the removal of ammonia from distilled water.

Second, to use batch adsorption isotherms to evaluate the same five IE media for the removal of ammonia from EIMWW. A comparison of these two experiments would allow a quantification of the magnitude of competitive sorption. Third, to assess the impact of the regenerant solution's KCl and NaCl concentration on the removal of ammonia. And finally, to evaluate the treatment of EIMWW using a continuous flow column system, similar to those used in full-scale systems, to reassess the impact of competitive ion exchange and evaluate the suitability of batch tests to predict the performance of continuous flow systems through direct comparison of performance between batch and dynamic conditions.

1.3 Thesis Layout

The layout of this thesis is consistent with the research paper format, rather than the traditional format. There are six chapters in total, the first chapter being the introduction chapter. It includes background information on the problem at hand, the related environmental concerns as well as the objectives of the research. The second chapter is a literature review focusing on ammonia removal; i.e. it's cause and effects in an environmental setting, various methods of treatment and finally an in-depth review of the ion exchange process. The portion related to ion exchange provides a brief history, an explanation of the basic mechanisms of IE, as well as a brief account of the research conducted for the improvement of ion exchange processes. The third chapter consists of a description of the materials and procedures used in the experiments that were conducted.

Chapter four is a technical paper presenting the results of the batch sorption experiments conducted on the five different ion exchange materials and examining the implications of competitive adsorption. This paper, entitled “Removal of Ammonia from explosive impacted mining wastewater by ion exchange” serves as the base work to develop an understanding of the interactions between various ion exchange materials and the various cations present within the mining wastewater. Furthermore, it allowed to shape the direction taken by the second technical paper presented in this thesis. Chapter five is a second technical paper entitled “Ion exchange of TAN in mining wastewater: implications of batch regeneration cycles and column performance on modified zeolites”. It studies the effectiveness of five different solutions for the regeneration of a modified as well as a natural zeolite. Furthermore, this second paper investigated the effects of running a flow through column system using a modified zeolite by comparing a synthetic ammonia wastewater solution to that of the mining wastewater. Finally, chapter six presents the conclusions of the study and provides suggestions for future works involving ion exchange in complex multi-component systems.

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Chapter 2: Literature Review

This following section provides a summary of background information ammonia and the implications of its presence can affect the aquatic environment. Furthermore, it includes various treatment methods, for the removal of ammonia from various water sources.

2.1 Ammonia

Ammonia is a hydrogen and nitrogen compound which can occur naturally but is also is one of the most produced chemicals in industry (New York State Department of Health 2005). Ammonia exists in two different states depending on the pH and temperature: the first form, composed of one nitrogen atom joined to three hydrogen atoms, is referred to as unionized ammonia and has a nomenclature of NH_3; and the second form, which is referred to as ionized ammonia or ammonium ion and has a nomenclature of NH_4^+. The equilibrium equations linking both compounds are presented in the following equations:

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

$$pH = pK + \log\left\{{[NH_3]}\middle/{[NH_4^+]}\right\} \qquad \text{(eq 2.2)}$$

Equation 2.2 demonstrates the process equilibrium constant pK which dictates the concentration of each species. The process equilibrium constant for ammonia is approximately 9.24-9.30 for water with a temperature of 18-25 ^{o}C (Halling-Sørensen and Jorgensen 1993). Figure 2-1 demonstrates the balance of the two-species relative to the pH at 20 ^{o}C. The sum of these two compounds is called the total ammonia nitrogen (TAN). Neither concentration of these two components are in constant in equilibrium and variations in pH and temperature can sway the total concentration towards either form (Appl 1999; Environment Canada 2001; New York State Department of Health 2005). The concentration of NH_3 can be calculated by applying the following formulas (Environment Canada 2010):

$$pKa = 0.0901821 + \frac{2729.92}{T} \qquad \text{(eq 2.3)}$$

$$f = \frac{1}{\left[10^{(pKa-pH)}+1\right]} \qquad \text{(eq 2.4)}$$

Where T is the temperature in Kelvins and f is the fraction of ammonia present in the unionized form.

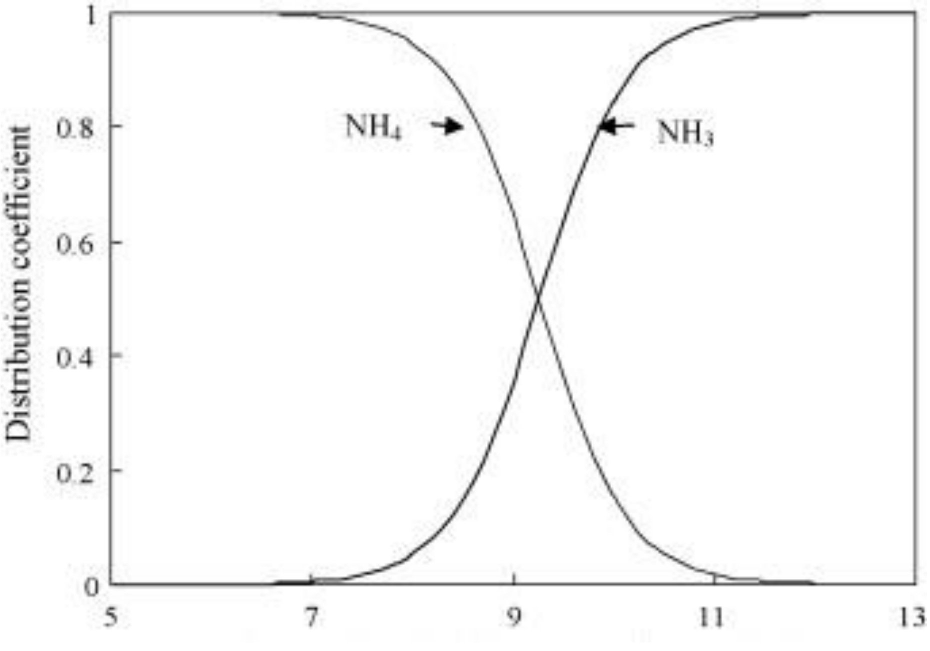

Figure 2-1. Ammonia Ionization Relative to pH at 20 °C (Lin et al. 2009)

The single largest use of ammonia stems from the fertilizer industry as nitrogen is one of the main nutrients for plant growth along with phosphorous (Appl 1999; Nett and Aggrochemicals

2008). Ammonia is also used in the production of explosives, dyeing agents, and household cleaners and industrial cleaners, all of which can find their way into the ecosystem and more specifically the aquatic ecosystem (Appl 1999). Another significant contributor to the release of ammonia is the effluent of municipal wastewater treatment plants which in 2001 was estimated at approximately 62 000 tonnes NH_3-N/year (Environment Canada 2001).

2.1.1 Ammonia in the Environment

The release of ammonia into the aquatic environment has four principal detrimental effects:

1. Eutrophication of natural waterways;
2. Major consumption of dissolved oxygen;
3. Toxicity in aquatic lifeforms; and
4. Nitrate contamination of groundwater sources.

(Mercer et al. 1970; Nehring et al. 1990; Halling-Sørensen and Jorgensen 1993; Green et al. 1996; Guo et al. 2008; Nett and Aggrochemicals 2008; Li et al. 2011)

The first point refers to nitrogen's natural capacity to act as a nutrient for plant-based lifeforms. As previously mentioned, nitrogen is one of the two main fertilizers used to accelerate plant growth; but when too much is introduced into the aquatic environment in the form of ammonia, it can result excessive growth of algae. The build-up of algae on the surface impedes the penetration of sunlight which in turn prevents any plants at the bottom of the waterway from synthesising solar rays. Like any other living entity without a food source the aquatic flora dies off in mass quantities, which leads to aerobic decomposition of matter on a large enough scale that can deplete the waters of dissolved oxygen. This is especially prevalent in the lake bottoms, where most game fish reside. As most aquatic species survive on dissolved oxygen, its presence is critical to their well-being (Hasler and Swenson 1967; Lund 1967; Scholten 2005; Webber 2010; Ansari editor and Gill editor 2014). One excessive growth of concern is that of cyanobacteria or blue-green algae due to ammonia consumption. Cyanobacteria blooms lead to discolored surface waters which pose serious health concerns, either through direct human contact such as drinking or swimming within the waters, or indirect contact such as the consumption of contaminated aquatic species like oysters (Anderson 1994; Landsberg 2002). Cyanobacteria is of specific concern due to certain unique properties such as its potential to release powerful toxins (Haselkorn 2009). The city of Toledo, OH, was required to issue a drinking water ban for more than two days due to cyanobacteria related toxins (Steffen et al. 2017).

Ammonia has officially been recognized as a prevalent contaminant, requiring that all industrial wastewater sources implement some form of discharge control. The Canadian Council of Ministers of the Environment (CCME) has set a limit of 0.019 mg NH_3/L as the discharge criteria for unionized ammonia and 27.55 mg TAN/L (at pH = 6 and T = 25 ^oC) for the protection of aquatic life (Environment Canada 2010). The fisheries act lists four effluent discharge criteria's, one of which is a effluent target of 1.25 mg NH_3/L @ 15 $^oC \pm 1$ ^oC (Minister of Fisheries and Oceans 2012). This allows for the control of nutrient discharges, furthermore, this helps prevent the consumption of dissolved oxygen. When ammonia is released into the environment, the bacterial consumption of ammonia requires 4.6 mg of oxygen for every mg of ammonia (Halling-Sørensen and Jorgensen 1993). Therefore, elevated concentrations of ammonia can easily deplete oxygen levels.

As previously mentioned ammonia exists in two forms, the ionized form NH_4, and the unionized one NH_3. Previous studies have noted that while ionized ammonia does not pose significant threat to fish, its unionized counterpart is acutely toxic to several fish species (Thurston et al. 1981; Randall and Tsui 2002; Environment Canada 2010; Souza-Bastos et al. 2017). The government of Canada has performed extensive research on the effects of ammonia on fish and summarized the LC_{50}, or the concentration of un-ionized ammonia producing 50% mortality rate (Environment Canada 2001). The results for several fish species have helped shape the Environmental Protection Act of 1999 and the lowest tolerance listed is for white perch at 0.279 mg NH_3/L. The green sunfish are listed with the highest tolerance coming in at 1.860 mg NH_3/L (Environment Canada 2001). It has also been noted that large fluctuations of ammonia can be even more lethal to fish than a steady elevated concentration (Thurston et al. 1981). Finally, if ammonia is converted to nitrite and nitrate through the nitrification/denitrification process, there is potential for seepage into groundwater sources (Schnobrich et al. 2007; Tutmez and Hatipoglu 2010). The ingestion of nitrate has proven to be extremely detrimental to young infants and can often lead to death. This condition is called methemoglobinemia, often referred to as blue baby syndrome (Comly 1945). This further reinforces the notion that ammonia is a leading nuisance in the environment and should not be released untreated.

2.2 Treatment of Ammonia

2.2.1 Biological Treatment

Historically, biological treatment has been considered one of the most essential methods of treating ammonia (Tang and Chen 2015). This is accomplished through a process named the nitrification/denitrification process (Tchobanoglous et al. 2003). This process can be broken into two distinct segments: the first is called nitrification and involves the use of bacteria named nitrosonomas which converts ammonia into nitrite (NO_2); a second bacteria, named nitrobacter then converts the nitrite into nitrate (NO_3) (Gerardi 2002) . This is accomplished as demonstrated by the following equations (Gerardi 2002):

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4\,H^+ \qquad \text{(eq 2.5)}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad \text{(eq 2.6)}$$

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \qquad \text{(eq 2.7)}$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad \text{(eq 2.8)}$$

From the previous equations, the nitrification step consists of the oxidation of both ammonia ion and unionized ammonia thus resulting in an aerobic process, ie. requiring the presence of oxygen. This process is very oxygen-intensive and is one of the common culprits for the depletion of dissolved oxygen in natural waterways (Lahav and Green 1998; Karadag et al. 2008; Conley et al. 2009; Müller et al. 2012)

The second step is denitrification, which consists of a reduction reaction that proceeds as heterotrophic bacteria function in an anoxic state. During this step, the nitrate is reduced to nitrogen gas which is in turn released into the air. Gerardi (2002) has documented this reaction as taking the following form:

$$C_5H_{10}O_5 + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 7H_2O + 2N_2 \qquad \text{(eq 2.9)}$$

These processes are generally accomplished in one of two manners: through attached growth media, or suspended growth (Focht and Chang 1975). The former consists of any technology where the bacterial culture is attached to a fixed medium through which the water is brought into contact. The most common attached growth media are rotating biological contactors (RBC) and trickling filters. Both attached growth methods unfortunately feature disadvantages. RBCs tend to feature mechanically complex structures that can be difficult and expensive to maintain. These systems usually consist of large mounted disks, which upon rotation, allow continuous contact between the biomass attached to the disks and flowing wastewater. Shaft failures as well as failure of other mechanical components have historically been common issues (Davis 2010). An example of a typical RBC design is presented in Figure 2-2. Trickling filters generally consist of large circular beds, composed of a media that simultaneously allows the passing of water and encourages the growth of biomass upon the media surface. This allows for biomass-wastewater contact while inducing aeration through turbulence. An example of a typical trickling filter is presented in Figure 2-3, where the wastewater is being spread across a bed of media. Trickling filters are susceptible to accumulation of biomass on the media which can lead to clogging, furthermore, these systems require a large footprint when treating high volumes of water (Davis 2010).

In the case of suspended growth, the processes do not feature any media for bacterial growth but rather rely on aeration to keep the bacteria in suspension, with activated sludge being the most common (Gerardi 2002; Davis 2010). In the activated sludge process, bacteria consume the ammonia and reproduces, creating large colonies of bacteria which can flocculate, settle and then be collected at the bottom of the unit, thus effectively removing suspended solids. The collected waste stream of flocculated bacteria is referred to as sludge. Limitations of the activated sludge process include low pH values due to nitrification as well as the production large volumes of sludge, which require further treatment (Davis 2010). Figures 2-2, 2-3 and 2-4 respectively demonstrate RBCs, trickling filters and activated sludge processes.

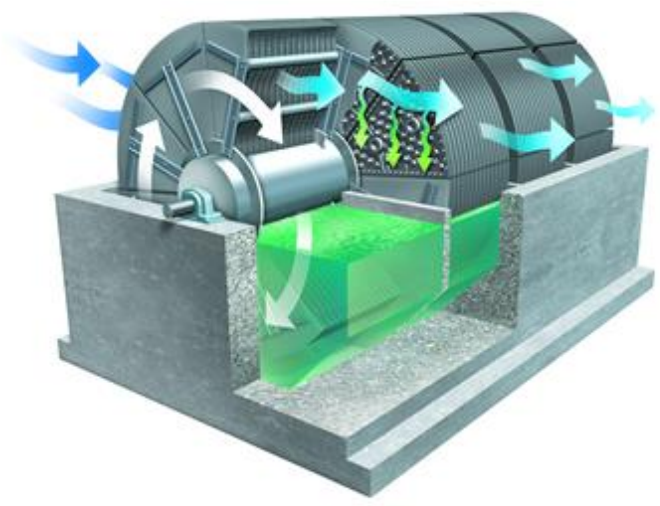

Figure 2-2. Rotating Biological Contactors (RBC’s) (The Mcnish Corperation 2012)

Figure 2-3. Trickling Filter (Bansal 2017)

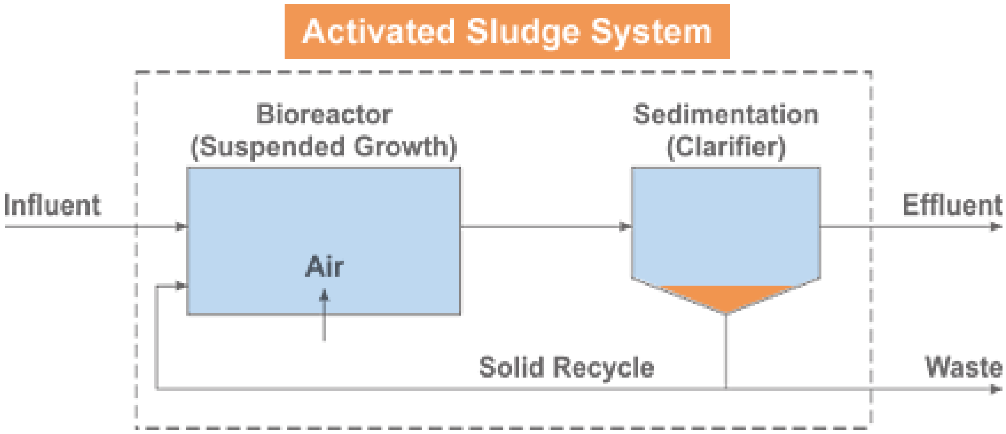

Figure 2-4. Waste Activated Sludge Process (Qualicom Solutions (P) LTD 2017)

Nitrification/denitrification does have potential disadvantages, such as bacteria toxicity due to heavy metals. Additionally, biological processes do not perform as well when subjected to shock loadings, whether they are shocks due to purely volume-wise changes or in terms of ammonia concentrations (Wang et al. 2006; Miladinovic and Weatherley 2008; Kurniawan et al. 2010; Almutairi and Weatherley 2015). All bacterial processes are very susceptible to change, thus requiring very long start-up times, and constant conditions such as pH, high dissolved oxygen levels as well as higher solid retention times. These factors can lead to a certain lack of flexibility. Mining wastewater sources are not always constant and may feature large fluctuations which could lead to complications with start-up times. Furthermore, cold climates have been proven to pose operational issues as temperatures below 10 ºC have historically lead to complications due to greatly reduced biological kinetics (Jorgensen and Weatherley 2003; Wang et al. 2006; Widiastuti et al. 2011). Many Canadian mining projects run year-round thus operate in cold temperatures.

2.2.2 Air Stripping

Air stripping is an efficient and cost-effective physico-chemical process for removing dissolved compounds which are volatile or semi-volatile in nature and transfers them into an air stream. This process has been used extensively to remove volatile organic compounds (VOC's). This process involves introducing large quantities of air into a wastewater stream to allow the target compound to volatilize. There are two main types of air stripping; packed towers and diffused aerators (Crittenden et al. 2012a). The packed towers or columns are filled with packing material; generally composed of engineered plastic materials placed randomly within the column, the water is distributed along the top of the column and trickles down the packing material as air is blown from the bottom of the tower. The packing, disperses and randomizes the flow path of the water and helps increase the turbulence within the tower, this in turn increases the air-water interfacial area and facilitates the transfer of the volatile compound from the liquid phase to the gas phase (Halling-Sørensen and Jorgensen 1993). Figure 2-5 illustrates a typical packed tower configuration.

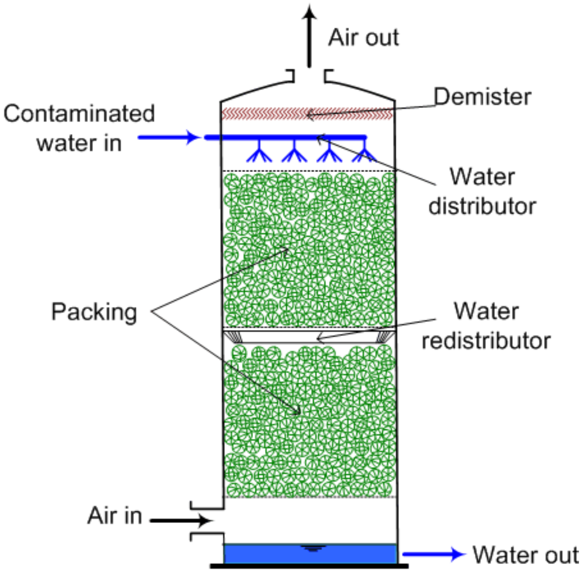

Figure 2-5. Air Stripping Tower (KudzuVine 2007)

The critical aspect as to the suitability of this process to remove a given compound is the compounds volatility, this property is quantified in terms of te Henry's Law Constant, which quantifies the gas-liquid equilibrium constant (Crittenden et al. 2012a).

The concentration of gas-liquid equilibrium constant (Yuan et al. 2016) can be found as follows:

$$C_L^* = \frac{C_G}{H_C} \qquad \text{(eq 2.10)}$$

Where, C_L^* is the gas-liquid equilibrium concentration in mg/L, H_c is the ammonia Henry's law constant and C_g is the gas phase concentration in mg/L.

As ammonia, in its unionized form is a highly volatile gas, USEPA recommends that air stripping of ammonia be conducted at high pH values of 10.8-11.5 (United States Environmental

Protection Agency 2000). Ammonia removal as high as 90% has been reported, but unfortunately when temperature is reduced the ammonia removal efficiency is substantially reduced because the Henry's Law constant decreases substantially with decreasing temperature (O'Farrel et al. 1973).

Other issues with air stripping involve the presence of surfactants, such as soap, which can greatly hinder the volatilization process. Furthermore, air stripping is not possible in freezing conditions, therefore there is the potential of incurring large power demands for heating the water or air streams (Crittenden et al. 2012a). For example, reducing the temperature of the air stream from 20 ^{o}C to 10 ^{o}C can reduce ammonia removal efficiency from 95 % to 75 % (United States Environmental Protection Agency 2000).

2.2.3 Ion-Exchange

Ion-exchange (IE) is most often described as a process where charged ions within a given solution are selectively exchanged for those attached to an insoluble solid material (Helfferich 1962; Davis 2010; Diwekar 2014). The exchangers themselves have the ability to release ions that are in the solid phase and proceed to exchange them for other ions that are in the soluble phase.

2.2.3.1 Historical Introduction

Lucy (2003) states that the earliest accounts of IE can arguably be found within the Old Testament, which claims that Moses converted undrinkable water into a potable water source. While some believe these ancient texts refer to the phenomena of ion-exchange, two soil chemists named H. S. Thompson and J. T. Way are credited as the first to truly investigate the science of IE in 1848 (Lucy 2003). This was accomplished by studying the exchange of ammonium with calcium in clay columns. They determined that ion-exchange could potentially became a viable option for selective removal of charged ions (Harland 1994). The first IE materials were all of natural origins such as clays and soils possessing alumino-silicate lattices, the latter eventually led to the discovery of natural zeolites by Thompson and Way in 1848 (Crittenden et al. 2012b).

2.2.3.2 Natural Zeolites

Natural zeolites, stemming from crushed minerals were an important discovery as they possessed higher capacities than previously used materials and were comprised of many different types including, but not limited to, chabazite, faujasite and clinoptilolite (Ames 1960; Jorgensen et al. 1976; Montégut et al. 2016). Natural zeolites have porous structures composed of interlacing aluminosilicates attached by covalent bonds to oxygen atoms forming tetrahedral structures (Smith and Smith 2015).

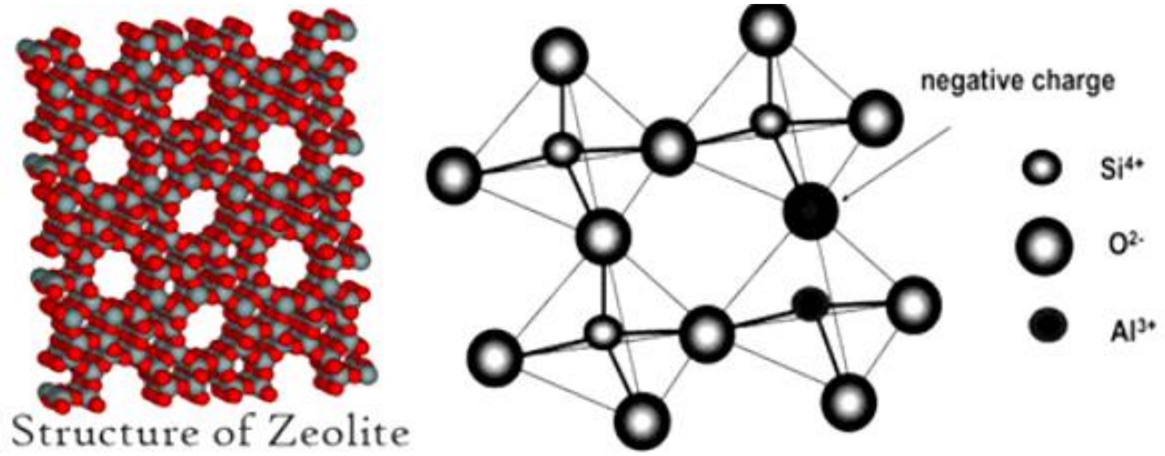

Figure 2-6. Potential Zeolite Structural Matrix (Gordes Zeolites 2014)

These structures can have variances in their atomic make-up which lead to different mineral configurations. Despite these variations, all zeolites share the same general atomic formula (Weatherley and Miladinovic 2004; Margeta et al. 2013; Casadellà et al. 2016).

$$(Na^{+}, K^{+}, Ca^{2+})_{6}(Si^{4+}, Al^{3+})_{36}O_{72} \cdot 2H_{2}O$$

In this formula both the Si/O_2 and Al/O_2 bonds represent the fixed-ion and the placement and/or presence of aluminum will determine the mineral type. Furthermore, the sodium, potassium and calcium component represent the counter-ions that can be exchanged with ions in solutions. If the amount of aluminum present within the aluminosilicate lattice decreases, then the overall charge of the mineral will increase, therefore it will preferentially adsorb higher charge cations (Margeta et al. 2013). From this it can be surmised that a zeolite with higher silicon content will prefer monovalent cations. Unfortunately, zeolites have low resistances to acidic or basic solutions and can easily degrade. Ultimately natural zeolites have wide use in water/wastewater treatment whether it be for ammonia removal or the removal of heavy metals such as cadmium and lead (Jamil et al. 2010).

2.2.3.3 Synthetic Ion-Exchange Resin

Limitations in the performance and durability of zeolites led to the creation of one of the first synthetic ion-exchange resin by Leibknecht in 1935 (Crittenden et al. 2012b) followed by Adams and Holmes in 1935 (Adams and Holmes 1934). These functional groups are mostly composed of vinyl polymers such as polystyrene and polyacrylics; divinylbenzene (DVB) is used as the cross-linking agent (Crittenden et al. 2012b). Resins with higher cross-linking lead to lower surface areas and less micropores whereas lower cross-linking resins have more internal ‘space’ which creates many useable micropores. Synthetic resins are most commonly classified by their functional group, from which there are four main categories (Davis 2010):

1. Strong-acid cation (SAC) exchangers will feature a sulfonate (SO_3^-) functional group;
2. Weak-acid cation (WAC) exchangers will feature a carboxylate (COO^-) functional group;
3. Strong-base anion (SBA) exchangers will feature a quaternary amine ($N^+(CH_3)_3$) functional group; and
4. Weak-base anion (WBA) exchangers will feature a tertiary amine ($N^+(CH_3)_2$) functional group

Acid cation exchangers will feature a negatively-charged fixed ion and selectively exchange positively-charged counter-ions and vice versa for the basic anion exchangers. Acid cation exchangers are known to readily remove TAN from solution (Jorgensen and Weatherley 2003; Malovanyy et al. 2013). Figure 2-7 shows the general appearance of a typical IE resin particle. It is important to note that synthetic ion exchange resins have the ability to swell and reduce in size in order to accommodate certain cations of different sizes. This swelling ability is directly proportional to the level of cross-linking, where higher cross-linking leads to less swelling and vice-versa (Helfferich 1962).

Figure 2-7. Amberlite IR120 Na Ion-Exchange Resin

2.2.3.4 Equilibrium Theory

In its simplest form, IE consists of a small particle with a surface charge (either positive of negative) - which is often called the fixed-ion. The free-ions in solution that have the opposite charge will adhere to the fixed-ion and are referred to as free-ions or counter-ions. When a fluid is passed through exchange resin, certain ions within the fluid will be selectively exchanged for those present on the fixed-ion thus transferring molecules from a solution to a solid (i.e., resin), while at the same time the exchanged ion originally on the resin becomes part of the flowing fluid. This can be written out through the following equation provided by Harland (1994):

$$n_B R_{z_A} \cdot A^{n_A} + n_A \cdot B^{n_B} \leftrightarrow n_A R_{z_B} \cdot B^{n_B} + n_B A^{n_A} \qquad \text{(eq 2.11)}$$

Where *R* represents the resin's fixed-ion, *A* and *B* the exchangeable counter-ions and finally n the corresponding ionic charge for compounds *A* and *B*. It is worth noting that the reaction is reversible, a process often referred to as regeneration. The resin will continue exchanging counter-ions until equilibrium is achieved. As ion-exchange will always work towards equilibrium, there is a necessity for electro-neutrality, meaning that the net charge of the exchange media is zero (Crittenden et al. 2012b). Therefore, if the resin originally holds counter-ions with a valence charge of 2^+ and is exchanging for a 1^+ liquid form ion, one freed 2^+ ion will be exchanged for two 1^+ ions. This rule is true for both anion and cation exchangers

2.2.3.5 Selectivity

As with all chemical reactions whether in nature or the laboratory, certain elements will have preferences for which other elements which they react with. This statement also holds true for IE and is referred to as affinity or selectivity (Davis 2010). The selectivity of a resin, K_A^B allows users to predict which ion is most likely to be exchanged for the counter-ion. It is important to note that while the selectivity of a resin is denoted by K, it is not the same as the equilibrium constant, a distinction that is sometimes incorrectly used in scientific literature (Helfferich 1962). It can be quantified as follows:

$$K_A^B = \frac{(A^+)^n(RB^{n+})}{(RA)^n(B^{n+})} \qquad \text{(eq 2.12)}$$

where A and B represent the aqueous phase equivalent concentration of respective counterions, RA and RB the resin phase (or solid phase) equivalent concentration of respective counter-ions, and finally n is the valence charge of exchanging ion (Davis 2010). Therefore, the higher the selectivity coefficient the higher the preference said resin will have for the counter-ion in question. It is worth noting that while the valence charge of an exchangeable ion does play an important role in the IE process, concentration is also considered in the previously mentioned equation. Therefore, it is possible to circumvent the general valence charge selectivity with a large concentration differential. For example, if the concentration of a +1 ion is much larger than that of a +3 ion in the same mixture then the ion exchanger may selectively remove the +1 ions. This is the fundamental basis upon which the regeneration process is founded.

2.2.3.6 Separation Factors

When evaluating an ion exchange material's selectivity for various elements, it is common to calculate a parameter entitled the separation factor (α_j^i). This parameter is defined by the following equation:

$$\alpha_j^i = \frac{X_i Y_j}{X_j Y_i} \qquad \text{(eq 2.13)}$$

where *i* represents the original counter-ion and *j* a presaturated ion within solution. *X* is the resin phase equivalent concentration and *Y* the aqueous phase equivalent concentration of a given ion. The separation factor allows to quantify the preference an ion exchanger may exhibit for one ion over another (Crittenden et al. 2012b). A high separation factor would result in a much larger exchange of ion *i* in comparison to equivalent concentration of ion *j*. The separation factor differs from selectivity in the sense that selectivity considers an IE media's affinity for one molecule versus the initially adsorbed counter-ion, whereas the separation factor compares the preference of an IE media for two molecules in solution.

2.2.3.7 Process Operation

Ion-exchange processes mainly occur under two different configurations. The first system consists of batch operation, where the solution requiring treatment is subjected to the IE media in a closed environment and allowed a predetermined amount of time, thereby providing sufficient contact time to allow for mass transfer. Because of their simplicity, batch tests are used extensively in IE research. The second system is that of a continuous flow system, where the solution is passed through a large vessel at a continuous rate and the contact time is determined by the flowrate entering the vessel. For industrial IE processes the main form of operation is continuous flow through large cylindrical vessels filled with a fixed bed of resin, they are also often called ion-exchange columns (Helfferich 1962).

The kinetics behind column operation are very complex and while certain models exist such as the Thomas and Adams-Bohart models (Malovanyy et al. 2013) it is often better to determine outcomes through experimentation. The transfer of ions is generally explained as a moving front, that works its way along the length of the column as counter-ions are exchanged with the ions present in the solution. Figure 2-8 demonstrates the generalized process of the mass transfer zone (MTZ) in an activated carbon adsorption column. The generalized process is the same for IE.

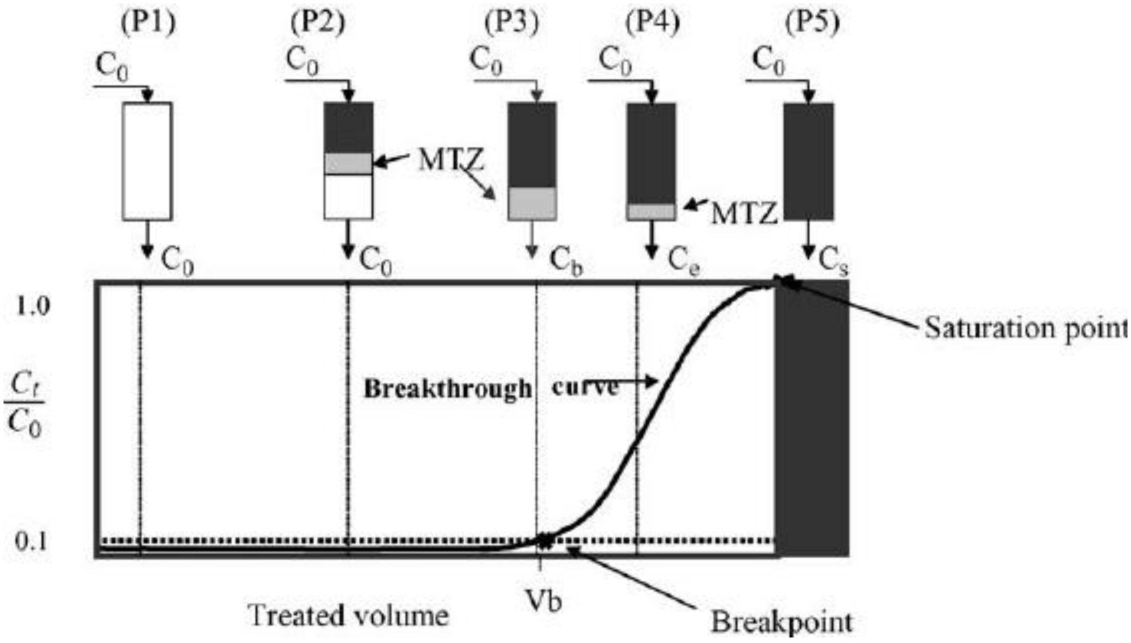

Figure 2-8. Generalized Column Operation Mass Transfer Zone in Activated Carbon Column (Christian Taty-Costodes et al. 2005)

As the solution progresses through the column, all ions are removed by the IE material resulting in an effluent concentration of approximately zero as seen under P1. The column will slowly become saturated resulting in a migration of the MTZ (P2). Once the column is sufficiently saturated, the MTZ will reach the end of the column and due to kinetics or diffusion limitations, will not allow sufficient time for the complete uptake of ions. This point is referred to as breakthrough or the breakpoint (P3). The breakpoint is often taken as 5-10 % of the influent concentration but can also be set for other concentrations depending on environmental effluent regulations. After breakthrough the concentration will rapidly increase until the saturation point, or when the effluent concentration is that of the influent concentration (Wachinski 2006).

During practical application, once the breakthrough point has been reached, the feed of untreated water is cut off and the column is regenerated (Helfferich 1962; Harland 1994; Davis 2010; Crittenden et al. 2012b)

2.2.3.8 Regeneration

One of IE's most attractive features is the ability to regenerate the resin once equilibrium has been achieved (Klieve and Semmens 1980; Milan et al. 1997; Bochenek et al. 2011). This process is called regeneration and involves circulating a regeneration fluid through the resin to remove all the previously exchanged ions. IE resins pose a certain selectivity for various species. This means a resin will preferentially exchange an element or compound with a higher selectivity coefficient. This selectivity can be overcome using a much larger concentration deferential, meaning that if species A is more favorable to the resin but species B has a much higher concentration, the resin will select species B instead. For example, clinoptilolite has a greater affinity for ammonia then it does for sodium, but during the regeneration process, extremely high concentrations (>10,000 mg/L) of sodium are used to replace the exchanged ammonia with sodium, allowing for further IE cycles (Ames 1960; Jung et al. 2004; Miladinovic and Weatherley 2008; Almutairi and Weatherley 2015). Following this basic principle, a resin may theoretically be reused indefinitely. For SAC/WAC exchangers, the regeneration fluid will be either a brine solution or an acidic solution, while SBA/WBA exchangers will use basic solutions.

2.2.3.9 Modelling of Batch Ion-Exchange Systems

The duration of batch tests is generally chosen so that there is sufficient time to reach equilibrium, thus the general basis for batch IE modelling is to use equilibrium models normally referred to as isotherm models. They are named isotherms because the equilibrium tests are conducted at constant temperature, but their main feature is that they are equilibrium tests. In general, isotherm model equations relate the equilibrium solid phase concentration (q_{eq}) and the equilibrium liquid phase concentration (C_{eq}). q_{eq} is calculated by conducting a mass balance of the contaminant of concern (considering both the solid and liquid phase) between the initial and final conditions of the batch test. The mass balance for contaminant X is:

$$\left(M_{liquid}^{X}\right)_{initial} + \left(M_{solid}^{X}\right)_{initial} = \left(M_{liquid}^{X}\right)_{final} + \left(M_{solid}^{X}\right)_{final} \qquad \text{(eq 2.14)}$$

$$V * C_i + M * q_i = V * C_{eq} + M * q_{eq} \qquad \text{(eq 2.15)}$$

Where M is the mass of contaminant X in mg, X is the contaminant in question, V is the volume of the system in L, C_i is the initial aqueous phase concentration of the pollutant in question in mg/L and C_{eq} is the equilibrium aqueous phase contaminant concentration in mg/L. Finally, q_i and q_{eq} are the initial and equilibrium solid phase contaminant concentration respectively in mg/g.

By isolating for the equilibrium capacity term (q_{eq}) and assuming q_i equals zero, it is possible to arrive at:

$$q_{eq} = \frac{(C_{eq} - C_i) * V}{M} \qquad \text{(eq 2.16)}$$

This equation is used to calculate the solid phase concentration achieved at the end of the batch experiment.

This allows us to plot the equilibrium solid phase concentration on the y-axis versus the equilibrium liquid concentration on the x-axis. There are countless models, and each have their own strengths and weaknesses depending on the desired application. Two of the most basic single-component isotherm models are the Langmuir isotherm and the Freundlich isotherm (Helfferich 1962; Wachinski 2006; Crittenden et al. 2012b; Diwekar 2014). Through regressions it is possible to determine the constants used by the previously mentioned models, which in turn can serve as an aid to predict the behaviour of the system.

2.2.3.9.1 Langmuir Model

The Langmuir model was developed by Irving Langmuir in 1916 and is based on four principal assumptions (Helfferich 1962; Diwekar 2014). The first assumption is that all adsorption sites are equivalent; secondly all adsorbed materials do not interact with each other; thirdly all adsorbed materials are adsorbed through the same mechanism; and finally only a monolayer of sorbed molecules will form on the surface of the adsorbent, meaning there is only one molecule per adsorption site (Diwekar 2014). Langmuir proposed the following equation with its corresponding linearization.

$$q = \frac{Q_m * b * C_{eq}}{1 + b * C_{eq}} \qquad \text{(eq 2.17)}$$

Where q is the equilibrium solid phase concentration of contaminant X (mg X/g resin), Q_m is the Langmuir monolayer constant (mg/g), b is the Langmuir adsorption model constant (L/mg) and C_{eq} is the aqueous equilibrium concentration (mg/L). The Langmuir model has found success in modelling ammonia exchange onto natural zeolites and is widely documented in modern literature (Leyva-Ramos et al. 2004; Widiastuti et al. 2011; Ding and Sartaj 2015).

2.2.3.9.2 Freundlich Model

The Freundlich model is another common adsorption model, which is especially popular for liquid-solid phase extractions (Helfferich 1962), and is frequently considered for modelling the sorption of ammonia (Weatherley and Miladinovic 2004; Widiastuti et al. 2011; Ding and Sartaj 2015). Unlike the Langmuir model, the Freundlich model does not pose the monolayer of sorbed ions restriction. Derived by Freunldich in 1926 (Diwekar 2014), its equation is:

$$q = K_f {C_{eq}}^{1/n} \qquad \text{(eq 2.18)}$$

Where q is the equilibrium solid phase concentration of contaminant X (mg X/g resin), K_f is a Freundlich model constant (L/mg), C_{eq} is the liquid equilibrium constant of contaminant X (mg/L) and 1/n is a Freundlich model constant.

2.2.3.10 Other Methods

Several other methods exist for the removal of ammonia from water streams. Some of the most common ones include, but are not limited to, struvite precipitation, reverse osmosis and breakpoint chlorination (Halling-Sørensen and Jorgensen 1993; Weiner 2000; Kurniawan et al. 2006; Ledda et al. 2013; Liu et al. 2015)

2.3 TAN Related Ion-Exchange Developments

The process for the removal of ammonia from aqueous solutions by use of IE, especially using natural zeolites, is well documented (Weatherley and Miladinovic 2004; Li et al. 2011; Montégut et al. 2016; Huang et al. 2017). Ames (1960) is generally considered responsible for the initial work concerning ammonia as the primarily exchanged cation present within solution (Hedström 2001; Guo et al. 2008). The general order of cation selectivity for Clinoptilolite, the most common natural zeolites, was extensively studied (Ames 1960) and was determined to follow this general rule:

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

This has further been confirmed by several other studies and is considered the accepted standard (Ames 1967; Koon and Kaufman 1975; Jama and Yücel 1989; Leyva-Ramos et al. 2004; Guo et al. 2008; Widiastuti et al. 2011). According to these studies, this material seems to prefer potassium over ammonia

2.3.1 Biological Ion-Exchange Processes

A large portion of IE research has been devoted to combining IE technology with other already existing technologies with the aim of simultaneously improving both. For example, Semmens and Porter (1979) investigated making use of a combined biological and IE system with the goal of introducing nitrifying bacteria onto the resin itself. The goal was to convert the ammonia into nitrate. This would permit the denitrification of the regenerant stream. Their experiments produced a resin capacity of 0.22 meq TAN/g of clinoptilolite, resulting in ammonia reductions of approximately 90-97 % (Semmens and Porter 1979).

Lahav and Green (1998) performed a similar experiment where preloaded zeolites acted as active biofilm carriers for nitrifying bacteria with the aim of nitrifying ammonia upon regeneration. They concluded that while the biofilm did not hinder the adsorption process the zeolite preloaded with potassium did feature shorter and less favorable breakthrough times: 160 bed volumes vs the 260 bed volumes featured by the sodium regenerated system (Lahav and Green 1998). This indicated that potassium acted in direct competition with TAN for active sorption sites. Ultimately a removal efficiency of 95% was achieved with an initial concentration of 40mg NH_4^+/L. Furthermore, Miladinovic and Weatherley (2008) also studied the interactions between nitrifying bacteria and the ion exchange process, namely mordenite and clinoptilolite zeolites. One key component to their research was to establish whether the aeration necessary for nitrification had any impact on the ion exchange process. This was determined by comparing breakthrough capacities in one column operated with aeration and the lack thereof in the other. The general conclusion was that the presence or lack of aeration posed no noticeable effects upon the ion exchange process itself. Furthermore, a secondary finding was that the addition of nitrifying bacteria improved performance for both zeolites: 50 % and 36 % for both clinoptilolite and mordenite respectively. Clinoptilolite's capacity was increase from 0.15 meq TAN/g to 0.22 meq TAN/g (Miladinovic and Weatherley 2008). The presence of nitrifying bacteria increased the mordenites capacity from 0.30 meq TAN/g to 0.41 meq TAN/g, suggesting a better TAN removal performance by mordenite than the clinoptilolite.

Others have tried to use powdered zeolites in an attempt to combine ion exchange, nitrification/denitrification and flocculation in sequential batch reactors (Jung et al. 2004). The addition of powdered zeolites did improve nitrogen removal from 70-82 % for the same hydraulic and solids retention time as well as providing an ammonia capacity of 0.33-0.41 meq TAN/g fixed suspended solids (Jung et al. 2004). The powdered zeolites featured the advantage of potential repurposing as a fertilizer with slow release ammonia capabilities. Unfortunately, as this method is a sequencing batch reactor type, the reactors are filled and subsequently emptied, resulting in difficulty of full recovery of zeolites for regeneration.

These biological methods can prove very beneficial for the treatment of ammonia by ultimately increasing treatment efficiency as well as reducing the cost of chemical regeneration (Jung et al. 2004) and can potentially deal with shock loadings if these are not too extreme. Ultimately, they are best suited for non-industrial purposes where contaminants are of a biological nature such as municipal wastewater treatment or swine manure as examples. This is due to bacteria's living nature and while it thrives when used to treat biologically produced contaminants, non-organics such as heavy metals continuously pose a threat to active bacteria colonies (Jorgensen et al. 1976) as well as the environmental constraints such as extreme pH values and low temperatures.

2.3.2 Pre-Treatment of Ion-Exchange Materials

In addition to potentially combining processes for the purpose of increasing efficiency, other research has been invested in physically, chemically or even thermally treating ion-exchangers to achieve the same end.

Klieve and Semmens (1980) performed pre-treatment studies on erionite, mordenite, phillipsite and clinoptilolite to evaluate their respective TAN uptake capacities and the impact of repeated sodium chloride regeneration cycles. These repeated regeneration cycles served as a form of pre-conditioning while attempting to achieve uniformity in the free-ions present on each zeolite. It has been stated that a homogenous distribution of counter-ions can greatly increase the overall performance of an IE material (Koon and Kaufman 1975; Semmens and Goodrich 1977; Klieve and Semmens 1980; Townsend and Loizidou 1984; Booker et al. 1996; Baykal and Guven 1997; Milan et al. 1997; Hedström 2001; Panayotova and Velikov 2003; Leyva-Ramos et al. 2004) Other methods of pre-treatment include the application of heat, nitric acid and sodium hydroxide. Experiments concluded that the pre-treated clinoptilolite performed similarly to mordenite with capacities of approximately 1.6 meq NH_4^+ /g. This contradicts works accomplished by Miladinovic & Weatherley (2008) where mordenite was found to be superior to clinoptilolite. It can be hypothesized that the lack of pre-treatment in most literature concerning clinoptilolite could have an impact on overall TAN capacity. Another finding was that erionite performed poorly with a capacity of 0.3 mg NH_4^+ /g whereas phillipsite had the best capacity at 2.64 meq NH_4^+ /g (Klieve and Semmens 1980). Unfortunately, phillipsite is a very fragile material with low crushing resistance. The price of the material is also considerably higher than other zeolites; approximately double that of clinoptilolite (Klieve and Semmens 1980). These experiments also support previously stated findings concerning repeated loading/regeneration cycles and how they've been known to increase TAN uptake capacities of clinoptilolite (Jorgensen et al. 1976).

2.3.3 Multi-Component Systems

More recently, researchers have begun to consider increasingly complex blends of wastewaters. This has led to the study of competitive adsorption between multiple species, notably, between TAN and other species.

Because wastewaters from farming industries tend to be extremely high in organics, it is important to understand how these affect the IE process. Jorgensen and Weatherley (2003) investigated the implications of the presence of organics such as citric acids and whey proteins on TAN sorption. The results obtained with clinoptilolite were compared with results from two synthetic ion-exchangers (Dowex 50w-x8 and Purolite MN500) operating under the same conditions. The Dowex resin featured the strongest affinity for TAN. It had no noticeable increase of capacity in the presence of organics whereas both the purolite and clinoptilolite experienced large increases in TAN sorption capacities. These increases were attributed to changes in surface tension resulting from the organics contacting with the counter-ions (Jorgensen and Weatherley 2003).

Furthermore, recent investigations have begun characterizing the impact of potassium’s presence in wastewater, and more specifically, on TAN sorption capacities. As previously mentioned, clinoptilolite’s affinities for potassium and ammonia are quite close. Crittenden (2012b) lists TAN and potassium’s respective selectivity’s as 2.6 and 2.9 for strongly acidic cation exchange resins. There is limited work which has focused on the implications of zeolites and commercial IE resins performances when in the presence of potassium and whether or not it would impede the removal of TAN. Montégut & al. (2016) compared three forms of zeolites, two natural and one synthetic for the removal of ammonium from swine manure which has historically proven high in potassium. Chabazite, clinoptilolite and the synthetic NaX faujasite were used in batch sorption experiments with the swine manure at 25ºC and 40ºC to establish TAN sorption as well as the effects posed by potassium. The clinoptilolite featured the largest reduction in capacity: from 2.6 to 0.11 meq TAN/g when swine manure was treated. The chabazite also featured a substantial drop in capacity, from 3.4 to 1.1 meq TAN/g when subjected to swine manure. Finally, the synthetic zeolite faujasite had the largest final capacity of 3.33 meq TAN/g, exactly half of its initial TAN capacity of 6.6 meq TAN/g (Montégut et al. 2016). Consequently, Torracca et al. (1998) studied ammonia uptake in the presence of potassium and lead on Chabazite and found an ultimate exchange capacity of approximately 2.4 meq TAN/g. It was also noted that the kinetics for potassium and ammonium were extremely fast especially in contrast to that of lead (Torracca et al. 1998). Finally, Wang et al. (2007) compared the effects on TAN uptake on Chinese zeolites when either calcium or potassium were present in the solution. The reduction in capacity was not as drastic as with the Montégut et al. (2006) findings. The initial sorption capacities of the clinoptilolite used were 0.56 meq TAN/g and the presence of potassium and calcium reduced the TAN capacities to 0.44 meq TAN/g and 0.50 meq TAN/g. The same experiment was performed with the synthetic faujasite and the capacity was reduced from 1.05 meq TAN/g to 0.98 meq TAN/g and 1.00 meq TAN/g respectively. Interestingly these results are not in good agreement, as the Chinese zeolites featured much smaller initial sorption capacities but also experienced much smaller reductions when the presence of competing ions were included. This could be attributed to the natural origins of zeolites and thus not providing any form of quality control as far as consistency in atomic configuration. Ultimately, there is still a large gap in the research with concerns to simultaneous sorption and elution of potassium and ammonia (Guo et al. 2013). This gap is further extended when considering the topic of TAN sorption in the presence of multiple competing ions.

2.4 Research Summary and Knowledge Gap

Ammonium removal from wastewaters by use of ion-exchange has been investigated by many different scientists over the last 50 years or so. While traditional methods revolve around biological treatment, every method has its drawbacks and the ever-changing landscape of environmental concerns and industry conditions have called for alternative treatment methods. IE materials have proven to be very successful for TAN removal especially in temperatures below 10 ^{o}C or when dealing with toxic substances. However, the presence of various dissolved ions may hinder the adsorption capacities of ion exchange materials and it is therefore important to understand the implications of competitive adsorption. The majority of competitive ammonia ion exchange research has revolved around the presence of potassium as well as the use of natural zeolites, more specifically clinoptilolite. However, very little published work involves the use of synthetic resins for the removal of TAN in the presence of potassium. Furthermore, there is a lack of research material concerning the removal of ammonia in the presence of multiple competing cations, as well as the regeneration of zeolites by alternate regeneration solutions. Therefore, this study will attempt to focus on the mixed interactions between both natural and synthetic ion exchange materials and TAN in the presence of dilute ions; namely potassium and calcium. It will also further the understanding of zeolite regeneration by alternative regeneration solutions such as potassium-based ones. This will be accomplished by an in-depth analysis of both batch systems as well as a continuous flow system and will involve the use of both a single solute TAN wastewater and a mining wastewater which will likely cause competitive sorption effects.

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Chapter 3: Materials and Experimental Procedure

The experimental research portion of this thesis was conducted to determine the best ion-exchange (IE) materials for the treatment of a complex blend of explosive impacted mining wastewater (EIMWW). Five different IE materials were selected with the purpose of determining through experimentation which would provide the best results. To consider a wide range of IE materials, three synthetic IE resins were selected along with one natural zeolite and finally one modified zeolite.

The research consisted of several different experiments with the selected materials running in the batch or in a continuous flow column reactor. The first set of batch experiments were run with a synthetic ammonium sulfate solution to establish how much time was required to achieve equilibrium in the batch equilibrium IE tests. Following the kinetics experiment, batch equilibrium adsorption tests (i.e., isotherms) were performed for the five IE materials using both a synthetic ammonium sulphate solution and EIMWW. These tests served as the basis for the comparison of all materials, with special considerations to the detrimental effects of competitive adsorption and ultimately allowed for the selection of two materials which displayed the least amount of performance impact as well as the highest total ammonia nitrogen (TAN) exchange capacities; the natural and modified zeolites. Batch regeneration studies were then performed on these two IE materials using different concentrations of potassium chloride and sodium chloride solutions.

Finally, based on its performance in the batch regeneration studies, the modified zeolite was used in continuous flow column experiments, using both the synthetic wastewater as well as the EIMWW. This served as a comparison between the synthetic wastewater and EIMWW in column configuration, as well as with regards to their batch system performances.

3.1 Materials

3.1.1 Ion-Exchangers

Five different ion-exchangers were selected for this research project, three of which were synthetic IE resins, one modified zeolite: which for the sake of simplicity will be considered a synthetic material, and the fifth and final: a natural zeolite. The goal was to explore as many different scenarios as possible. The description of IE materials will be broken into two sections corresponding to the exchangers origins; synthetic or natural.

3.1.1.1 Natural IE Material

The natural zeolite (mineral clinoptilolite), shown in Figure 3-1 was obtained from a fertilizer company (The Seed Supply, Saint Anthony, ID). This zeolite is marketed as an natural fertilizer all purpose adsorbent due to it’s high capacity for water and essential plant growth minerals.

Figure 3-1. Clinoptilolite, Natural Zeolite

According to the manufacturer this product is 85 % clinoptilolite with a cation exchange capacity of 1.4-1.65 meq/g and a maximum water retention of 55 % of its weight. The bulk density is approximately 881-961 kg/m^3 (The Seed Supply 2017). The following table summarizes the rock analytical content of the zeolite.

Table 3-1. Zeolite Elemental Composition (The Seed Supply 2017)

Compound	Percentage (%)
SiO_2	67.40
MgO	0.45
K_2O	4.19
MnO	< 0.01
Al_2O_3	10.60
CaO	2.23
TiO_2	0.27
Fe_2O_3	1.70
Na_2O	0.59
P_2O_5	0.10
LOI (@925^{o}C)	11.40

The Brunauer-Emmet-Teller (BET) surface area was analysed at Chemistry Department, University of Ottawa, with a result of 24.2 m^2/g. The samples were degassed under a vacuum at 1x10^{-5} Torr followed by drying in an oven for 5 hours at 100 ^{o}C. Then nitrogen adsorption was measured at a temperature of 77 K with a Micrometrics ASAP 2020 adsorption analyser. From the relative pressure adsorption isotherm, the surface area was determined.

Prior to each experiment set the clinoptilolite was thoroughly rinsed 8-10 times with deionized water to remove fine dusts and debris. This was accomplished by placing the clinoptilolite in an Erlenmeyer flask, filling it with deionized water and shaking the mixture. The water was then drained, and the process repeated until no turbidity was visible in the water. Not only did this allow for better access to sorption site but also prevented the zeolites from adding color to the water; resulting in error of measurements when applying colorimetric methods. The samples were then dried in an oven at 65 ^{o}C for 4 hours and placed in a desiccator until it was time to begin adsorption tests.

3.1.1.2 Synthetic IE Materials

The first synthetic resin is the Purolite SSTC60, shown in Figure 3-2 was supplied by Purolite (Purolite, Bala Cynwyd, PA), which is a strong acid cation resin in the Na^+ form. SST is the acronym for shallow shell technology and features a non-reactive core and a uniform depth of exchange sites among different resin beads. This ensures that reaction time is the same for all produced resin and the reduced reactive depth reduces the distance travelled by exchangeable cations thus reducing the amount of chemical regenerant required during the regeneration step. Purolite claims this results in sodium savings of 32.04-64.07 kg/m^3 per regeneration cycle (Purolite 2015). The technical data listed in the following table was obtained from the resin's technical brochure.

Table 3-2. Purolite SSTC60 Technical Data (Purolite 2015)

Polymer structure	Gel polystyrene crosslinked with divinylbenzene
Functional group	Sulfonic Acid
Whole bead count functional groups	90 %min.
Ionic form as shipped	Na^+
Total exchange capacity	3.8 meq/g
Moisture retention	36-46 % meq/g
Particle size range	300-1200 µm
<300 µm	1 %
Uniformity coefficient	≤ 1.7
Reversible Swelling, $Na^+ \rightarrow H^+$ (max)	6 %
Specific gravity	1.20
Shipping weight	775-825 g/l
Maximum Temperature limit	60 °C

Figure 3-2. Purolite SSTC60

The second synthetic resin used was the Amberlite IR120 Na^+ form, shown in Figure 3-3. It is a strong acid cation exchange resin; whose main use is for water softening and serves as a good comparison to the SSTC60's shallow shell build. The technical properties are listed in the following table provided by the DOW chemical company (DOW chemical company, Midland, MI).

Table 3-3. Amberlite IR 120 Na+ Technical Properties (Dow Chemicals 2017)

Polymer structure	**Styrene divinylbenzene copolymer**
Functional group	Sulfonate
Ionic form as shipped	Na^+
Total exchange capacity	≥ 2.0 eq/L
Moisture retention	45-50 %
Shipping weight	840 g/L
Uniformity coefficient	≤ 1.9
Particle size range	600-800 μm
≤300 μm	2 % max
Reversible swelling, $Na^+ \rightarrow H^+$ (max)	≤ 11 %

Figure 3-3. Amberlite IR120 Na^+

The third synthetic resin was a strong acid cation exchange resin manufactured by Bojie Resin (Suzhou Bojie Resin, Suzhou city, Jiangsu). The BC121H is a hydrogen form resin manufactured for dealkalinisation and demineralization. As this resin is primarily shipped in hydrogen form it was necessary to be converted it into Na^+ form. This was accomplished by two loading/regeneration cycles. A synthetic solution with ammonia concentration of 1000 mg TAN/L was combined with the resin (1 g to 125 ml) and allowed to react overnight on an orbital shaker. The resin was then separated from the ammonia solution, rinsed thoroughly with deionized water and then regenerated (1 g to 125 ml) with a 10 % w/w NaCl solution to replace the ammonia with sodium as the free ion. This process was then repeated once more. Conversion was tracked by monitoring the pH; as the release of H^+ ions drastically reduced the pH. Once the pH no longer dropped upon ion uptake it was established that the resin was no longer releasing H^+ ions. The technical information obtained from Bojie resin is presented in the following table.

Table 3-4. Bojie resin BC121H Technical Properties (Suzhou Bojie Resin Technology Co. 2017)

Polymer structure	Styrene cross-linked with divinylbenzene
Ionic form as shipped	Hydrogen
Total exchange capacity	1.9 meq/ml min
Moisture retention	53-57 %
>1.19mm	< 5 %
<300µm	< 1 %
Uniformity coefficient	≤ 1.6
Reversible Swelling, $Na^+ \rightarrow H^+$ (max)	Approx. 10 %
Shipping weight	0.75-0.79 g/l
Maximum Temperature limit	120 ºC

The fourth and final IE material was the SIR-600 produced by Resintech. This is a modified zeolite (clinoptilolite) prepared for ammonium and cesium removal.

Table 3-5. Resintech SIR-600 Technical Properties (ResinTechInc 2017)

Material structure	Zeolite
Functional group	Aluminosilicate
Ionic form as shipped	Na^+, K^+
Total Capacity Sodium form	>0.5 meq/ml
Moisture retention	< 10 %
Screen Size Distribution (US mesh)	12 to 40
< 300µm	1 %
Shipping weight	64 lbs/ft^3
Maximum Temperature limit	100 ^oC

Other than converting the BC121H from hydrogen to sodium form all ion exchangers were prepared in the same manner. They were carefully rinsed 2-3 times in distilled water by manual shaking in an Erlenmeyer flask and then placed in an oven at 55 ^oC for 4 hours. Once dried, they were placed within a desiccator to avoid moisture adsorption from the ambient air. The different IE materials will henceforth be referred to in the following manner Purolite, Bojie, Amberlite, SIR-600 and clinoptilolite.

3.1.2 Synthetic Wastewater

For initial kinetics and single component batch IE tests a synthetic wastewater was prepared by dissolving approximately 260 mg certified American Chemical Society (ACS) ammonium sulfate in 1 L of distilled water to obtain an initial concentration of approximately 3.87 meq TAN/L (70 mg/L). The volumetric flask was covered by parafilm for the duration of the mixing (30 minutes) to avoid any potential contamination. A new solution was created for each set of sorption experiments.

3.1.3 Explosive Impacted Mining Wastewater (EIMWW)

The EIMWW was obtained courtesy of Newterra. The preliminary analysis was accomplished both at the University of Ottawa's Geochemistry and at Paracel Labs in Ottawa for trace metals and elemental composition as well as basic anions. Both laboratories performed Inductively Coupled-Plasma (ICP) elemental and metal analysis. This gave a basis of comparison and validation between both sets of 5data. Upon further comparison it was concluded that both laboratories results were within 10 % of each other.

The wastewater was stored in plastic buckets to avoid any leeching of metals and stored at room temperature of approximately 22 ^{o}C. The EIMWW was filtered through a 0.45 µm filter membrane prior to any experiments to avoid fouling the resin and to present ideal conditions for the water quality analysis (shown in Figure 3-4). Newterra would include sand filtration and potentially cartridge or bag filters to achieve a solids concentration of <1 mg TSS/L therefore the filtering of samples was believed to represent real world conditions.

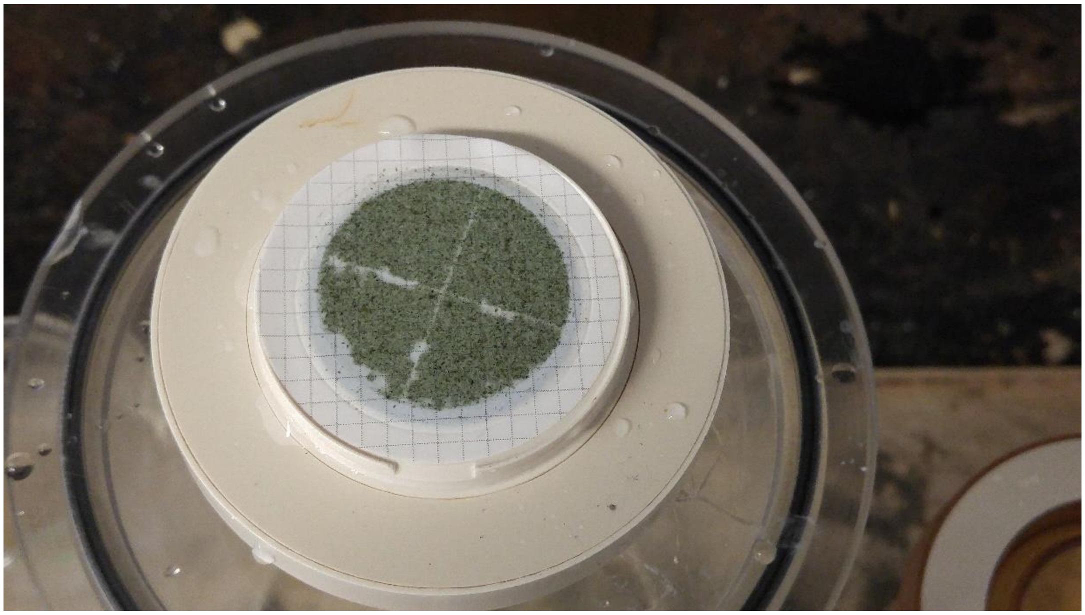

Figure 3-4. Residue Removed from EIMWW Following Filtration

As TAN concentrations of the EIMWW had decreased after 1 year of storage time, likely due to biological activity, the wastewater was spiked prior to tests through the addition of approximately 230 mg of $(NH_4)_2SO_4$ per liter of distilled water. The solution was mixed on a magnetic stirrer for approximately 30 minutes prior to experiments in a volumetric flask covered with parafilm prior to the experiment. A new solution was created for each set of sorption experiments.

3.2 Analytical Methods

3.2.1 Measurement of Ammonia

Ammonia was principally measured by direct nesslerization standard methods 4500-NH_3 (American Public Health Association 2005) and confirmed with the use of HACH TNT 832 test vials. Both, methods are spectrophotometric methods and the absorbances were measured on a spectrophotometer (DR600, HACH, Loveland, CO)

The Nessler technique requires the addition of a stabilizing salt to prevent precipitation followed by the addition of Nessler reagent to react with ammonia. The TAN present in the solution will turn yellow and can then be measured as a form of wavelength absorbance at 425 nm. In this case, Rochelle Salt (Potassium Sodium Tartrate) was used as the stabilizing salt. Nessler reagent consists of Mercuric Iodide, Potassium Iodide, Sodium Hydroxide and water.

A calibration curve was constructed prior to the actual testing. This was accomplished by measuring triplicates of samples of ten standard solutions ranging from 1-10 mg NH_3-N/L in concentration. The use of triplicates ensured quality data, from which an equation was derived for the calculation of ammonia. At this point all concentrations were converted from NH_3-N to the ionized form (NH_4) for the sake of consistency by multiplying their molecular weight fraction; or a factor of $\frac{18}{14}$. Figure 3-5 shows the calibration curve along with the regressed ammonia concentration equation and R^2 value.

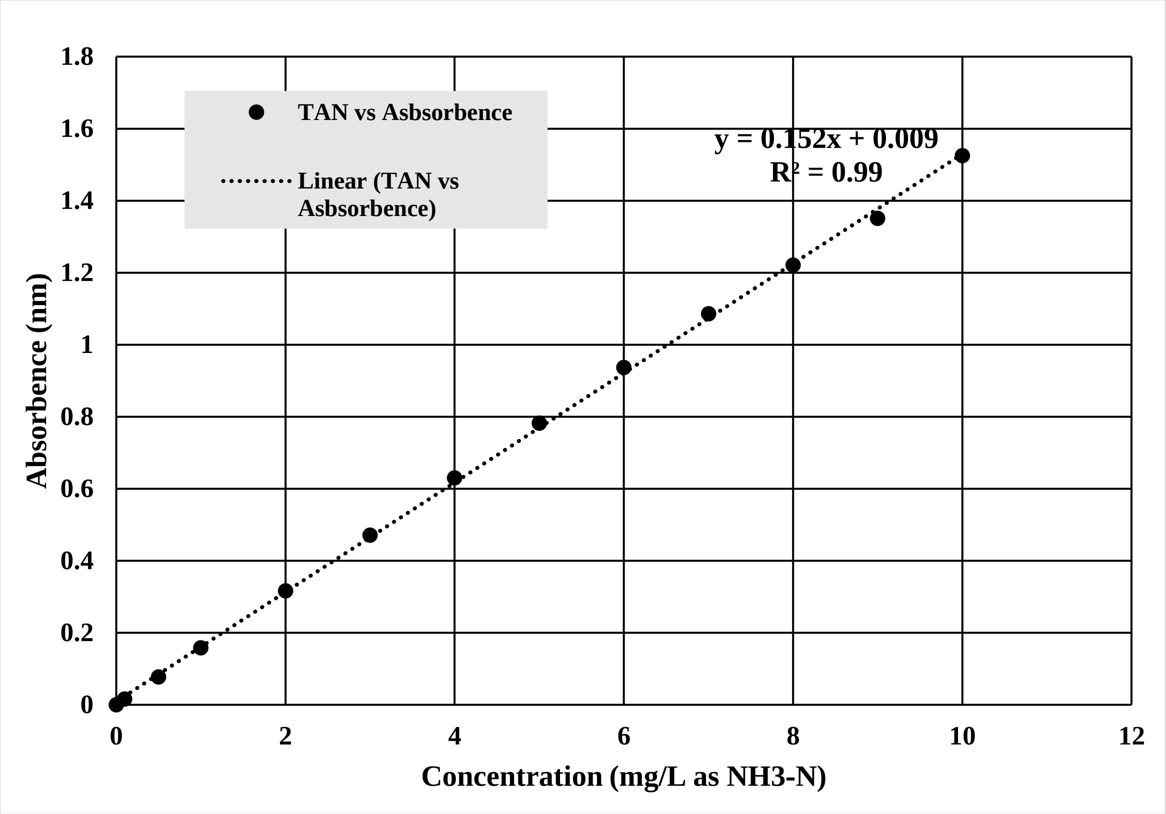

Figure 3-5. Nesslerization calibration curve

For each test, a blank sample consisting of distilled water, Rochelle Salt and Nessler reagent was used to zero the spectrophotometer along with a 10 mg TAN/L standard for quality control. Furthermore, repeat readings of samples were performed to ensure instrument accuracy and strategic duplicates were prepared for each experiment to ensure sample consistency.

In all cases 10 mL of each sample was taken (dilutions were performed when necessary) and combined with 0.25 mL of Rochelle Salt. A timer was set for 5 minutes after which 0.20 mL of Nessler reagent was added and allowed to react for 10 minutes. Once reaction time was completed, the samples were measured on the spectrophotomer.

For HACH based ammonia measurements, a prepackaged version of the salicylate method, the HACH TNT-832 vials were used to perform this colorimetric test. In this method, the ammonia reacts to create monochloramine due to a reaction with chlorine followed by a reaction with salicylate to form 5-aminsalycate. Sodium nitroferricyanide will then allow for the oxidation of 5-aminsalycate which gives the liquid a blue-green colour liquid which can in turn be measured on the spectrophotometer at 650 nm.

0.20 mL of each sample was added to the vials along with a reagent powder pillow compartment built into the cap. After proper mixing, the solution was allowed to react for 15 minutes. Due to the proprietary bar code included by the vial no reagent blank was required. Once inserted in the spectrophotometer the concentration in NH_3-N was read directly.

3.2.2 pH

The pH was taken with a pH probe (PHC201, HACH, Loveland, CO) 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. pH was taken during each experiment both before and after contact with ion exchange media to evaluate any effects the resin might have.

3.2.3 Temperature

Temperature was measured with the built-in temperature sensor of a pH probe (PHC201, HACH, Loveland, CO) connected to a potable benchtop meter (HQ40d, HACH, Loveland, CO).

3.2.4 Conductivity

The conductivity of all real mining wastewater samples was measured using a conductivity probe (89231-616, VWR, Radnor, PA, United States) connected to a benchtop meter (B40PCID, VWR, Radnor, PA, United States). Values were recorded in µS/cm. For initial single component isotherms, no conductivity was measured as experiments consisted only of distilled water, ammonium sulfate and the given sorbent.

3.2.5 Metal Analysis

As previously mentioned, the initial mine water characterization was performed by external labs. All potassium and calcium analysis for the IE tests was accomplished on a flame atomic absorption spectrometer (PinAAcle 500, PerkinElmer, Waltham, MA, United States) located at the Dept. of Civil Engineering of the University of Ottawa, shown in Figure 3-6, following standard methods 3111B (American Public Health Association 2005). Samples were aspirated through a capillary tube which then sprayed the fluid as a mist into the spray chamber where it was atomized by an air-acetylene flame. The flame is passed through the emission of a hollow cathod elemental lamp and absorbance is measured. A calibration curve was created each time experimental measurements were taken, and standards were prepared freshly prior to each analytical session.

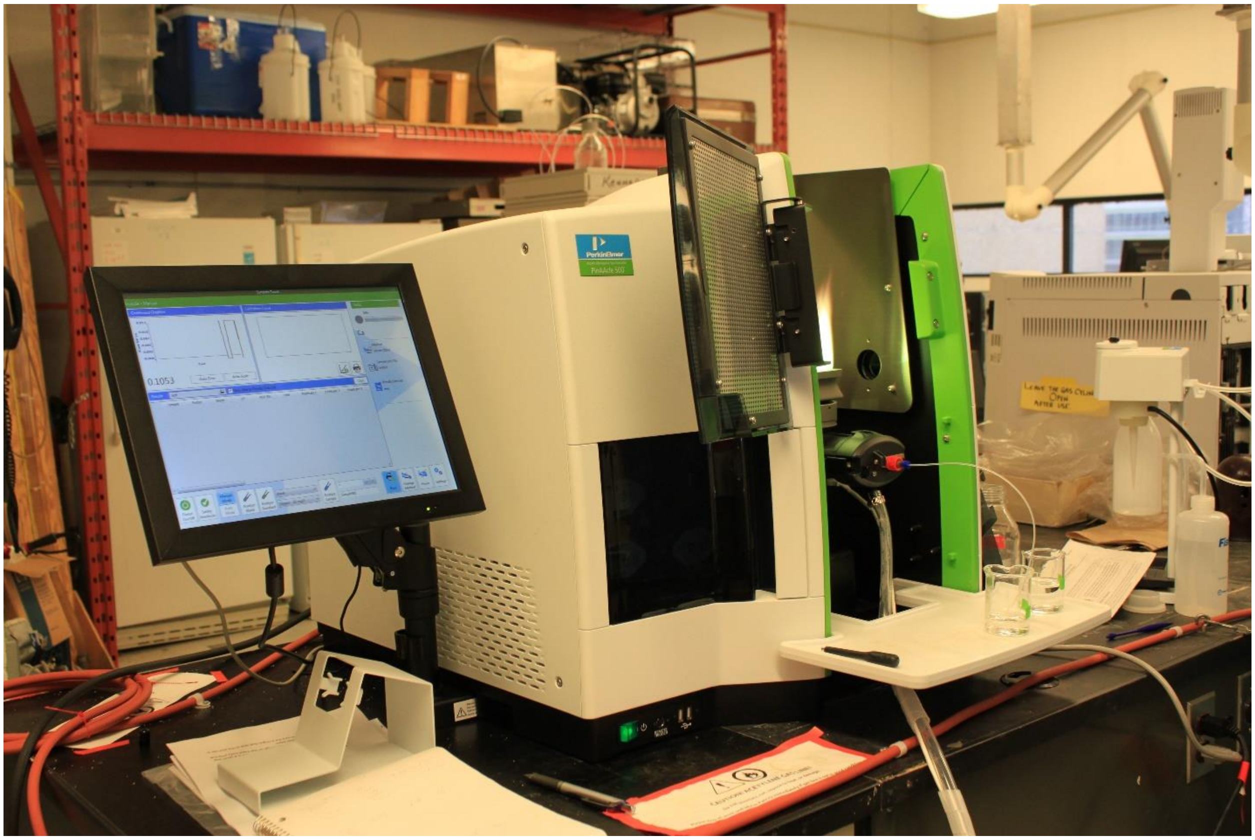

Figure 3-6. PerkinElmer PinAAcle 500 Flame Atomic Adsorption Spectroscopy Metal Analysis Unit

The instrument required careful alignment prior to each elemental measurement sessions. This was accomplished by varying the height of the burner head until a reading of 0 absorbance was registered by the spectrometer. The flame was then turned on and the capillary inserted into a 5 % nitric acid solution to properly clean out the apparatus. The instrument was allowed to aspirate approximately 80 mL of this nitric acid solution prior to any measurements. This was accompanied by regular disassembly and soap cleaning of the entire burner assembly. Once the 5 % nitric acid solution was consumed, the highest concentration standard was then aspirated and once absorbance had stabilized, the depth of the burner and nebulizer were adjusted to read the maximum stable absorbance. Once this was achieved, a blank sample was read to establish the baseline concentration. This was followed by the analysis of the standards once again to be able to create the calibration curve and finally all samples of unknown concentration were measured. Two quality control steps were taken. First, after completing the calibration curve, the analysis of one of the standards was repeated for confirmation purposes. Second, after half the samples (5 to 10 samples) were analyzed, another standard was measured to ensure no drift had occurred. These steps were performed for each experiment. Four repeats of each sample were measured, the instrument in turn provided the mean value. This was the value used as the basis for all calculations. Residuals and standard deviation of each measurements were recorded and used to evaluate the validity of readings.

All samples were filtered through a 0.45 µm filter membrane to avoid the uptake of any sediments or larger particles. The capillary tube was thoroughly cleaned with a Kimwipe ® between each sample to avoid dilution or contamination of samples. It should be noted that at least 20 seconds were allowed to pass prior to the next measurement of concentration as once the sample was aspirated the absorbance would spike above real reading and slowly reduce to a stable value. The use of a 5 % nitric acid solution between samples helped reduce this measured spike.

For both calcium and potassium, it was observed that using only 1 calibration standard was favorable for desired ranges. Extensive testing showed that when several standards were used it often resulted in an unfavorable S shaped curve, which has the tendency to over or underestimate values and ultimately reduce the validity of readings. When plotting the calibration curve, the software will ensure that the curve is fitted to every point by assuming there is no error in the calibration standards. Therefore, too many standards may lead to a curvature in the calibration curve, leading to errors in measurements.

To avoid interferences from dissolved metals, a solution of lanthanum chloride was added to each of the samples prior to analysis. The lanthanum chloride solution was created by combining 58.65 g of lanthanum oxide, 250 mL's of concentrated Hydrochloric acid and 750 mL's of distilled water.

3.2.5.1 Potassium

All potassium measurements were performed with a single element potassium hollow cathode lamp (HCL) (N3050139XX Lumina™ 2, PerkinElmer, Waltham, MA, United States) using a wavelength of 769 nm, a slit width of 0.7 and flowrates of 2.5 L/m and 10 L/m of air and acetylene respectively. The linear range for this wavelength is 0-2.00 mg/L, therefore a single standard of 1.00 mg/L was chosen for calibration and samples were diluted by factors of 1:200, 1:100 and 1:25.

As the wastewater contains several other dissolved species, a 0.1 % Lanthanum solution was added. Furthermore, to ensure metals remain dissolved upon dilution 1 % concentrated nitric acid was added to each sample, blanks and standards. The nitric acid also served as a cleaning agent for the capillary, spray chamber and burner head, preventing any residual metals trapped within the instrument from causing reading fluctuations.

3.2.5.2 Calcium

For the measurement of calcium, a calcium single element HCL (N3050114XX Lumina™ 2, PerkinElmer, Waltham, MA, United States) was used. The 422 nm line was selected along with a slit width of 0.7 and the following gas flowrates: 2.5 L/min for air and 10 L/min for acetylene. This wavelength was linear between 3-5 mg/L but by turning the burner head on a slight angle the sensitivity of the instrument was reduced and could therefore increase the linear range up to approximately 20.00 mg/L. For this analysis, a maximum standard of 10.00 mg/L was chosen. The alignment of the machine was accomplished in similar fashion to what was previously stated but with an intermediary step after turning on the flame and before adjusting burner head depth and nebulizer. This step consisted of slowly turning the burner head away from the optical path until the absorbance reading was just below 0.2, or within the linear range.

The wide variety of metals found within the sample caused significant interferences (absorbance < 2x noise of measurement) and therefore 10% lanthanum solution was added to prevent ionization. It was seen that 1 % concentration nitric acid depressed the calcium signal, therefore only 0.1 % concentrated nitric acid was added.

3.3 Ion-Exchange Experimental Methods

3.3.1 Kinetic Experiments

Timed sorption tests were conducted for each IE material to determine the amount of time each IE material required to reach equilibrium. This was accomplished by using several 125 ml Erlenmeyer flasks and allowing different contact times and measuring resulting equilibrium concentrations. All kinetic tests were conducted with a synthetic TAN solution containing only ammonium sulfate and distilled water. The Erlenmeyer's were placed on an orbital shaker (New Brunswick Innova 2000, Eppendorf, Hamburg, Germany) set to 120 rpm's. Selected design contact times ranged from 10 minutes to 3 days. This was to ensure that equilibrium was met.

Different contact times were started at staggered intervals allowing the measurement of the TAN levels for varying contact time. Each set of sample analysis featured one blank sample simply containing only deionised water and the IE material in question, one control sample with only synthetic TAN solution and various Erlenmeyer's with corresponding contact times. All samples were filled to approximately 25 mL and contained 2 g's of resin. Once the sample was removed for analysis it was filtered through a glass microfiber filter to separate the liquid sample and resin, then placed within a clean Erlenmeyer flask. The pH, temperature and TAN concentrations were then measured.

3.3.2 Single Component Batch Adsorption Isotherm Tests

Isotherms are constant temperature (~22 ^{o}C) equilibrium batch adsorption tests. The single component batch isotherms yield the maximum capacity that can be expected at the given temperature without the presence of the competing ion. Competing ions can decrease the exchange capacity of the target ion. The tests served two purposes; first, they quantified the TAN sorption of the various IE materials allowing for comparisons; and they helped evaluate the impact of the supplementary elements found within the EIMWW after the EIMWW isotherms are performed. Single component isotherms were obtained by placing 50 mL of synthetic ammonia solution in numerous Erlenmeyer flasks, adding different amounts of IE materials to each, placing the flask in an orbital shaker and mixing them overnight. Since the kinetic test results showed that all the studied IE materials reached equilibrium within an hour, mixing them overnight assured that equilibrium was reached. The samples were then passed through a glass microfiber filter. Finally, the liquid phase ammonia concentration was measured. All experiments included two blank samples of simply distilled water and IE material as well as two control samples which consisted of simply synthetic ammonia solution. The blanks were to evaluate if the resin leached any color or contaminants which would provide false positives. The controls were to account for any potential contamination from glassware or losses due to volatilization. The chosen masses of ion-exchanger ranged from 0.1-1.5 g with the use of strategic duplicates to ensure quality control. Furthermore, the lowest and highest dosages (0.1 g and 1.5 g) along with a middle dosage (0.5 g) were all performed in duplicates to ensure that the results obtained were consistent and accurate. This was meant to be a form of quality control.

The adsorption capacity or equilibrium solid phase concentration was calculated by using an integral mass balance (between the initial and final, liquid and solid phase masses of solute) with each individual sample considered their own system.

$$q_{eq} = \frac{(C_i - C_{eq})V}{M} \qquad (3.1)$$

Where q_{eq} is the capacity of the ion-exchanger (meq TAN/g), C_i is the initial TAN concentration (meq TAN/L), C_{eq} is the equilibrium TAN concentration (meq TAN/L), V is the volume of the sample (L) and M is the mass of resin (g).

The results were then plotted using the traditional isotherm graphs, i.e. q_{eq} versus C_{eq}. All results were plotted in Excel and the Freundlich model coefficients were determined through linearization and regression. The Langmuir model was also evaluated, although it did not provide acceptable results and was therefore not used further.

3.3.3 Multi Component Batch Adsorption

Batch IE experiments were performed on the EIMWW which was spiked with ammonium sulfate to allow an approximate TAN concentration of 3.87 meq TAN/L or 70 mg TAN/L. A similar methodology to the single component batch adsorption was used.

Different dosages of ion-exchange material, ranging from 0.1 g to 1.5 g's were added to 50 mL's of spiked EIMWW samples and placed on the orbital shaker over night. The samples were then filtered through a glass microfiber filter to separate the solid and liquid. The following morning the pH, temperature and conductivity were measured along with the equilibrium concentrations of ammonia, potassium and calcium. Using equation (3.1) it was possible to calculate the contaminant equilibrium solid phase concentrations (i.e. capacities).

3.3.4 Regeneration Studies

This phase of the research aimed at: a) quantifying the regeneration efficiencies of the IE materials; b) establishing the long-term IE sorption capacities through several loading cycles; and c) determining the impact of different regeneration solutions. As these regeneration cycles are time consuming, experiments proceeded with only two of the original five resins; the Resintech SIR-600 and the clinoptilolite, natural zeolite. This was due to the Resintech's superior performance with regards to ammonia capacity as well as a lower degree of competitive sorption. The natural zeolite was selected as it represents the most unique of the five materials, it is the least expensive, and it did not feature as high an affinity for calcium or potassium as the Bojie, Purolite or Amberlite resins.

For proper regeneration characterization, five different regeneration fluids were studied. Three of them were NaCl based solutions (2.5 %, 5 % and 10 % NaCl), one a KCl solution and the other a combination of KCl and NaCl. Finally, a deionized water solution (entitled 0 % solution) was also used as a regenerant for two reasons: first to evaluate repeated loading cycles which allowed to understand the loss in capacity, and second to establish if the resin leached any sorbed ions. The NaCl regeneration featured a 2.5 % by weight, a 5 % and a 10 % by weight brine solution. This was accomplished by mixing 25 g, 50 g and 100 g of NaCl respectively in a 1 L volumetric flask. The KCl solution was a 5 % solution as well. Finally, the NaCl+KCl was a 50/50 combination of the 5 % NaCl and 5 % KCl. The potassium centric regenerations had a secondary goal of evaluating the feasibility of the IE materials developing somewhat of an equilibrium point with the ion exchanger itself. Therefore, upon subsequent loading cycles the material would already have its maximal potassium capacity achieved and would simply exchange potassium for TAN, ultimately reducing the quantity of regenerant required.

To accentuate ammonia desorption the pH of each solution was raised to a value of approximately 10, using a 0.2 M solution of NaOH for the sodium based regenerants and a 0.2 M solution of KOH for the potassium based one. For the NaCl + KCl solution all pH adjustments were made prior to the combination of both solutions. Due to the elevated pH, an effort was made to avoid volatilization of any TAN by replacing the 125 mL Erlenmeyer's with 125 mL head-space-free bottles. This was accomplished by filling the bottles until the liquid 'spilled' over the top of the bottle and sealed shut with a cap so that there was no head-space into which the ammonia could volatilize. To avoid leakage Teflon tape was used to cover the threading of the bottle and once the cap was applied, electrical tape was wound around the top of the cap.

Batch loadings were accomplished with ammonium sulphate spiked EIMWW in similar fashion to multi-component batch tests. Approximately 0.5 g of resin was added to the bottles, which were then subsequently filled as previously stated. Bottles were prepared in triplicates for each regenerants and consisted of a 2.5 % NaCl, 5 % NaCl, 5 % KCl, 10 % NaCl, NaCl + KCl as well as one 0 % deionised water, 2 blanks with IE material and deionized water and two controls with only spiked EIMWW. Conductivity, pH and temperature were measured prior to loadings as well as ammonia, potassium and calcium concentrations. The bottles were then loaded in the end-over-end tumbler which rotated the bottles at 10 rpm. This ensured gentle mixing of the resin allowing for proper solid/liquid contact. For the loading cycles, the bottles were left in the tumbler for 24 hrs, then they were removed and filtered through a glass microfiber filter to separate the liquid from the ion exchange material. As in previous experimental stages; pH, temperature, conductivity, ammonia, potassium and calcium were measured. The IE material was then rinsed off with deionized water to remove any residual water.

Figure 3-7. Tumbler Used in Regeneration Studies

Regeneration fluids were prepared in advance for each regeneration cycle and bottles were once again filled in the same manner as with the loading cycles. The tumbler speed was again set to 10 rpm but in this case, the bottles were allowed to equilibrate in the tumbler for 48 hrs to ensure complete regeneration. After 48 hrs the contents of the bottle were once again filtered to separate the IE materials from the respective regeneration fluid. pH, temperature, conductivity, TAN, potassium and calcium were again measured. This allowed for monitoring any variations and interactions the resin had with the regenerant. Since the volumes of each bottle varied, concentrations were converted to mass based to allow for direct comparisons using the following equation.

$$Mass\ of\ Species = Conc * Volume \qquad \text{(eq 3.3)}$$

Where Mass of species is in meq, the concentration of species in meq/L and the volume of solution in L.

It was then possible to conduct a mass balance over the system and quantify how much mass was being removed during the initial loading cycle and then how much was subsequently released upon regeneration. A total of three loading/regeneration cycles were accomplished for both the natural zeolite and the Resintech adsorbent. Additionally, a batch of "virgin" resin was included in the final cycle which consisted of un-loaded resin within a 10 % NaCl regeneration solution to establish whether any ammonia, calcium or potassium was present on the material.

3.3.5 Column Studies

Continuous flow column studies were applied to evaluate the performance of the ion exchange material in a setting more applicable to typical industry configurations. This was accomplished with an acrylic column, with an internal diameter (I.D.) of 28.75 mm and a length of 150 mm. Glass wool was placed in the bottom of the column to ensure the ion-exchange material remained within the column without inhibiting liquid flow. Small perforated acrylic diffuser chips were placed above and below the ion exchange material for two purposes. The first purpose was to ensure the ion exchange material remained in a constant bed and was not transported through the bottom of the column or into the glass wool. The second goal was to adequately diffuse the flow of liquid and attempt to prevent or minimize channeling through the resin. Channeling would result in inadequate liquid-solid contact and ultimately reduce the sorption performance of the column. A reservoir allowing for 2.0 L was placed on top of the column thus allowing for a constant head of liquid above the top portion of the bed volume and reduced the chances of flow channeling. Initially a pump was used to refill the reservoir and an overflow port was added however due to low volume requirements the pump was removed in favor of manually refilling the reservoir. Exactly 40 g's of IE material was used in the column resulting in an empty bed volume of 46.09 ml and bed depth of 71.00 mm.

Flow control was accomplished by connecting rubber tubing to the bottom of the column and velocity was controlled with the help of a metal clamp. Flow rate was determined by adjusting the clamp, allowing the flow to stabilize, and collecting liquid for exactly one minute in a beaker. The volume of water was measured and recorded as the flow rate. The clamp was then adjusted for the desired flow rate. During the sorption phase, a flow rate of 8-40 bed volumes per hour was desired. After experimentation, a design flow rate of approximately 29 ml/min was selected. Figure 3-8 demonstrates the experimental set-up of the column used for all experiments.

Figure 3-8. Column Experimental Setup

Following the loading cycles, extensive backwash was accomplished in a similar manner to the loading cycle. Using a top down flow, the column was backwashed with at least 30 bed volumes (BV) of distilled water to ensure no residual wastewater remained on the resin. Once backwashing was completed the column was regenerated in the same manner using a 10 % NaCl solution. The technical sheet for the selected ion exchange material recommended a contact time of 30 minutes, which resulted in a flow rate of approximately 1 ml/min. This flow rate was measured in the same manner as previously mentioned. It is worth noting that while regenerating, samples were periodically measured for TAN concentration and that complete desorption was never reached as the levels of regenerant required are non-practical. This was more representative of column operations in industrial settings. Once regeneration was completed, the column was again extensively backwashed with distilled water to eliminate any residual regenerant.

Analysis of effluent was determined by pre-selecting several times at which a sample would be taken in an Erlenmeyer flask. In general, samples were approximately 50-60 ml to ensure that a complete analysis was possible, which consisted of pH, temperature, conductivity, TAN analysis and finally metals analysis. All of these were measured following the procedures outlined earlier in this chapter.

All effluent was collected in a container and measured each time a sample was taken. This permitted the determination of the total volume of liquid which had passed through the column prior to the sample being measured, thus establishing the total bed volumes treated for given effluent concentrations. With these values, it was possible to plot breakthrough curves for both the EIMWW and a synthetic wastewater solution containing only ammonium sulphate.

For initial characterization, the EIMWW was run through the column until TAN exhaustion and subsequently regenerated. This allowed for a generalized preview of column performance and served as a basis for bed volumes treated before TAN breakthrough. In this case a breakthrough of 10 mg TAN/L or 0.55 meq TAN/L was selected. The same experiment was then performed with the EIMWW, but the flow was cut off when the effluent had reached breakthrough. After regeneration, the experiment was repeated once again with a synthetic TAN solution to compare the difference in performance and establish the effects of competitive sorption. This was accomplished by directly comparing sorption capacities with regards to TAN using the following equation:

$$q = \frac{Q}{M} \int_{t=0}^{t=breakthrough} \left(C_{feed} - C_{eff}\right) dt \tag{eq 3.5}$$

$$q = \frac{Q}{M} * \sum \left(C_{feed} - C_{eff}\right) \Delta t \tag{eq 3.6}$$

Where q is the capacity of ion exchange material (meq/L), Q is the liquid flow rate passing through the column (ml/min), M is the mass of ion exchange material (g), C_{feed} is the influent concentration of species in question (meq/L), C_{eff} is the effluent concentration of species in question (meq/L) and Δt is the time step between subsequent readings (minutes).

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Chapter 4: Assessment of Ion-Exchange Process and Impact of Competing Ions on Removal of Ammonia from Explosive Impacted Mining Wastewater

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Abstract

Mining is economically an important industry, but it has a number of detrimental environmental impacts such as the production of explosive impacted mining wastewater (EIMWW) from the use of ammonium nitrate explosives. This EIMWW contains high total ammonia nitrogen (TAN) concentrations as well as other species, such as potassium and calcium.

Ion-exchange (IE) was considered for the treatment of EIMWW and the effects of competitive adsorption between TAN, potassium and calcium were investigated. Batch single component isotherms were performed with a single-solute TAN solution, followed by batch multi-component isotherms for a EIMWW. This allowed for direct comparison of five different IE materials; three different synthetic resins (Purolite SSTC60, Amberlite IR120 Na, Bojie BC121 H) and two zeolites (natural clinoptilolite and a modified clinoptilolite (SIR-600)). All materials were used in sodium form. The synthetic resins suffered the largest reduction in capacity from the presence of competing ions, with capacities of 0.22-0.25 meq TAN/g for multi-component (EIMWW) versus ~1.8 meq TAN/g for single component synthetic solution at an equilibrium concentration of 3.5 meq TAN/L. The two zeolites had the highest TAN capacities when treating the real wastewater, 0.32±0.04 meq TAN/g for the clinoptilolite and 0.42±0.01 meq TAN/g for the SIR-600 at equilibrium concentrations of ~3.6 meq TAN/L. Finally, separation factors were calculated to compare TAN-K affinity, they were strongly ion-exchanger dosage dependent. SIR-600 featured higher selectivity towards TAN for all dosages (α_K^{TAN}= 1.63 and 2.95 for dosages of

0.1 g and 1.5 g respectively), whereas the clinoptilolite had a higher selectivity towards TAN only in the lower dosages (α_K^{TAN}= 1.57 for 0.1 g).

Keywords: Ammonia, natural zeolite, modified zeolite, clinoptilolite, synthetic resin, competitive adsorption, separation factor, batch tests

4.1 Introduction

The Canadian mining industry is one of the largest in the world and it was the first worldwide in the exportation of potash, second for uranium, nickel and nobium and third for cobalt, aluminium and platinum group metals (Marshall 2016). In 2015 Canada produced a gross domestic product of \$24.6 billion in mineral extraction and \$30.9 billion in mineral processing and manufacturing (Marshall 2016). However, mining operations and processes could lead to serious environmental impacts, including elevated levels of total ammonia nitrogen (TAN) due to explosive impacted mining wastewaters (EIMWW).

Ammonia is a naturally occurring nitrogen-hydrogen compound that can exist in two forms, unionised NH_3 as well as ionized or ammonium NH_4. Distribution between these two compounds depends on temperature and pH (Environment Canada 2001). The sum of these two species is referred to as TAN. Environmental concerns associated with elevated TAN concentrations include the depletion of dissolved oxygen as a result of nitrification, toxicity to aquatic life as well as nitrate contamination of groundwater sources and contribution towards the eutrophication of natural waterways due to excess of nutrients (Thurston et al. 1981; Halling-Sørensen and Jorgensen 1993; Lee et al. 2000; Burow et al. 2010)

Conventional treatment methods for TAN include biological nitrification/denitrification, adsorption, ion-exchange, ammonia stripping and breakpoint chlorination (Jorgensen et al. 1976; Halling-Sørensen and Jorgensen 1993; United States Environmental Protection Agency 2000; Hedström and Rastas Amofah 2008; Malovanyy et al. 2013; Ding and Sartaj 2015). While nitrification/denitrification is viewed as the traditional biological TAN removal method for municipal and industrial wastewaters, IE has gained popularity for a few noteworthy reasons, especially in cold climates such as the harsh Canadian winters. These include that IE is simple and easy to implement and is not susceptible to shock loadings and it does not require large quantities of dissolved oxygen as is the case with the nitrification process. Furthermore, the effects of temperature are not as severe for IE as is the case with biological processes (Almutairi and Weatherley 2015). The use of IE has also led to the possibility of nutrient recovery, which in turn can later be recycled for multiple industrial purposes (Hedström 2001; Smith and Smith 2015). Finally, TAN toxicity can result in inhibition of microbial activities (Lee et al. 2000)

The majority of research concerning the removal of TAN by use of IE has focused on the use of natural zeolite, commonly clinoptilolite. These natural minerals are easy to obtain, and are relatively inexpensive (Jorgensen et al. 1976; Casadellà et al. 2016). According to Ames (1960) the general selectivity of clinoptilolite was proposed to as the following:

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

This selectivity order has been confirmed on several occasions and is accepted as the standard order of selectivity for clinoptilolite (Leyva-Ramos et al. 2004; Widiastuti et al. 2011). This selectivity is of crucial importance as it may be used during the screening process to construct an initial idea of how a system might behave. If a cation with a higher selectivity than the target ion is present, it may hinder the uptake of the desired cation. Furthermore, concentration also plays a role in this selectivity order, where if the concentration difference between two cations is substantial enough, then it is possible to circumvent this selectivity order and preferentially adsorb an ion that is situated lower on the selectivity order. Based on the above selectivity, it is very challenging to use clinoptilolite to remove ammonia from waters that contain potassium.

Tables 4-1 and 4-2 list the TAN exchange capacities that have been reported for different clinoptilolite samples and several commercial IE materials respectively. It should be noted that these studies have not been conducted under the same conditions, i.e. the same TAN concentration, pH, etc. Also, most often these conditions have not been properly reported. Nevertheless, several facts are evident from these tables. First, as zeolites are natural in their origins and originate from different locations, there are significant inconsistencies in recorded IE capacities. Second, there is a substantially smaller amount of published works for TAN sorption onto synthetic resins compared to natural zeolites such as clinoptilolite. Third, the majority of the studies used synthetic wastewaters as opposed to real wastewaters. The only wastewaters tested were municipal wastewaters, so there is a need to study IE TAN removal from wastewater from different characteristics such as EIMWW. Fourth, the TAN exchange capacities from municipal wastewaters were significantly lower than those of the synthetic wastewaters, presumably due to competing ions. And finally, the sorption capacity of TAN from synthetic wastewaters was generally higher by the synthetic resins than by clinoptilolite.

Table 4-1. Selected Clinoptilolite TAN Sorption Capacities in meq TAN/g of Clinoptilolite

Zeolite Origins	TAN capacity (meq TAN/g)	TAN concentration (meq TAN/L)	Wastewater type	Reference
Hungary	0.62	0.71	Municipal WW	(Jorgensen et al. 1976)
Hungary	0.51	0.24	Municipal WW	(Hlavay et al. 1982)
Mexico	0.95-1.35	3.87	Synthetic TAN	(Leyva-Ramos et al. 2004)
Australian	0.35	0.28	Synthetic TAN	(Widiastuti et al. 2011)
Canada	0.44	5.53	Synthetic TAN	(Ding and Sartaj 2015)

Table 4-2. Selected Ion-Exchange Resins TAN Sorption Capacities in meq TAN/g of Resin and Equilibrium Concentration of 3.87 meq TAN/L

Resin Origin	TAN Capacity (meq TAN/g)	Wastewater type	Reference
Purolite MN500	~0.94	Synthetic TAN	(Jorgensen and Weatherley 2003)
Dowex 50w-x8	~0.94	Synthetic TAN	(Jorgensen and Weatherley 2003)
Amberlite IR120 H	~0.61	Synthetic TAN	(Ding and Sartaj 2016)

There is limited literature on TAN uptake in the presence of multiple competing cations (Wang et al. 2007; Montégut et al. 2016). Potassium has been known to result in strong competition during simultaneous uptake with TAN. Using a Chinese clinoptilolite, capacities of 0.44 meq TAN/g and 0.50 meq TAN/g were found for TAN uptake in the presence of potassium and calcium respectively for an equilibrium TAN concentration of 6.10 meq TAN/L (Wang et al. 2007). The single-solute TAN exchange capacity for the same zeolite was 0.57 meq TAN/g when only TAN was present (Wang et al. 2007). Similarly, another study performed on New Zealand mordenite found that both potassium or calcium reduced the TAN capacity from 0.60 meq TAN/g to 0.55 meq TAN/g in both cases (Weatherley and Miladinovic 2004).

The goal of this study was to investigate the removal of TAN from real EIMWW in the presence of various competing elements, notably potassium and calcium which have been known to be favorably adsorbed by both synthetic and natural ion-exchangers (Harland 1994). This was accomplished through batch sorption tests for single solute ammonia solutions (synthetic wastewater) and a real mining wastewater using one natural zeolite, one modified zeolite and three synthetic IE resins. An attempt was also undertaken to model the performance of these IE materials for the removal of TAN from real wastewater.

4.2 Experimental Methods

Batch lab-scale tests were performed with five different IE materials, which were natural clinoptilolite (zeolite), Amberlite IR120 Na, Purolite SSTC60, Bojie Resin BC121 H and a modified clinoptilolite (SIR-600 from Resintech) to establish if TAN removal from EIMWW was possible in the presence of calcium and potassium as competing ions. All IE materials except the Bojie BC121 H (hydrogen form) were shipped in the sodium form. The Bojie resin was subjected to repeated contact cycles with a high sodium content (>10,000 mg Na/L) solution to convert all exchange sites to the Na form. The natural clinoptilolite was obtained by a fertilizer company based in the United States (The Seed Supply 2017).

Batch IE tests were carried out in 125 mL Erlenmeyer flasks with 50 mL of either single solute or real wastewater and varying dosages of IE material, ranging from 0.1 g to 1.5 g. No pre-conditioning treatment was applied other than rinsing the materials 4-5 times with distilled water to remove any excess dirt or debris. The flasks were placed on an orbital shaker (New Brunswick Innova 2000, Eppendorf, Hamburg, Germany) and agitated at 120 rpm over night to ensure proper mixing and that equilibrium was achieved. Preliminary kinetic tests indicated that all the ion exchange materials tested reached equilibrium within 1 hour (see Chapter 3). The samples were then vacuum filtered through a 47 mm glass microfiber filter (CA28333-129, VWR, Radnor, PENN) to separate solid phase from liquid phase constituents. All experiments and analysis were performed at a room temperature (22-23 ^{o}C). Select experiments were performed in duplicates to ensure accuracy.

The first set of batch experiments used synthetic wastewater containing only distilled water and ammonium sulfate (230 mg in 1 L solution); aiming for a liquid TAN concentration of approximately 3.87 meq NH_4/L (70 mg TAN/L). These single component isotherms were performed as a reference and to quantify the effects of competition. The pH of the synthetic wastewaters remained constant at a pH of approximately 7 for every material. The second set of batch experiments utilized actual EIMWW rather than a synthetic solution. A list of species present, in the EIMWW as well as corresponding concentrations can be found in Table 4-3. All concentrations were measured at the University of Ottawa by Inductively Coupled-Plasma (ICP) analysis.

Table 4-3. List of Species and Corresponding Concentrations Present in the EIMWW

Species	Concentration (mg/L)	Concentration (meq/L)
Si^{+4}	3.56	0.51
Al^{+3}	0.08	0.01
Fe^{+3}	0.70	0.04
B^{+3}	0.07	0.02
Ca^{2+}	78.1	3.90
Mg^{+2}	12.7	1.04
Sr^{+2}	2.10	0.05
Na^{+}	270	11.8
K^{+}	112	2.85
HCO_3^{-}	300	4.92
SO_4^{-2}	1050	21.9

All measurements of TAN were accomplished through Nesslerization standard methods 4500-NH_3 (American Public Health Association 2005) on a spectrophotometer (DR6000, Hach, Loveland, CO). The pH and temperature were measured with a temperature enabled pH probe (PHC201, HACH, Loveland, CO) and the electrical conductivity quantified with a conductivity probe (89231-616, VWR, Radnor, PA). Ca and K were measured by direct air-acetylene flame atomic absorption spectroscopy (PinAAcle 500, PerkinElmer, Waltham, MA) following standard methods 3111B (American Public Health Association 2005).

All isotherms were modeled with the Freundlich model:

$$q = K_f C_{eq}{}^{1/n} \qquad \text{(eq 4.1)}$$

Where q is the equilibrium solid phase capacity (i.e., the capacity of IE material (meq/g))), K_F is the Freundlich constant of adsorption capacity at unit concentration, C_{eq} is the equilibrium liquid phase concentration of species in questions (meq/L) and 1/n is the dimensionless coefficient quantifying the strength of adsorption. The solid phase concentration is calculated by a mass balance of the batch test. The Freundlich parameters were obtained through a log-transformation of the Freundlich equation and subsequent linear regression.

The data was also modelled using the Langmuir isotherm equations:

$$q = \frac{Q_m b C_{eq}}{1 + b C_{eq}} \qquad \text{(eq 4.2)}$$

Where Q_m is the Langmuir monolayer constant in meq/g and b the Langmuir adsorption constant in L/meq. The Langmuir constants were obtained in similar fashion to the Freundlich constants, through linearization of the Langmuir equation followed by a linear regression.

Two methods were used to determine if a model was a good fit. First, following the linearization the R^2 value of each model was obtained. A higher R^2 value can generally signify a close fit of the data to a regression model. As the R^2 value is a simple statistical tool it is possible for a ‘good fit’ of data without the final isotherm resulting in an accurate model. For this reason, the modelled isotherms were also plotted versus experimental data and a visual inspection was accomplished to ensure the models properly conformed to measured data.

Finally, for the EIMWW isotherm data the separation factors were calculated to serve as a direct comparison of relative elemental preference exhibited by each IE material. This was accomplished with the following equation:

$$\alpha_j^i = \frac{X_i Y_j}{X_j Y_i} \qquad \text{(eq. 4.3)}$$

Where α is the relative separation factor, X is the resin phase concentration in meq/g, Y the aqueous phase concentration in meq/L and the subscripts i and j are the counter-ion and pre-saturated ions respectively. Note for multi-component systems it is important to consider all species, therefore weighted values are calculated, and X and Y become:

$$\bar{X}_i = \frac{X_i}{X_{Total}} \qquad \text{(eq. 4.4)}$$

$$\bar{Y}_i = \frac{Y_i}{Y_i + Y_j + Y_k + \ldots} \qquad \text{(eq. 4.5)}$$

4.3 Results and Discussion

Preliminary kinetic experiments determined that materials reached equilibrium within 1 hour. As all materials performed similarly only the clinoptilolite and the Amberlite were presented in Figure 4-1.

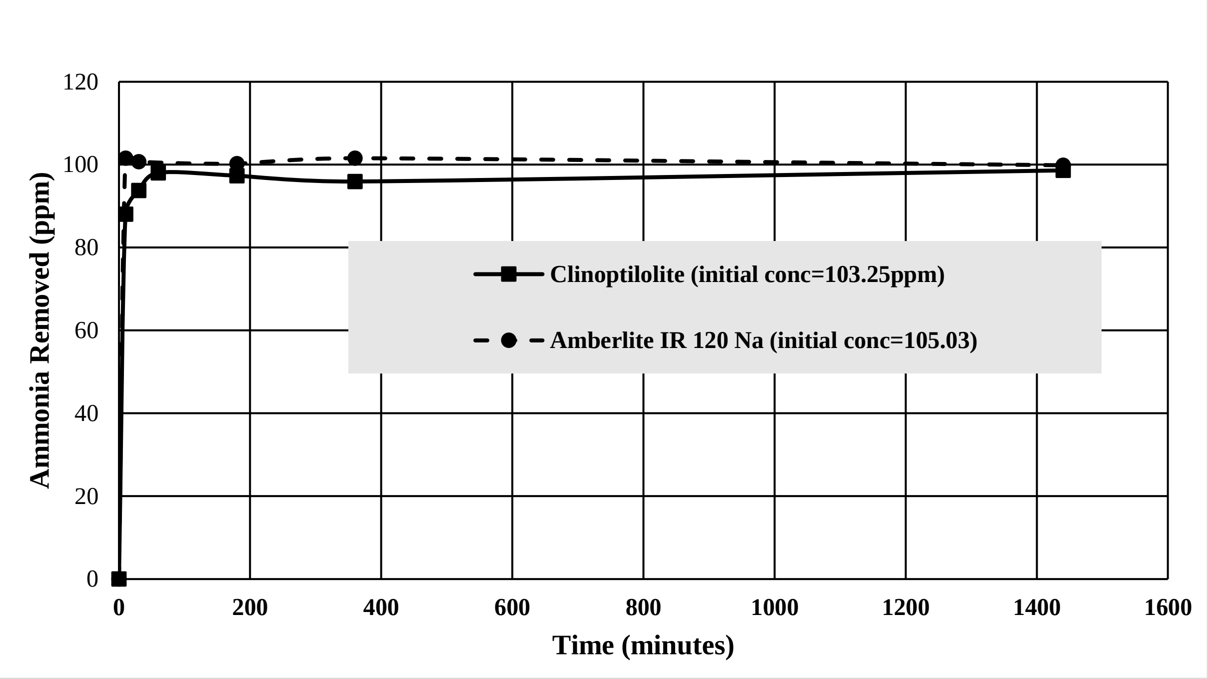

Figure 4-1. Example of Kinetic Experiments

4.3.1 Effects of IE Dose

The batch equilibrium test with EIMWW and the five IE materials yield the equilibrium TAN, potassium and calcium concentration for the five IE materials. The dosages of 0.1±0.01 g, 0.5±0.01 g and 1.5±0.01 g were performed in duplicates and the average concentrations are reported. Representative examples of these results are presented in Figure 4-2a, b and c. The main results were that as expected in most cases, both the TAN and K liquid phase concentrations decreased with increasing IE material dosage. The percent removal of K was higher than that of TAN for all resins except the SIR-600. Furthermore, the Bojie resin featured a strong affinity for potassium. The Purolite SSTC60 featured almost identical profiles for all three species and similar equilibrium concentrations.

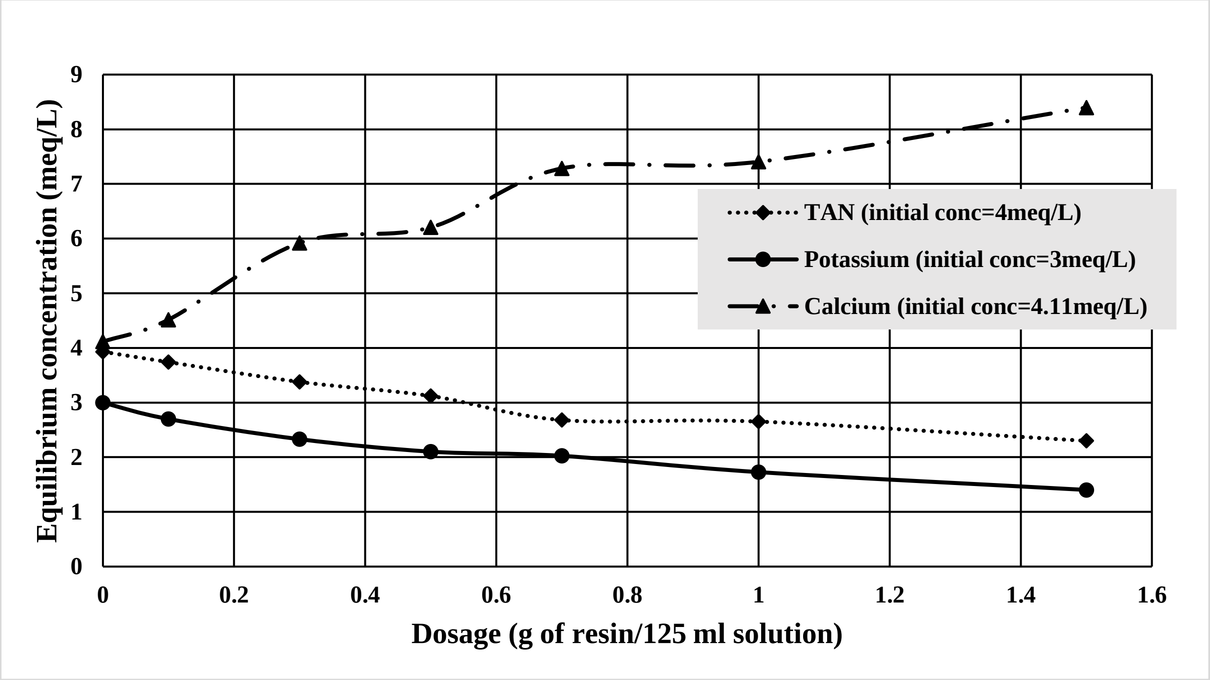

Figure 4-2a. Clinoptilolite Averaged Equilibrium Liquid Phase Concentrations for EIMWW

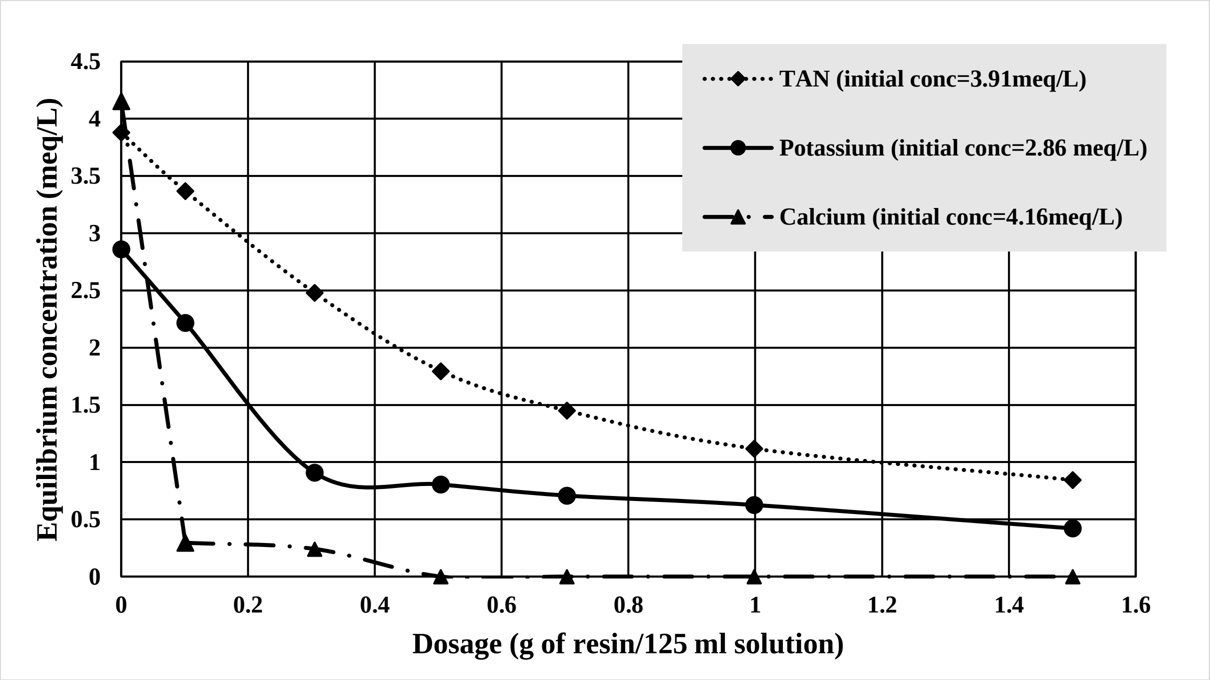

Figure 4-2b. Amberlite IR120 Na Averaged Equilibrium Liquid Phase Concentrations for EIMWW

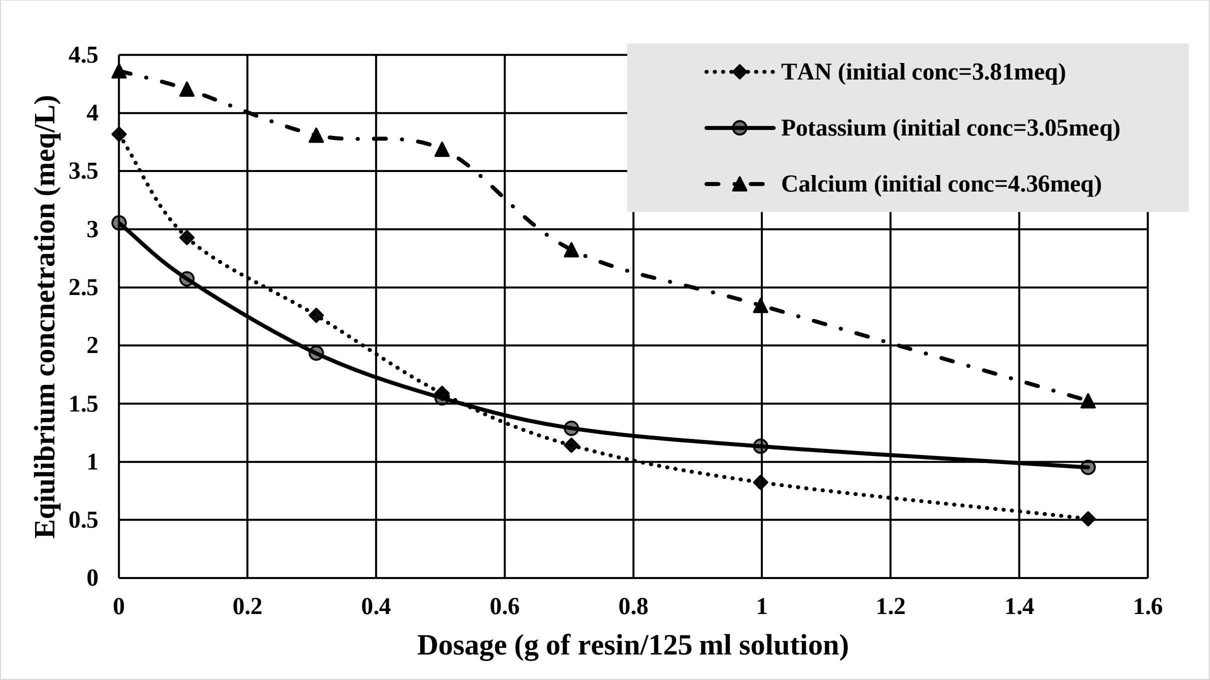

Figure 4-2c. Resintech SIR-600 Averaged Equilibrium Liquid Phase Concentrations for EIMWW

Considerable differences on how the different IE materials impacted the Ca equilibrium liquid phase concentrations were noticed. The three synthetic materials behaved as expected, resulting in a decrease of Ca liquid concentration with an increase of sorbent dosage as illustrated by Figure 4-2b. Furthermore, the Bojie resin also had similar results but the potassium removal was slightly higher and the TAN removal lower. Unexpectedly, for clinoptilolite (Figure-2a), there was an increase in the calcium concentration corresponding to an increase in dosage, culminating in an equilibrium concentration of 8.40±0.07 meq Ca^{2+}/L, approximately double its initial concentration. This suggests unaltered clinoptilolite contained substantial amounts of calcium as a readily exchangeable ion which was then leached out in favor of TAN and potassium, confirming the general order of selectivity initially determined by Ames (1960) and subsequently confirmed through experimentation. Furthermore, it has been documented that clinoptilolite has a higher affinity for TAN than it does for calcium, even when calcium is present in higher concentrations (Jung et al. 2004). The pH of the solution was raised, gradually increasing from 5.3 to 7.0. This effect increased proportionately with the increase in dosage. The conductivity of the solution did not change significantly for any of the dosages, which indicates electroneutrality was maintained.

The Purolite and Amberlite (Figure 4-2b) removed all the calcium when the resin dosage was increased above 0.3 g / 125 ml solution whereas the Bojie resin experienced near complete removal of calcium with a dosage of 0.1 g in 125 ml solution. This represents a strong affinity for calcium in all three cases. Finally, the SIR-600 (Figure 4-2c) featured removal of all three cations, with the TAN concentration experiencing the largest reduction of 2.31 meq TAN/L for a dosage of 1.5 g/125 ml solution.

The equilibrium concentration of all materials for a dosage of 1.5 g in 125 ml solution are presented in Table 4-4. Plus, or minus represent one standard deviation (SD). Compared to synthetic resins, natural clinoptilolite showed far less exchange capacity for both TAN (39.4% removal vs 54.6-86.6%) and K (54.1% removal vs 68.9-86.2%). The Bojie featured a higher TAN equilibrium concentration (~50 %) than the other synthetic resins but lower than natural clinoptilolite. This indicates that the Bojie resin had a lower exchange capacity for TAN compared with other synthetic resins (54.6% TAN removal compared to 77.2-86.6%). This could potentially be the result of incomplete conversion from H^+ to Na^+ form but is more likely the result of competition from some of the other ions present in solution. Previous studies have suggested that in the presence of calcium or magnesium, strongly acidic cationic ion-exchangers should be avoided (Harland 1994; Malovanyy et al. 2013). Once again, the sorption tests of all three resins had minimal impact on the electrical conductivity of the solution.

Table 4-4. Equilibrium Concentration (Average ± SD in meq/L) and Percent Removal of TAN, K and Ca for Dosages of 1.5 g of Resin/125 mL Solution

Ion exchange material	TAN (meq TAN/L)	K (meq K/L)	Ca (meq Ca/L)
Clinoptilolite	2.30 ± 0.04 (39.6 %)	1.40 ± 0.14 (54.1 %)	8.40 ± 0.07 (-92.7 %)
Amberlite IR120 Na	0.84 ± 0.02 (78.0 %)	0.42 ± 0.02 (86.2 %)	0.00 (100 %)
Purolite SSTC60	0.87 ± 0.02 (77.2 %)	0.57 ± 0.22 (81.3 %)	0.00 (100 %)
Bojie BC121 H	1.73 ± 0.04 (54.6 %)	0.57 ± 0.22 (81.3 %)	0.00 (100 %)
Resintech SIR-600	0.51 ± 0.07 (86.6 %)	0.95 ± 0.07 (68.9 %)	1.5 ± 0.04 (65.6 %)

Finally, from Table 4-4 it was noticed that the SIR-600 modified zeolite had the highest TAN removal (~87 %) with an equilibrium concentration of 0.51 ± 0.07 meq TAN/L for a dosage of 1.5 g in 125 ml solution. The electrical conductivity of the solutions was nearly identical after exchange tests for all dosages. SIR-600 was also the only IE material that showed higher removal of TAN than K. This indicated that it had a higher affinity for TAN than K relative to the other materials. Furthermore, the SIR-600 had a slight neutralizing effect on the pH of solution, increasing from the initial pH of 5.3 to between 6.4-7.0 for all dosages.

4.3.2 Ion-Exchange Isotherms

Figures 4-3 through 4-7 compare the single solute (synthetic wastewater) TAN IE isotherms versus the EIMWW simulated TAN IE isotherms for the IE materials. Furthermore, the pH values for the EIMWW are the same as those reported in the previous section. Plotted values represent the averaged IE materials capacity (meq TAN/g resin) versus the equilibrium liquid phase concentration (meq TAN/L). The IE capacities (i.e., the equilibrium solid phase concentration) were calculated using a mass balance of the batch tests. The points represent the experimental data while the curves correspond to Freundlich modeled isotherms. The Langmuir isotherms were also computed. A summary of all parameters as well as R^2 for the synthetic wastewater results are presented in Table 4-5.

Table 4-5. Langmuir and Freundlich Parameters and R^2 Results for TAN Sorption from the Synthetic Wastewater

Material	**Langmuir**			**Freundlich**		
	Q_m (meq/g)	b (L/meq)	R^2	K (L/meq)	1/n	R^2
Clinoptilolite	1.23	0.18	0.98	0.23	0.71	0.99
Amberlite IR120	110.62	0.005	0.98	0.55	0.92	0.99
Purolite SSTC60	9.54	0.07	0.64	0.53	0.93	0.99
Bojie BC121	N/A	N/A	N/A	0.34	1.33	0.97
Resintech SIR-600	1.18	0.54	0.95	0.39	0.57	0.97

The following observations can be made from this table. First, except for the Langmuir regression of the Purolite isotherm, all the models gave excellent simulations of the data as the R^2 values are very close to 1 (in the range of 0.95 – 0.99). The Langmuir constants for the Bojie resin were unsatisfactory (negative coefficients) and were therefore not included. Regardless, the visual fits for the Freundlich model were superior in every case. Ding and Sartaj (2016) calculated the Langmuir and Freundlich parameters for the Amberlite IR 120 in the H form using a synthetic wastewater (Q_m = 1.65 meq/g, b=0.09 L/mg for Langmuir, K=0.55 L/meq, 1/n = 0.92 for Freundlich). These results are completely different than those obtained by this study. However, the experimental conditions were different as they focused on much higher equilibrium concentrations (up to 2500 mg TAN/L) therefore, the comparison is not necessarily valid. Furthermore, they used the Amberlite resin in H^+ form, indicating there was a strong behavioral change associated with converting the resin from the H form to the Na form. Using the same clinoptilolite as this study and a synthetic TAN solution, Ding and Sartaj (2015) found the nearly identical Langmuir model constants (Q_m = 1.23 meq/g, b = 0.05 L/meq versus Q_m = 1.23 meq/g, b = 0.18 in this study) and different Freundlich model parameters (K = 0.28 L/mg, 1/n = 0.280 versus K = 0.23 L/mg and 1/n = 0.71 in this study). Once again, a much higher range of concentration (25-3000 mg TAN/L) may be the cause for the deviation and is not concerning. In both cases the Langmuir featured poorer fits than the Freundlich model for the natural zeolite, which once again may be indication of the Freundlich model featuring better representation of experimental results for zeolite-based materials.

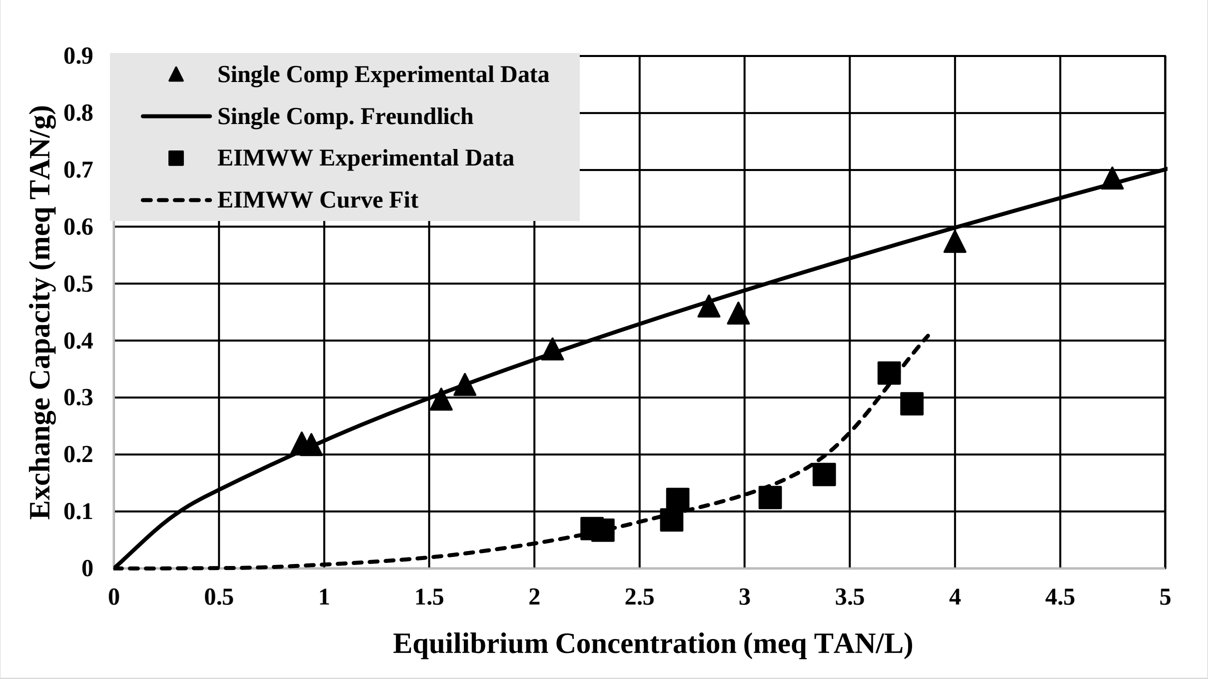

Figure 4-3. Single-Component (Synthetic Wastewater) Versus Multi-Component (EIMWW) TAN Exchange Isotherms for Clinoptilolite

Substantial work has been invested in the understanding of TAN exchange onto clinoptilolite. Due to the mineral's non-synthetic nature a wide range of variability has been noted in terms of TAN capacity, especially considering the interchangeability of exchangeable ions naturally present; which include, among others, potassium, calcium and magnesium (Leyva-Ramos et al. 2004). Furthermore, single solute TAN isotherms are well documented including the wide range of TAN adsorption capacities presented in Table 4-1. The clinoptilolite used from this study was from an American fertilizer company (The Seed Supply 2017) and featured a maximum recorded capacity of 0.81±0.02 meq TAN/g for the synthetic wastewater and 0.32±0.04 meq TAN/g for the EIMWW. While some of the clinoptilolite mentioned in Table 4-1 featured higher capacities such as the Mexican (41 %) source, the overall trend is closer to the clinoptilolite used in this study. As it has been suggested previously, the natural presence of various exchangeable counter-ions have led to a reduction in capacity and a pre-treatment of the clinoptilolite in such that a homogenous ionic form results in an overall increase of TAN sorption. These phenomena may explain at least in part the differences in the capacities reported in literature.

For every IE media the TAN exchange capacity from EIMWW was smaller than that for the single-solute synthetic wastewater. This was attributed to the supplementary cations present in solution, resulting in intense competition for the sorption sites. From Figure 4-2a. it is evident that a large amount of potassium was removed during the isotherm tests. The potassium present in the solution was acting as the main competitor for the exchange sites, and ultimately reduced the clinoptilolite's capacity for TAN. Capacity reductions of 50% at certain instances were observed. For example, from Figure 4-3., the 0.1 g dosage had an equilibrium concentration of 0.9 meq TAN/L, which resulted in an exchange capacity of 0.22±0.001 meq TAN/g clinoptilolite. For the same dosage, the identical experiment with EIMWW yielded an equilibrium concentration of 2.3 meq TAN/L and a capacity of 0.07±0.002 meq TAN/g clinoptilolite. This represents a 68 % reduction in exchange capacity due to the competitive interactions. These reductions in TAN capacities were expected given that potassium has frequently been documented as a source of competition when treating TAN with clinoptilolite, often resulting in inferior performance (Milan et al. 1997; Hedström and Rastas Amofah 2008). These findings indicate that the clinoptilolite featured a strong affinity for potassium which detrimentally impacted the TAN exchange capacity. Figures 4-4 and 4-5 represent the comparison of TAN uptake by the Amberlite and Purolite respectively, for both the single-solute synthetic wastewater and real EIMWW.

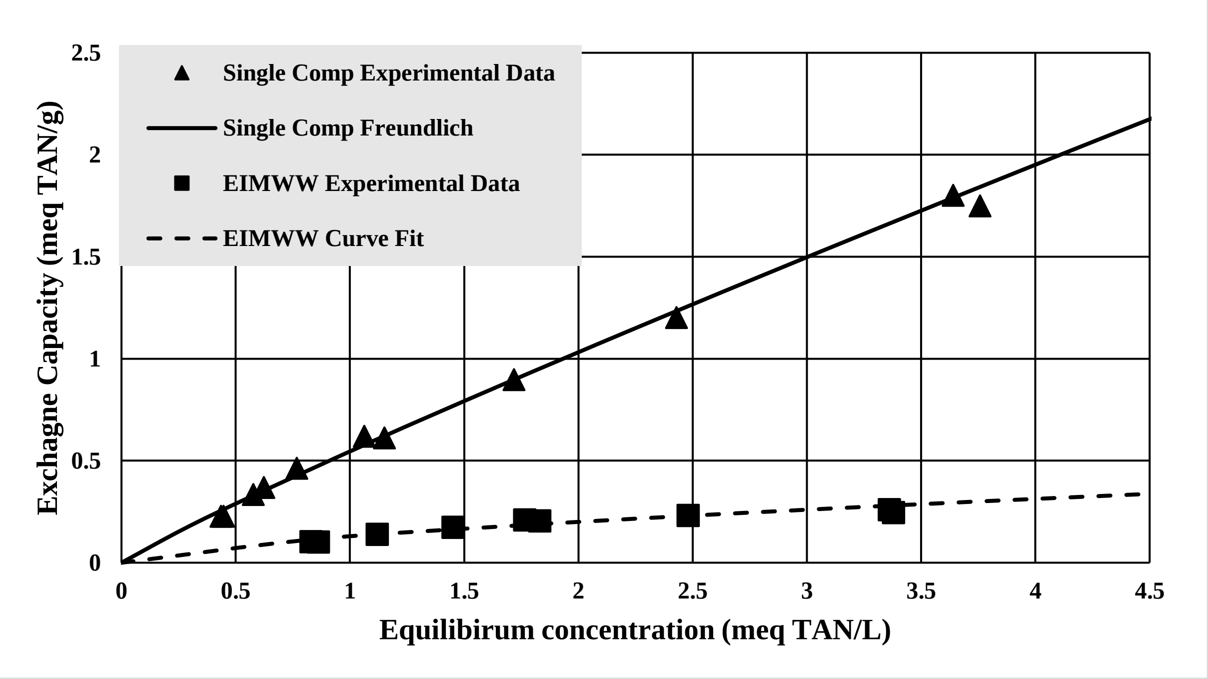

Figure 4-4. Single-Component Versus Multi-Component TAN Exchange Isotherms for Amberlite IR120 Na

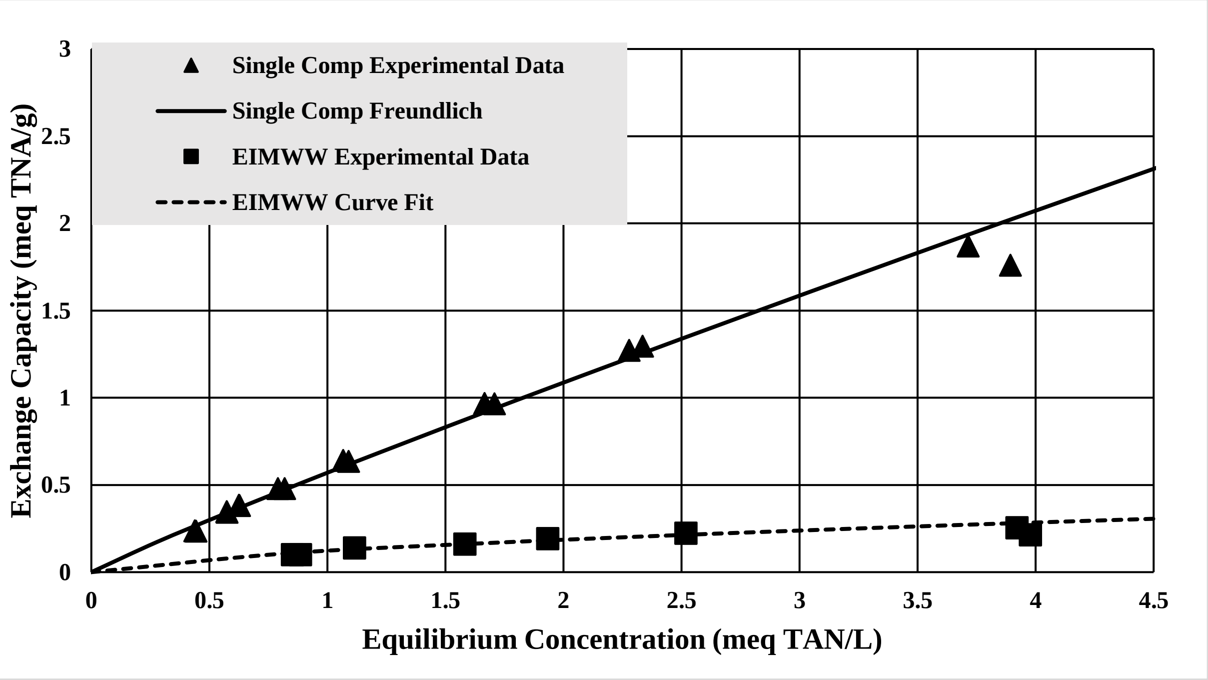

Figure 4-5. Single-Component Versus Multi-Component TAN Exchange Isotherms for Purolite SSTC60

Figures 4-4 and 4-5 demonstrate that both IE materials performed similarly, both resins are competing industrial products targeting hardness removal which could explain these results. The maximum single-solute TAN capacity obtained was approximately 1.78±0.04 meq TAN/g for the Amberlite and 1.81±0.08 meq TAN/g for the Purolite, both at equilibrium concentrations of approximately 3.6 meq TAN/L. Unfortunately, when treating the EIMWW, both resins performance decreased significantly. The maximum capacities were of 0.25±0.01 meq TAN/g for the Amberlite and 0.24±0.03 meq TAN/g for the Purolite. As both of these resins were designed for the removal of hardness, calcium was almost entirely removed with a dosage of 0.3 g as discussed earlier. As a cation with a charge of +2, calcium requires 2 exchange sites (Harland 1994), leading to a larger occupation of capacity than potassium or TAN, thus adding a further element of competition that was not present for the clinoptilolite. Furthermore, the presence of potassium once again resulted in competition. These results confirm the limited published works (Malovanyy et al. 2013) on the co-adsorption of potassium and TAN or calcium and TAN on synthetic IE resins. Figure 4-2b has shown the following selectivity orders:

$$Ca^{2+} > K^{+} \gg NH_4^{+}$$

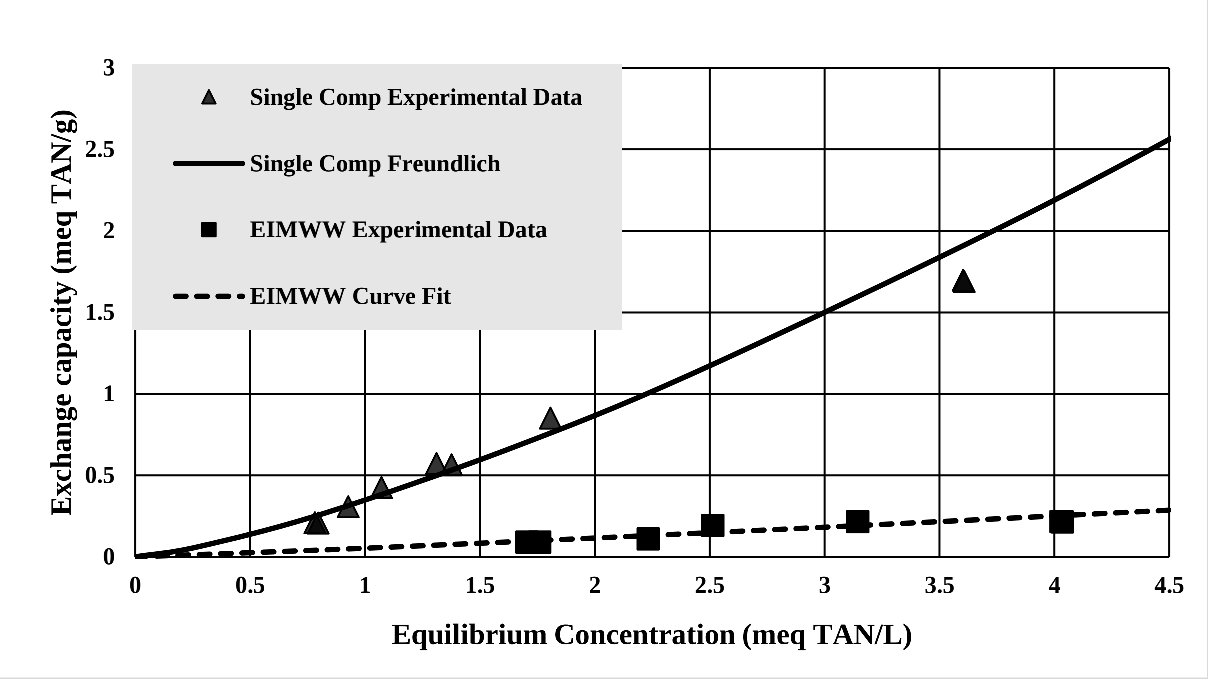

Figure 4-6. Single-Component Versus Multi-Component TAN Exchange Isotherms for Bojie BC121 H

The manufacturer of Bojie BC121 (Suzhou Bojie Resin Technology Co. 2017) claims it is equivalent to the Amberlite IR120 and the Purolite C100. Thus, a similar performance was expected. However, the maximum TAN capacity of the Bojie resin when treating the EIMWW was lower than that of the Amberlite (0.22±0.001 meq TAN/g versus 0.25±0.01 meq TAN/g) but it also came at a higher equilibrium concentration of 4.0 meq TAN/L as compared to the Amberlite's capacity of 3.4 meq TAN/L, indicating a lesser performance for the same quantity of material. Previously hypothesized reasons for this difference include an incomplete conversion to Na^+ form for the Bojie resin. Another potential explanation is that the Bojie BC121 performs better for it's stated objective, hardness removal. While treating the EIMWW with the Bojie resin, calcium was completely removed with a dosage of 0.3 g of resin whereas the Amberlite had 0.24 meq Ca^{2+}/L remaining in solution for the same conditions. Therefore, it is likely that the Bojie resin has a higher affinity towards calcium relative to TAN than the Amberlite resin, which could explain why the TAN capacities were at a higher equilibrium concentration.

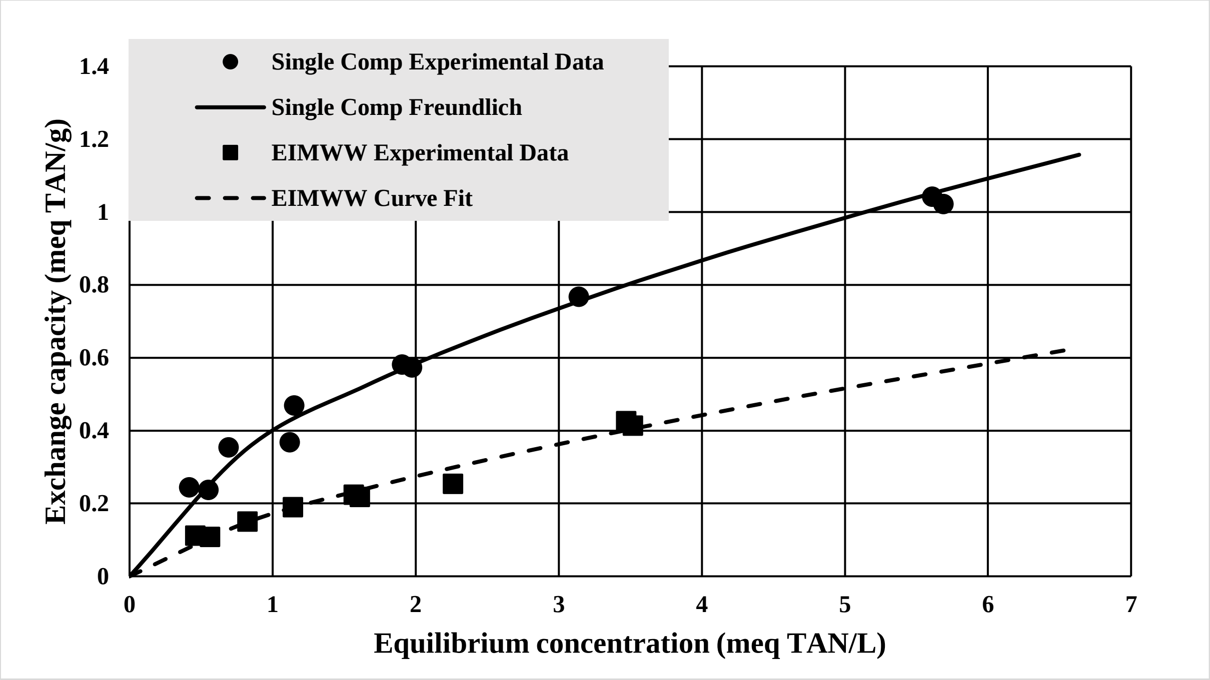

Figure 4-7. Single-Component Versus Multi-Component TAN Exchange Isotherms for Resintech SIR-600

The final IE material studied was the Resintech SIR-600, a clinoptilolite modified specifically for the enhanced removal of TAN. Figure 4-7 shows that while TAN capacities for SIR-600 are also impacted by the other IE materials the competition was not as significant a factor on the performance of SIR-600 as for the otherIEmaterials. It featured the highest TAN capacity during the EIMWW exchange tests with a capacity of 0.42±0.01 meq TAN/g for the EIMWW at an approximate equilibrium concentration of 3.5 meq TAN/L. This is an increase of approximately 50 % over the Bojie resin, 42 % for the Purolite, 40 % for the Amberlite and finally 20 % more than the clinoptilolite for the 1.5 g dosage and similar equilibrium concentrations. From Figure 4-

2c. it is evident that although calcium was exchanged, it was not as prevalent as with the synthetic resins. The clinoptilolite did not exchange any calcium yet still resulted in a lower TAN capacity than the SIR-600, which would perhaps suggest that the SIR-600 simply has a larger total cation exchange capacity, allowing for the exchange of an overall larger number of cations.

The SIR-600 features aluminosilicates as a functional group and is a modified clinoptilolite (ResinTechInc 2017). The highest single-solute TAN capacity measured with the SIR-600 in this study was approximately 1.0±0.01 meq TAN/g, which is higher than 0.5 meq TAN/g mordenite for a similar equilibrium concentration of 3.5 meq TAN/L (60 mg TAN/L) obtained by Wang et al. (2007). While this experiment featured both potassium and calcium, it is evident from Figure 4-2c that potassium results in higher competition than calcium and ultimately played a larger role in the reduction of TAN capacity. Regardless, the capacity of 0.42±0.01 meq TAN/g SIR-600 for the EIMWW is comparable to the range of TAN capacities in the presence of calcium and potassium presented in the introduction (such as 0.55 meq TAN/g by Weatherley and Miladinovic 2004) in the presence of calcium of potassium. This reduction in capacity could be attributed to the simultaneous presence of potassium and calcium and to a higher equilibrium concentration of 4.98 meq TAN/L (90 mg/L) used by Weatherley and Miladinovic (2004). Based on this equilibrium liquid phase concentration and the multi-solute curve fit in Figure 4-7, the SIR-600 was expected to yield a very comparable TAN exchange capacity. Furthermore, TAN uptake capacities at 25 ^{o}C on chabazite, another natural zeolite have been reported as high as 2.5 meq TAN/g in the absence of potassium, and 1.5 meq TAN/g with potassium present in solution (Montégut et al. 2016). This would indicate that chabazite has a higher affinity for TAN.

Interestingly, this study found a great difference between TAN capacities of clinoptilolite and the SIR-600, single solute solution capacities of 0.68 meq TAN/g and 1.00 meq TAN/g, respectively. Yet when referring to Table 4-1 certain sources of clinoptilolite, namely the Mexican zeolites featured a higher maximal capacity than the SIR-600. This once again reinforces the notion that the source of the zeolite is extremely important and relevant to the overall performance.

4.3.3 Relative Separation Factors

The relative selectivity of each IE material was also studied with the goal of directly comparing the preference each exchange material possesses for one cation in solution versus the other cations also present. Unfortunately there is a lack of consistency in literature concerning separation factors, a term which is often used interchangeably with selectivity or equilibrium constant (Helfferich 1962). During a single component exchange experiment, the separation factor is generally equal to the selectivity, but during multicomponent exchange, as is the case with these experiments, that is no longer true. Therefore, for the sake of clarification, Table 4-6 summarizes the separation factors for TAN relative to potassium, calcium and as well as that of potassium relative to calcium for dosages of 0.1g and 1.5g. This is in order to determine if a certain cation is preferentially exchanged for different amounts of resin present, and while not equal to selectivity in this case, can still indicate a cationic preference exerted by an IE material. Relative separation factors above 1 indicate that exchange of the first ion is preferred over that of the second ion.

Table 4-6. Relative Separation Factors of each Ion-Exchange Material at Doses of 0.1 and 0.5g

Ion exchanger	α_{K}^{TAN}		α_{Ca}^{TAN}		α_{TAN}^{Ca}		α_{Ca}^{K}	
	0.1g	**1.5g**	**0.1g**	**1.5g**	**0.1g**	**1.5g**	**0.1g**	**1.5g**
Clinoptilolite	1.57	0.80	-	-	-	-	-	-
Purolite SSTC60	0.45	0.56	0.01	0.00	100	DIV/0	0.03	0.00
Amberlite IR120	0.53	0.62	0.01	0.00	100	DIV/0	0.02	0.00
Bojie BC121	0.42	0.22	0.01	0.00	100	DIV/0	0.03	0.00
Resintech SIR-600	1.63	2.95	9.18	3.54	0.12	0.29	1.10	2.67

A review of Table 4-6 shows that the different ion-exchange media have different preferential uptake of certain ions. Several columns contain zero values, all of which are present for the synthetic resins and the calcium separation factors. This was a result of a complete uptake of calcium and indicates that these resins have a complete preference for calcium over TAN and potassium. When considering the equation for calculation of separation factors (eq 4.3) the liquid concentration of calcium is present as the numerator, therefore if all calcium is removed from solution the relative separation factor is zero. This is reflected in the α_{TAN}^{Ca} column, where the separation factor for all three synthetic materials is 100 Furthermore, as the clinoptilolite desorbed Ca, the clinoptilolite separation factors relative to calcium could not be computed. Therefore, the clinoptilolite's preference is tremendously in favor of potassium and TAN over calcium. This resulted in the assumption of complete calcium exchange and a division by zero in the calculation of the separation factor.

The TAN separation factors relative to potassium (α_K^{TAN}) for the three synthetic resins were well below 1, the Bojie BC121 had the lowest separation factors. This confirms the general consensus in the literature, strongly acidic cation exchangers have a larger selectivity for potassium than TAN (Jung et al. 2004). The Bojie resin had a decrease in separation factor from the 0.1 g dosage to the 1.5 g dosage. The reason was believed to stem from the nature of synthetic resins and their crosslinked structures. The main driving force during ion exchange is the concentration differential between the aqueous and resin concentrations, which is opposed by the resins ability to swell and accommodate the ions (Arden 1968). This suggests that the resins ability to accept ions is partially controlled by the radii of exchanged cations and is further impactful when considering the less accessible exchanges sites. It is believed that with an increase in dosage, the overall concentration of TAN within the solution was reduced, leading to a smaller driving force, which was no longer strong enough to counter the Bojie's restrictive swelling abilities, explaining why the separation factor was reduced by half when increasing the dosage from 0.1 g to 1.5 g. Therefore, for higher dosages a lower degree of cross-linking (i.e., higher resin swelling) would be beneficial.

The clinoptilolite yielded encouraging TAN vs K^+ results for both dosages. For a dosage of 0.1 g the clinoptilolite had a separation factor of 1.57±0.45, but for a dosage of 1.5 g the separation factor was 0.80±0.17. This indicated a higher preference for TAN when a small dosage of clinoptilolite was applied, followed by a decrease in TAN relative to potassium selectivity proportional to the material dosage. These results further confirm information present in general literature which lists zeolites as having very similar affinities for potassium and TAN; with potassium's selectivity just slightly higher (Ames 1960; Dryden and Weatherley 1989; Weatherley and Miladinovic 2004; Wang et al. 2007; Widiastuti et al. 2011). Alternatively, Dryden and

Weatherley (1989) found an equal selectivity for TAN and calcium during their experiments, while in this case, calcium was completely eluded in favor of TAN. It is possible that the clinoptilolite obtained during Dryden's study featured a different atomic configuration leading to this difference. Furthermore, the α_K^{TAN} for clinoptilolite decreases with an increasing dosage, but as seen in Figure 4-8, using the 95% confidence intervals for the repeated tests there is overlap for all measured values, indicating that these results are statistically the same.

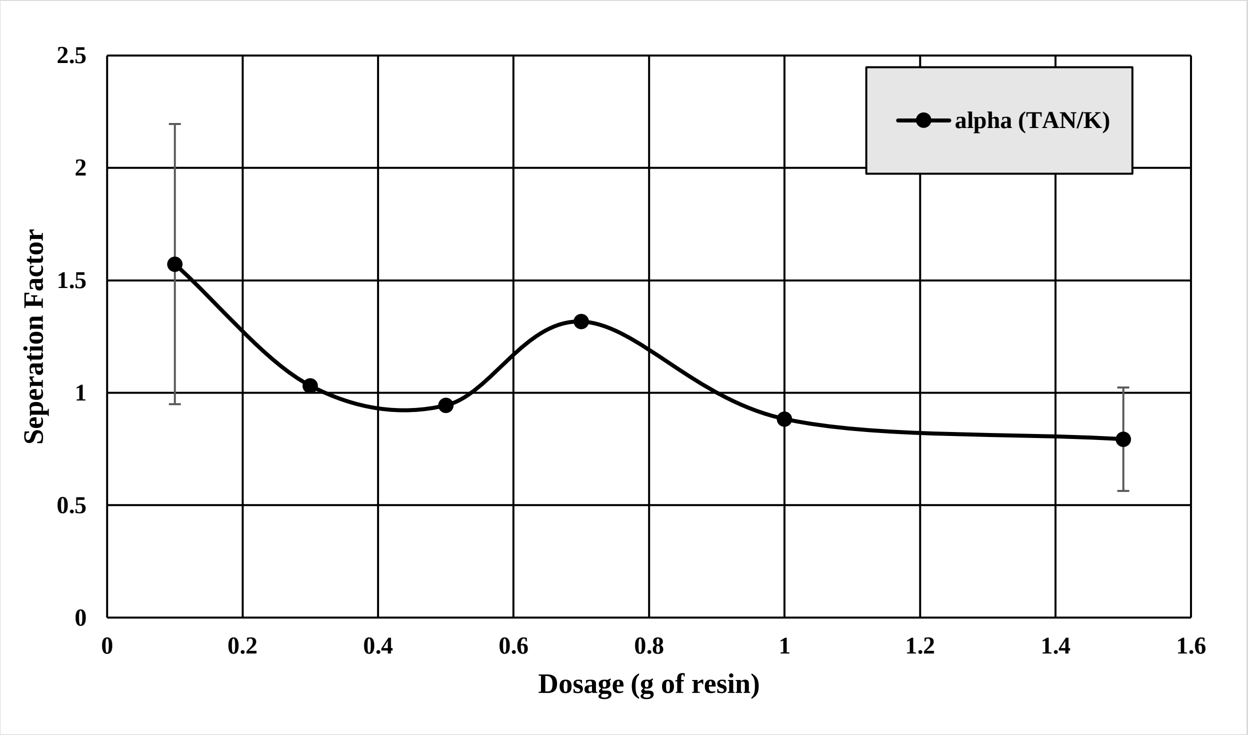

Figure 4-8. Clinoptilolite TAN/K Separation Factor Versus Dosage using a 95% Confidence Interval

This would indicate that the averaged value is slightly above 1.0, which suggests that the clinoptilolite exerts equal affinities for potassium and TAN and is somewhat constant for all measured dosages.

Finally, the SIR-600 media performed favorably with regards to TAN removal. For all dosage's, the α_K^{TAN} was above 1.0 which indicates a preference for TAN over potassium. This preference also increased with a larger dosage, as was seen in Table 4-6, where the 1.5 g dosage featured a α_K^{TAN} of 2.95±0.18. Suggesting that the dosage of ion exchange material and extent of competition were strongly linked, as the $\alpha_K^{TAN}$for 0.1 g was 1.63±0.08, slightly above half of the calculated value for the 1.5 dosage. The α_{Ca}^{TAN} featured a similar trend with the factor changing from 9.18 ±4.84 to 3.54±0.71 as the dosage increased from 0.1 to 1.5 g. This would once again imply that the dosage was strongly linked to competition. It is possible that this material featured different types of sorption sites, some of which only became prevalent at lower loadings. This could explain why the Langmuir model, which assumes all sites have the same energy of adsorption did not model the results adequately, whereas the Freundlich model featured better results. Regardless, TAN was found to be preferentially exchanged over calcium and almost equal to potassium. The above finding is in contrast to the generalized zeolite cation uptake selectivity's (Ames 1960; Dryden and Weatherley 1989; Widiastuti et al. 2011). There is no information on the modifications Resintech has applied to the SIR-600. Therefore, it is possible that the generalized zeolite selectivity no longer applies. The second important factor was the lack of any pre-treatment used to prepare the material. Hence, if there are any cations already present on the SIR-600 this could affect performance, i.e. if potassium is already present as an exchangeable cation, it could potentially cause the potassium capacity to appear as lower than reality. Thus, it is recommended that future studies pre-teat the IE media by applying repeated cycles of sodium or potassium-based brines.

4.4 Conclusion

The purpose of this study was to characterize the TAN uptake capacities of various IE materials by comparing a single component TAN synthetic wastewater with a complex blend of real EIMWW. This wastewater contained a wide variety of different dissolved ions, including high concentrations of potassium and calcium which posed as potential competition for the removal of TAN. For the synthetic wastewater the three synthetic resins; (Bojie BC121H, Purolite SSTC60 and Amberlite IR120 Na) had the highest TAN exchange capacities of 1.70-1.81 meq TAN/g for equilibrium concentrations of approximately 3.6 meq TAN/L. However, they also resulted in the highest competition with potassium and calcium within the mining wastewater as their maximum capacities decreased by 86-87 %. Their α_K^{TAN} were well below 1. These results confirm previous studies which have suggested avoiding synthetic IE resins when treating water mixtures containing potassium and calcium (Harland 1994; Malovanyy et al. 2013).

The TAN capacities of the two zeolites (natural clinoptilolite and SIR-600 modified clinoptilolite) were lower for the synthetic wastewater (without competing ions), however, they were significantly less impacted by the presence of K and Ca in the mining wastewater and achieved higher TAN capacities than the synthetic resins. The SIR-600 modified zeolite featured the highest TAN exchange capacity when treating the EIMWW; 0.42 meq TAN/g. Thus, the SIR-600 is the recommended IE material when attempting to treat wastewaters with several competing ions.

An important factor was the lack of any resin pre-treatment, thus no removal of any potentially pre-loaded ions such as the calcium in the case of the clinoptilolite. It is recommended that regeneration studies be performed to establish long term capacities and remove the possibility of interferences from competing pre-loaded cations. Regeneration studies would allow to determine the long-term effects of repeated loadings as well as simulate sodium/potassium pre-treatment through multiple brine regeneration cycles. Furthermore, column studies would help evaluate the impact of sorption kinetics of the competing ions and are relevant to real world applications. Finally, chabazite should be considered as a potential IE media.

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Chapter 5: Competitive Ion-Exchange of Ammonia in Mining Wastewater in the Presence of Ca and K: Implications of Batch Regeneration Cycles and Column Performance on Zeolites

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Abstract

Repeated batch loading-regeneration cycles were conducted for two ion-exchange (IE) media used in the treatment of ammonia-laden explosives impacted mining wastewater (EIMWW) to establish the effects of regeneration solution composition and concentration. The media included a natural clinoptilolite and a modified clinoptilolite (SIR-600). Five regenerant solutions were tested: 2.5 % NaCl, 5 % NaCl, 10 % NaCl, 5 % KCl and a 5 % NaCl + 5 % KCl mixture. The presence of potassium in the regenerant was found to hinder the total ammonia nitrogen (TAN) exchange capacity in both zeolites. The SIR-600 and the natural clinoptilolite used in conjunction with the 10 % NaCl solution featured the best TAN exchange capacities, 0.47±0.02 meq TAN/g and 0.36±0.05 meq TAN/g, respectively.

Continuous flow column tests were also performed using SIR-600 media and both a synthetic TAN solution and EIMWW. Competition with other ions severely impacted the TAN removal of the IE material. Breakthrough was reached after 274 bed volumes for the synthetic wastewater versus 50 bed volumes for the EIMWW.

Keywords: Ion exchange, ammonia, TAN, zeolite, clinoptilolite, SIR-600, competitive adsorption, potassium, calcium

5.1 Introduction

Due to increased awareness, an increasing number of regulations have been implemented in locales around the world in an attempt to curb the discharge of ammonia into the environment (Environment Canada and Health Canada 2001; Jorgensen and Weatherley 2003). This has led to the research and development of multiple treatment options for the removal and or transformation of ammonia, while aiming to minimize subsequent environmental consequences. Common treatment methods include biological processes such as the nitrification/denitrification process (Bashir et al. 2010; Halim et al. 2010), but it is also possible to achieve total ammonia nitrogen (TAN) removal through adsorption/ion-exchange, microwave radiation, sonification, air stripping, and chemical processes such as chemical precipitation or breakpoint chlorination (Halling-Sørensen and Jorgensen 1993; Zhang et al. 2012; Dong and Sartaj 2016). Ion-exchange (IE) removal of TAN from wastewaters is of interest because it is not susceptible to shock loadings (like biological processes) and it is not impacted by TAN toxicity which can lead to microbial inhibition in biological systems (Lee et al. 2000).

Removal of ammonia by IE is a well-documented process, especially in wastewater treatment (Hedström and Rastas Amofah 2008; Malovanyy et al. 2013; Ding and Sartaj 2016). In general, the exchange of TAN is performed using zeolites, due to their high affinity for TAN. Furthermore, zeolites are easily acquirable and generally inexpensive. Zeolites are natural minerals, formed by tetrahedral chains of aluminosilicates with high porosity and are characterized by their capacity for molecular sieving (Hlavay et al. 1982; Smith and Smith 2015; Montégut et al. 2016). Their negatively charged sites within the internal surfaces of the zeolite particles allow for the adhesion of positive counter-ions, which are readily exchanged for other cations in solution.

Ames (1960) proposed the following general order of selectivity for clinoptilolite, a common zeolite:

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

This order of selectivity has been studied and confirmed on numerous accounts (Leyva-Ramos et al. 2004; Guo et al. 2008; Widiastuti et al. 2011). While this list is considered the basic order in which most zeolites will preferentially adsorb species, it is dependent on species concentration and can be circumvented by greatly increasing the concentration of a less preferred ion (Hedström and Rastas Amofah 2008). While observing the generalized selectivity order, attention should be drawn to potassium. Since zeolites generally have only a slightly higher selectivity for K^+ than TAN, potassium has often resulted in competition with TAN for adsorption sites (Milan et al. 1997; Guo et al. 2008; Hedström and Rastas Amofah 2008). The TAN exchange capacities reported in the literature vary widely partially due to the many differences amongst zeolite types, testing conditions and the differences among the solutions being treated (Klieve and Semmens 1980; Hlavay et al. 1982; Weatherley and Miladinovic 2004; Ding and Sartaj 2015; Montégut et al. 2016)

Table 5-1 serves as an example of selected TAN exchange capacities exhibited by zeolites and draws the difference between liquid solutions used in terms of real wastewaters (WW), synthetic TAN solutions or synthetic multicomponent wastewaters (synthetic WW). The main conclusion was the difficulty in comparing amongst the various studies largely due to the differences among the zeolite types and the difference among the solutions treated. The difference among the zeolites can be attributed to the source of the zeolite, it’s atomic structure and the preconditioning. The natural origins of these materials lead to a lack of any form of industrialized quality control. Furthermore, it has been stated that the application of pre-treatment in the form of high concentration sodium baths or even repeated loading/regeneration cycles can lead to an increase in TAN capacity (Klieve and Semmens 1980; Leyva-Ramos et al. 2004). This has been attributed to the establishment of a homoiconic exchangeable counter-ion, which favorably increases TAN exchange capacities (Klieve and Semmens 1980; Leyva-Ramos et al. 2004). The majority of literature reported the use of synthetic solutions rather than real wastewater. In general, it is difficult to synthetically reproduce real blends of wastewaters as there are many potentially significant ions and environmental conditions. This can lead to artificially higher capacities by neglecting the interactions between unaccounted for dissolved species. Furthermore, the presence of these dissolved species can lead to supplementary competition during the IE process.

Table 5-1. Zeolite TAN Exchange Capacities in meq TAN/L

Zeolite Origins	Zeolite Type	TAN capacity (meq TAN/g)	Equilibium concentration (meq TAN/L)	Wastewater type	Reference
New Zealand	Mordenite	0.61	4.97	Synthetic WW	(Weatherley and Miladinovic 2004)
United States	Phillipsite	2.64	5.53	Synthetic TAN	(Klieve and Semmens 1980)
Canada	Clinoptilolite	0.44	5.53	Synthetic TAN	(Ding and Sartaj 2015)
United States	Mordenite	1.80	5.53	Synthetic WW	(Klieve and Semmens 1980)
Hungarian	Clinoptilolite	0.51	0.24	Municipal WW	(Hlavay et al. 1982)

Limited information was available for the regeneration of IE materials using potassium as the exchangeable cation (Guo et al. 2013). The majority of studies have focused on the conventional sodium or acid-based regenerations. Therefore, there is a need to investigate the implications of using high potassium concentrated brines for the regeneration of IE materials. Lahav and Green (1998) investigated the interactions of potassium pre-loaded clinoptilolite and sodium form clinoptilolite operating in a flow through column treating a synthetic wastewater. Ultimately, the column pre-saturated with potassium featured breakthrough after 160 bed volumes (BV), compared to its sodium counterpart which resulted in breakthrough after 260 bed volumes. Hlavay et al. (1982) compared the uptake of TAN from municipal wastewater with that of a synthetic wastewater on a natural clinoptilolite operating in column flow experiments. His experiments found that the TAN exchange capacity of the synthetic wastewater was much higher than those of the municipal wastewater even-though similar cationic conditions were created. The synthetic wastewater featured TAN exchange capacities of 0.33 meq TAN/g, which were more than twice those of the municipal wastewater 0.13 meq TAN/g. This indicated that it is important to evaluate real wastewaters as synthetic blends often do not adequately represent realistic conditions.

The mining industry extensively uses nitrogen-based explosives, and this results in wastewaters with TAN, Ca and K concentrations in the order of 100 mg/L. This study evaluates the performance of a natural clinoptilolite and a modified clinoptilolite (SIR-600) for the removal of TAN from explosive impacted mining wastewater (EIMWW). The focus of this work are batch experiments to study the effects of regeneration methods and the treatment of EIMWW using continuous flow column tests to further the competitive adsorption under dynamic conditions. Both potassium and calcium have been noted to reduce the exchange of TAN onto zeolites, particularly potassium due to a similar selectivity exerted by conventional zeolites for potassium and TAN. (Hlavay et al. 1982; Weatherley and Miladinovic 2004; Crittenden et al. 2012)

5.2 Experimental Methods and Materials

Both batch and continuous flow column experiments were performed using synthetic wastewater as well as real EIMWW in an attempt to assess the performance of an IE process and to establish the effects of ionic competition. The EIMWW was collected from a blasting operation in a mine. The EIMWW contained approximately 3.87 meq TAN/L (70 mg TAN/L). Thus, the synthetic wastewater was prepared by combining distilled water with ammonium sulphate (230 mg in 1 L) for a desired concentration of approximately 3.87 meq TAN/L (70 mg TAN/L). Furthermore, the EIMWW contained a complex blend of dissolved metals and anions. Full chemical analysis was accomplished via Inductively Coupled-Plasma (ICP) analysis.

TAN, potassium and calcium were determined to be the three cations presenting the largest concentrations for EIMWW, therefore their interactions were the central focus of the study. Furthermore, zeolites are known to exhibit very similar selectivity's for potassium and TAN as was determine by Ames (1960).

The two IE materials considered were both zeolitic in nature. The first material was a natural zeolite (clinoptilolite) obtained from an American fertilizer company (The Seed Supply, Saint Anthony, ID). Clinoptilolite is inexpensive and known for its molecular sieving abilities as well as its high affinity for ammonia (Hedström and Rastas Amofah 2008; Casadellà et al. 2016). The second studied IE material was a modified clinoptilolite (SIR-600, Resintech, West Berlin, NJ, USA). This modified clinoptilolite is typically utilized in the removal of cesium and ammonia from wastewaters (ResinTechInc 2017). The purpose of the regenerations studies was to establish which zeolite would yield the highest TAN removal in a continuous flow column. Furthermore, there was a desire to determine if a continuous flow column system could treat this real blend of EIMWW to meet the Canadian Council of Ministers of the Environment (CCME) standards for industrial wastewater discharges. The CCME requires effluent concentration for unionized ammonia of 0.019 mg NH_3/L to avoid acute toxicity for fish in receiving waters.

5.2.1 Analytical Methods

TAN measurements were accomplished by Nesslerization as per Standard Methods (4500-NH_3) with a spectrophotometer (DR6000, HACH, Loveland, CO, USA). pH was recorded on a pH probe (PHC201, HACH, Loveland, CO, USA) and electrical conductivity (EC) was measured with a probe (40PCID, VWR, Radnor, PA, USA) and a benchtop meter.

Potassium and calcium concentrations were measured by direct air-acetylene flame atomic absorption (AA) spectroscopy as per Standard Methods (3111B) with an AA spectrometer (PinAAcle 55, PerkinElmer, Waltham, MA, USA).

5.2.2 Experimental Setup

During the regeneration experiments, five different regeneration solutions were tested, containing different combinations of potassium and sodium as exchangeable cations. Using a batch configuration, the efficiency with which these different solutions could regenerate the loaded zeolites and the implications of regenerating cations on the long-term capacities were evaluated.

All exchange cycles for the regeneration studies were performed with the EIMWW. The five regeneration solutions were based on a percentage by weight ratio. Only two contained potassium; a 5 % KCl solution, and a 50/50 combination of a 5 % KCl and 5 % NaCl solution. The sodium-based regeneration solutions consisted of a 2.5 % NaCl solution, a 5 % NaCl solution and finally a 10 % NaCl solution. The purpose of the potassium centric regenerations was to establish if the IE material would find an equilibrium point within the particle with regards to potassium. This would result in the IE material constantly at it's maximal potassium capacity before exchange cycles had even begun as it would retain the already adsorbed potassium and not remove any more from the EIMWW. Finally, only TAN would be removed during the exchange cycle, and subsequently release less cations into regenerant streams. All results were referred to by the ion-exchanger regenerating salt (NaCl or KCl) and their percent concentration. The exception being the 5 % NaCl + 5 % KCl regenerations which were simply referred to as the NaCl+KCl.

Each regeneration experiment consisted of a loading, or exchange phase, followed by the regeneration phase. The sum of these two steps were referred to as cycles. 0.5 g of either zeolite was combined with 125 ml of solution (EIMWW for loadings and regenerant for the regeneration step). The pH of each batch regeneration solution was increased to approximately 10 by titration using 0.2 M NaOH or 0.2 M KOH solutions. Any pH adjustments for the NaCl+KCl solution were accomplished prior to combining respective K^+ and Na^+ regenerants. All batch experiments were performed at room temperature (approximately 23 ^{o}C). All experiments were performed in triplicates to allow for standard deviation statistical analysis.

Both the loading and regeneration phases were performed in 125 ml sealed glass bottles to avoid TAN volatilization. Teflon tape was wrapped twice around the threaded portion of the bottle and electrical tape around the cap of the bottle once screwed on. Volatilization was avoided by filling the bottles until the solution was overflowing, to avoid any head space. The bottles, once sealed, were placed in an end-over-end tumbler that rotated the bottles at a speed of 10 rpm to ensure gentle mixing and thorough solid-liquid contact, promoting IE.

During the loading cycles, the bottles were filled with the EIMWW, placed on the tumbler and rotated for 24 hrs to ensure equilibrium conditions were met. Once the desired contact time was achieved, the bottles were removed, and the content vacuum filtered through a glass microfiber filter (Whatman plc, Maidstone, Kent, England) to separate the solid and liquid phases. The IE materials were rinsed with distilled water and placed within a desiccator.

The regeneration cycles were performed following the same procedure as for the loading cycle, but with the previously mentioned regeneration solutions used to fill the bottles rather than the EIMWW. Furthermore, as desorption is a slower process, a contact time of 48 hrs was selected.

It was possible to determine the uptake and release of TAN, potassium and calcium by performing a mass balance around the entire system using the following equation:

$$q_{eq} = \frac{(C_i - C_{eq}) * V}{M} \qquad \text{(eq 5.1)}$$

Where q_{eq} is the equilibrium IE material capacity (meq/g); C_{eq} and C_i are the equilibrium and initial pollutant liquid phase concentrations, respectively (meq/L); V is the volume of solution (L) within the bottles and M is the mass of IE material (g).

The second set of experiments, consisting of column studies; used a 28.75 mm I.D., 150 mm long acrylic column. A total of 40 g of SIR-600 was placed within the column. The SIR-600 was selected for the column experiments as it featured a higher TAN uptake capacity as well as a lower Ca^{2+} uptake capacity compared to the natural clinoptilolite. To prevent loss of material, glass wool was inserted into the bottom of the column and two perforated acrylic disks, one placed overtop glass wool, the IE media was placed above the disk. To distribute the flow equally and reduce channeling, the second perforated disk was placed above the IE material. The total bed depth of the zeolite was 71.0 mm which resulted in an empty bed volume of 46.1 mL. Flow control was accomplished by placing a clamp on the rubber tubing used for the columns effluent. The feed to the column was introduced into the column by a 2.0 L plastic reservoir, which helped ensure a constant head above the IE material within the column. This was a gravity flow system where depth of water within the column was always above the media and always ensure a sufficient contact time.

A flow rate of approximately 29 mL/min was selected for the loading cycles and effluent was collected after various predetermined intervals for further analysis. The column was then regenerated using a 10 % NaCl solution at a flowrate of approximately 1 mL/min as per the manufacturers recommendations (ResinTechInc 2017).

During the first experiment, the column was loaded with the EIMWW, run until exhaustion and subsequently regenerated. The regenerated SIR-600 zeolite was then once again loaded with the EIMWW until breakthrough, which consisted of an effluent TAN concentration of approximately 0.55 meq TAN/L (10 mg/L). The experiment was repeated with the synthetic wastewater where the column was once again run until a breakthrough concentration of 0.55 meq TAN/L (10 mg/L).

To compare the performance of the column with regards to potassium, calcium and TAN, the respective capacities were calculated using a simplified numerical integration of the mass of the species removed as presented by Inglezakis (2006):

$$q = \frac{Q}{M} \sum (C_{feed} - C_{eff}) \Delta t \qquad \text{(eq 5.2)}$$

Where q is the capacity for a given species of the IE material at a given time (meq/g). Q is the flow rate for a given time interval (mL/min), M is the mass of IE material present in the column (g), C_{feed} and C_{eff} are the influent and influent pollutant concentrations respectively (meq/L) and Δt is the given time step (min).

5.3 Results and Discussion

Preliminary kinetic experiments determined that materials reached equilibrium within 1 hour. As all materials performed similarly only the clinoptilolite and the Amberlite were presented in Figure 5-1.

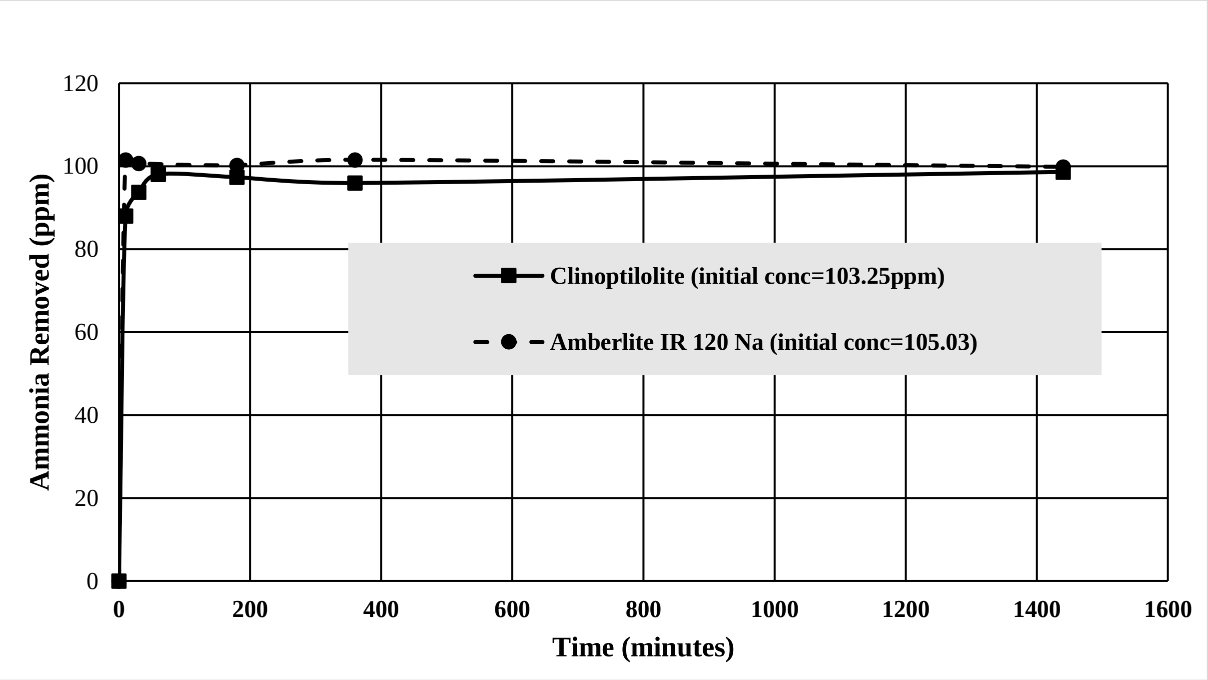

Figure 5-1. Example of Kinetic Experiments

5.3.1 Batch Regeneration Studies

The first phase of this study focused on the effects of loading natural and modified zeolites with real EIMWW and subsequently performing regeneration cycles with various regeneration fluids to establish the effects of regenerant concentration, composition as well as to determine the long-term performance of both materials. Analysis after every exchange and subsequent regeneration cycles allowed to evaluate regeneration efficiency. Table 5-2 summarizes the elemental composition of the EIMWW used for all experiments.

Table 5-2. List of Species and Corresponding Concentrations Present in the EIMWW

Species	Concentration (mg/L)	Concentration (meq/L)
Si	3.56	0.51
Al	0.08	0.01
Fe	0.70	0.04
B	0.07	0.02
Ca^{2+}	78.05	3.90
Mg	12.67	1.04
Sr	2.10	0.05
Na	270.29	11.76
K	111.5	2.85
SO_4	1050.0	21.86
HCO_3	300.0	4.92

Figure 5-2 illustrates the Ca^{2+} exchange capacities exhibited by both zeolites over four different loading cycles after being regenerated by a 10% NaCl regenerant. All error bars are one standard deviation.

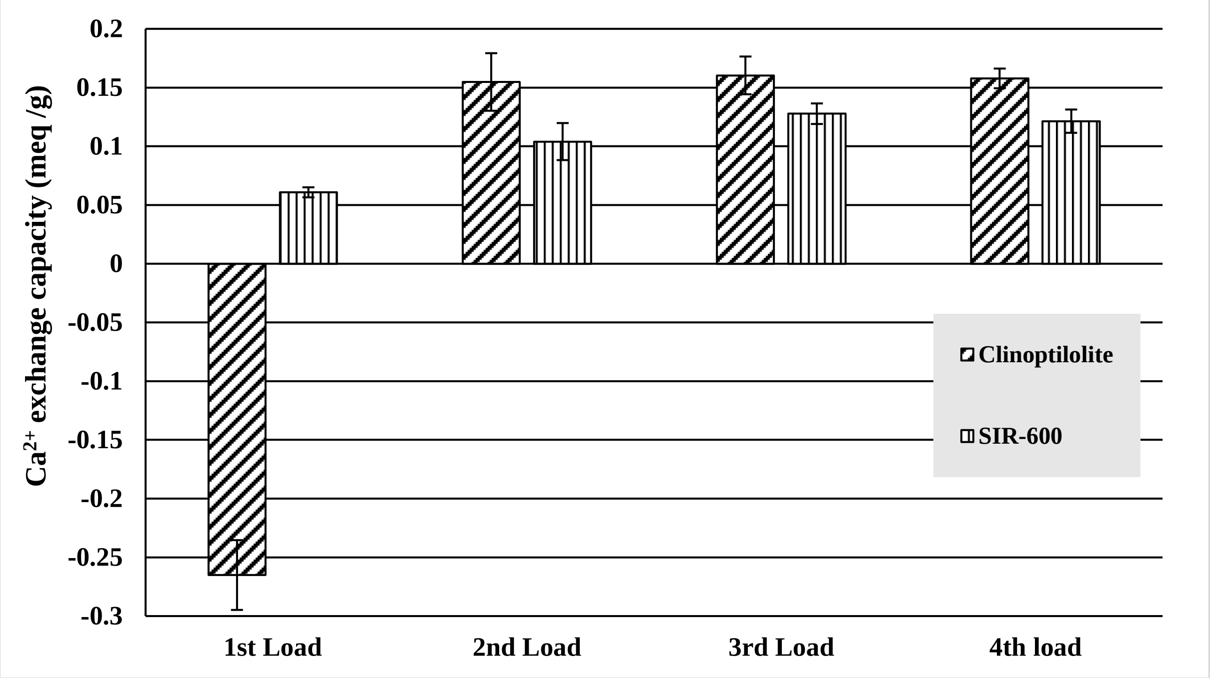

Figure 5-2. Successive Average Calcium Uptake Capacities for 10% NaCl Regenerant and EIMWW

On the first loading, there was a negative calcium capacity demonstrated for the clinoptilolite (natural zeolite). This indicated the presence of initial calcium present as an exchangeable cation, that leached during the first loading cycle. It has been reported in literature that clinoptilolite may feature several initial counter-ions, including calcium (Jama and Yücel 1989; Weatherley and Miladinovic 2004; Widiastuti et al. 2011; Montégut et al. 2016). Furthermore, the clinoptilolite featured a larger affinity for calcium than the SIR-600, as the second through fourth loadings resulted in larger calcium uptake capacities than the SIR-600. The clinoptilolite had an equilibrium capacity of 0.16±0.01 meq Ca^{2+}/g. The SIR-600 featured a slight increase in capacity between the first loading cycle and stabilized at 0.12±0.01 meq Ca^{2+}/g. As the purpose of the experiment was the removal of TAN, Figure 5-2 suggests that the SIR-600 is favorable as it removed less calcium. Similar results were observed for potassium over four loading cycles with 10 % NaCl as the regeneration solution, they are presented in Figure 5-3.

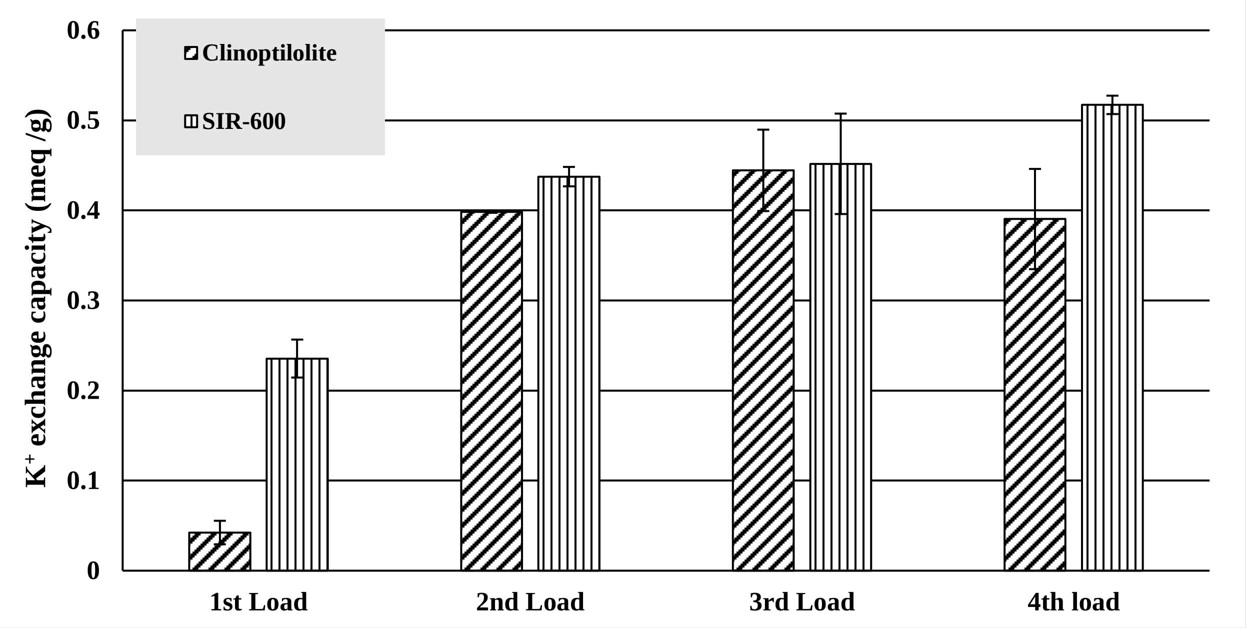

Figure 5-3. Successive Potassium Uptake Capacities for 10% NaCl Regenerant and EIMWW

Both IE materials experienced increased K^+ loading following the first exchange cycle. This was attributed to the presence of potassium as exchangeable counter-ions on the non pre-treated zeolite samples (i.e., they were preloaded with potassium) (Milan et al. 1997; Guo et al. 2008; Montégut et al. 2016) along with competition resulting from TAN present in the EIMWW. Therefore, it is possible that both materials had their potassium capacities saturated and since the two ion-exchangers have a high affinity for potassium neither featured a release of the initially adsorbed potassium. This would explain why the materials have noticeably higher potassium capacities in the second and subsequent cycles, which consequently would have released pre-loaded potassium during the regeneration step. Prior to the first test, the zeolites were only rinsed with distilled water to remove any dirt or impurities, therefore the second factor which caused the increase of K^+ uptake capacities were attributed to the conditioning of the zeolites. Several studies have stated that repeated loading/regeneration cycles can increase the capacity of a material, by creating a uniformity of counter-ions (Klieve and Semmens 1980; Milan et al. 1997; Leyva-Ramos et al. 2004; Hedström and Rastas Amofah 2008). These repeated regeneration cycles with high concentration of sodium, removed any pre-loaded counter-ions. Furthermore, Figures 5-2 and 5-3 confirm the generalized order of selectivity, which states a higher affinity for potassium than calcium in zeolites, approximately 74% for the SIR-600 and 61% for the clinoptilolite (Ames 1960; Jama and Yücel 1989; Leyva-Ramos et al. 2004; Guo et al. 2008).

The structure of zeolites plays an important role in defining the selectivity of materials and it has been stated that zeolitic structures containing high Si to Al ratio's in fact have a higher selectivity towards lower charge density elements (Margeta et al. 2013). Clinoptilolite is one such material and according to the supplier, the clinoptilolite used in this study had a Si/Al ratio of 22.4 (The Seed Supply 2017) which is much larger than typical clinoptilolites which have ratios ranging from 2.7 to 5.7 (Margeta et al. 2013). Thus, the higher Si ratio in this study, therefore explains the higher capacities for potassium. In contrast, the SIR-600 featured a smaller calcium capacity than the clinoptilolite and a much higher potassium capacity relative to it's calcium (high charge density cation) capacity. Figures, 5-4 and 5-5 present the average TAN exchange capacities of each loading cycles for both IE materials using the different regeneration solutions.

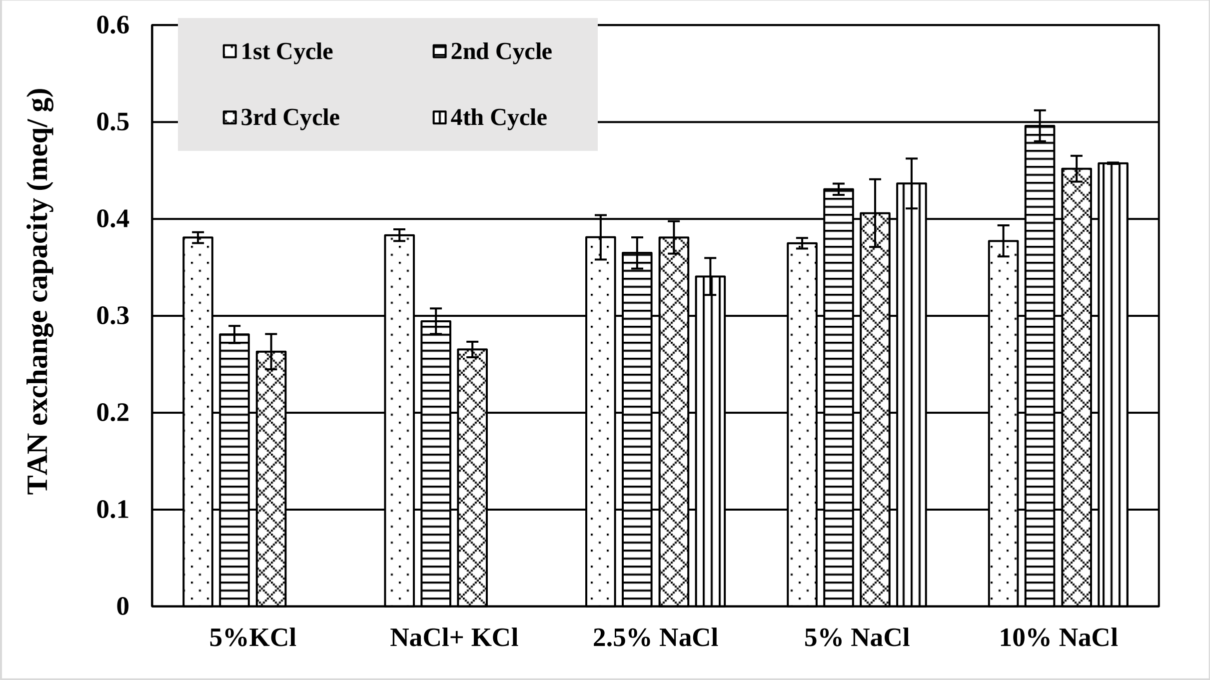

Figure 5-4. Averaged TAN Exchange Capacities for all Regenerants on SIR-600 with EIMWW

Comparing the two KCl regenerations for the SIR-600, see Figure 5-4, the TAN exchange capacities decreased by approximately 0.1 meq TAN/L over three cycles, or approximately 25 %, which suggested that the increase in potassium concentration within the regenerant was not as impacting on TAN uptake capacities as the mere presence of potassium itself within the regenerant. These reductions in capacity were likely caused by a high affinity for potassium and a high concentration of potassium. This would lead to a higher degree of exchange sites occupied by potassium. As previously mentioned, IE selectivity is partially based on elemental composition of the fluid. In this case, by exchanging potassium, the potassium concentration within the fluid was increased, thus increasing the concentration differential. Furthermore, this indicates that the regeneration solutions could not fully desorb potassium during the regeneration process, which is not unlike other studies accomplished with clinoptilolite (Jama and Yücel 1989; Milan et al. 1997; Guo et al. 2013). Therefore, the initially desired outcome of saturating the resin with potassium and removing only TAN were achieved yet the results were unsatisfactory from a maximizing TAN uptake performance objective, especially when compared to the exchange capacities achieved with the sodium based regenerants. Due to lower TAN uptake capacities for both IE materials, the regenerations using KCl based solutions were abandoned after 3 cycles and only the NaCl based regenerants were used for a 4th cycle.

Furthermore, the 2.5 % NaCl regenerant did not have enough sodium to increase the SIR-600 TAN exchange capacities, as exchange capacities remained constant between 0.34-0.38 meq TAN/g over the four cycles. The findings of Klieve and Semmens (1980) and Leyva-Ramos et al. (2004) suggest that a noticeable increase in exchange capacity due to the conditioning of the ion-exchanger should have been noticed, which was not the case for the 2.5% NaCl regeneration. Finally, the 10 % NaCl had the highest capacities ranging from 0.46-0.49 meq TAN/g, thus representing the expected increase in capacity resulting from multiple regeneration cycles and their conditioning effects. This represents an increase of approximately 9 % above the 5 % NaCl regeneration. Therefore, in a batch setting it could be beneficial to use a 5 % NaCl regenerant as it suffers only a minimal reduction in capacity while reducing chemical consumption in half.

Figure 5-5 presents the repeated averaged TAN uptake capacities for the same regeneration solutions applied to the clinoptilolite. The clinoptilolite regeneration cycles featured similar trends as those presented for the SIR-600 but had more variability in the results. By comparing Figures 5-4 and 5-5 it was immediately evident that the SIR-600 was more consistent. Not only are the error bars for the SIR-600 smaller in most cases, but the clinoptilolite's results are more variable.

This was attributed to clinoptilolite's natural origins, thus lacking any form of manufactured consistency, as was the case with the SIR-600.

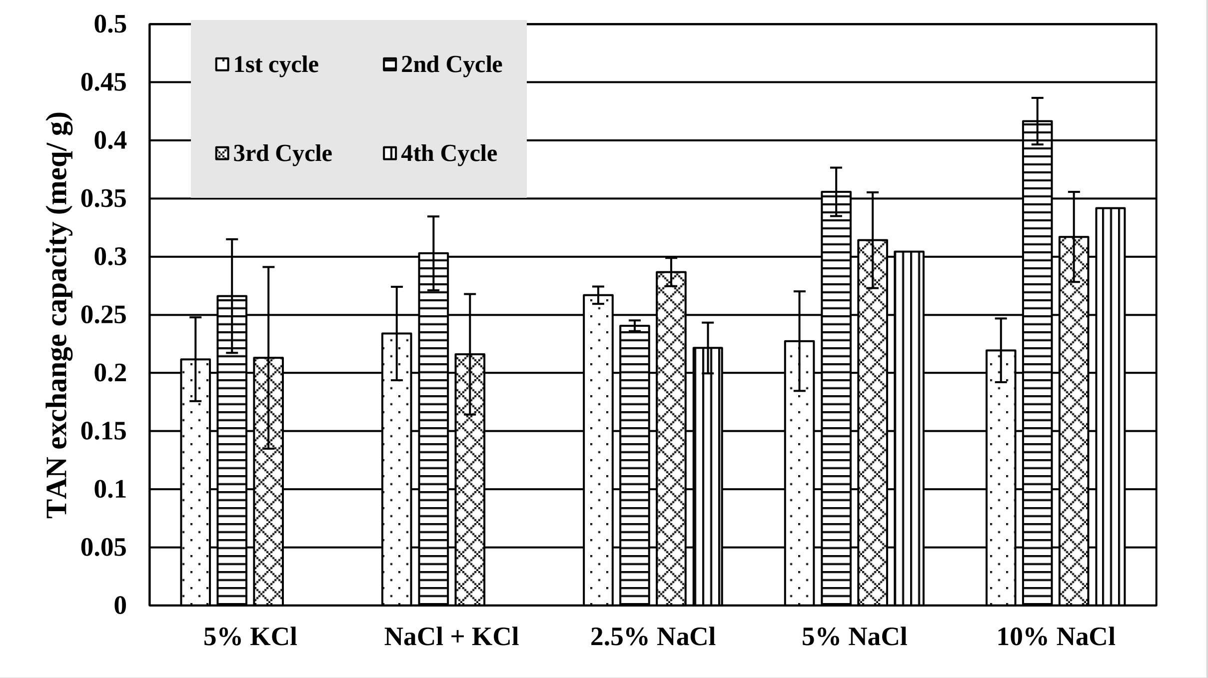

Figure 5-5. Averaged TAN Exchange Capacities for all Regenerants on Clinoptilolite with EIMWW

The clinoptilolite's TAN loadings using 5 % and 10 % NaCl regeneration cycles were comparable, with final capacities of 0.30 ± 0.02 meq TAN/g and 0.34 ± 0.02 meq TAN/g, respectively. This indicated that increasing the concentration of regenerant from 5 % to 10 % did not result in a significant increase of the clinoptilolite's TAN exchange capacity. This is in contrast to the SIR-600's TAN capacity which featured a slight improvement with each incremental NaCl dosage level. In similar fashion to the SIR-600, the clinoptilolite had low TAN capacities when regenerated with 2.5% NaCl solutions. The fourth cycle featured a capacity of 0.22 ± 0.03 meq

TAN/g, almost identical to those obtained with the potassium based regenerants or during the first cycle with virgin ion-exchanger.

Table 5-3 summarized the averaged calcium, potassium and TAN capacities for the 4th exchange cycle for 5 % and 10 % NaCl regenerations. As the potassium based regenerants and the 2.5 % NaCl regenerant featured lower results, they were omitted from the following table.

Table 5-3. Average 4th Exchange Cycle Capacity of Clinoptilolite and SIR-600 for 5 and 10 % NaCl Regeneration (± one SD)

Clinoptilolite		
Regenerant	**5 % NaCl**	**10 % NaCl**
meq Ca^{2+}/g	0.14 ± 0.02	0.16 ± 0.01
meq K^{+}/g	0.36 ± 0.01	0.39 ± 0.06
meq TAN/g	0.30 ± 0.02	0.34 ± 0.02
SIR-600		
Regenerant	**5 % NaCl**	**10 % NaCl**
meq Ca^{2+}/g	0.13 ± 0.06	0.12 ± 0.01
meq K^{+}/g	0.46 ± 0.04	0.52 ± 0.01
meq TAN/g	0.44 ± 0.03	0.46 ± 0.01

From Table 5-3 it was noticed that the SIR-600 featured higher TAN uptake capacities (0.46 ± 0.01 meq TAN/g for SIR-600 versus 0.34 ± 0.02 meq TAN/g for natural clinoptilolie) and that both materials featured a preference for potassium over TAN. The literature for the selectivity of zeolites such as clinoptilolite (Widiastuti et al. 2011; Guo et al. 2013) tend to be in agreement in suggesting that there is a defined order of selectivity, with a slight preferential exchange of potassium over TAN. However clinoptilolite has been documented to exhibit equal exchange capacities for TAN and potassium (Malovanyy et al. 2013). Clinoptilolite's potassium exchange capacity was higher than its TAN exchange capacity for both the 5 % NaCl and the 10% NaCl, 17 % and 13 % respectively. However, when considering for the 10 % NaCl clinoptilolite experiments the confidence limits of the K^+ and TAN loadings overlap, therefore, the difference is not statistically significant. In comparison, the results for the regeneration of SIR-600 with 5 % NaCl, the TAN and potassium capacities are statistically the same, whereas the 10 % NaCl regeneration favors potassium by 12 %. Based on the overlapping confidence limits of the K^+ and TAN loadings in the 5 % NaCl SIR-600, in this case the difference is once again not considered statistically significant.

The pH of all regeneration solutions was raised to a value between 9.5 and 10, and thus monitored before and after contact with IE materials (i.e. the regeneration process). It was noted that after contact with the ion exchange material the pH reduced by a similar amount for both IE materials, approximately 1-1.5. Figure 5-6 serves as an example of the averaged pH values for the 10% NaCl regenerations both before and after regeneration had occurred. The initial column represents the averaged pH values of the regeneration solution used in all experiments prior to any regeneration cycles. Error bars represent one standard deviation. All regeneration cycles featured similar pH reductions as illustrated in Figure 5-6 regardless of the regenerant used, therefore only the 10 % NaCl is shown.

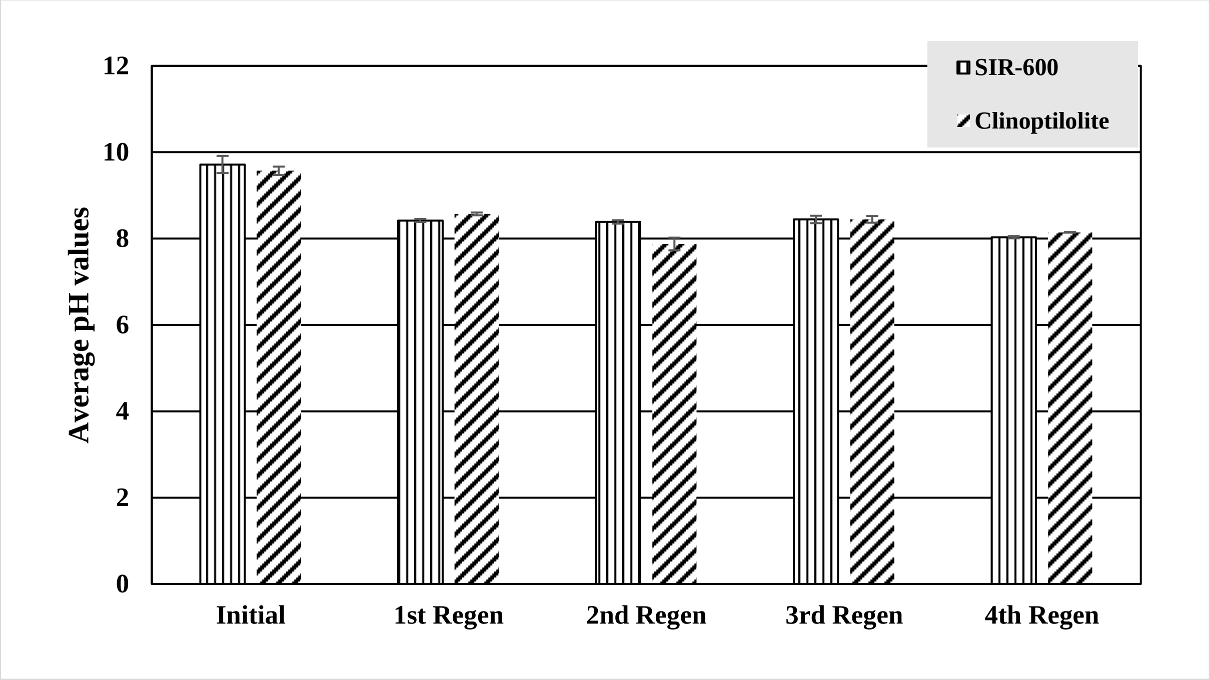

Figure 5-6. Averaged pH Values of 10% NaCl Regeneration Solutions

This reduction in pH was attributed to the following reaction, which represents the shift in TAN concentration from ammonium (NH_4^+) to ammonia (NH_3) due to the elevated pH.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \text{(eq 5.3)}$$

This was interpreted as the ammonium reacting to produce unionized ammonia as well as hydrogen in turn consistently reducing the pH of the regenerants. Similar results were presented by Guo et al. (2013).

Based on findings from the batch regeneration studies, the SIR-600 modified zeolite was selected as the better candidate for the subsequent column studies. This was based on the lower uptake of calcium, a potentially higher selectivity for TAN than potassium and finally an overall higher overall cation exchange capacity.

5.3.2 Column Studies

Full-scale IE applications generally consist of continuous flow column systems for practical reasons as well as to maximize operational efficiency. Therefore, it is important to determine if the EIMWW could be treated in a column system, particularly because in these systems the contact times are only in the order of minutes and the kinetics of the exchange may impact the selectivity. A second goal of this study was to quantify the reduction in TAN capacity of a continuous IE column resulting from the presence of multiple competing species by comparing performance when treating the EIMWW versus a synthetic TAN solution. Finally, a tertiary goal was to determine if the TAN levels could be reduced to below the CCME's required effluent. Figure 5-7 illustrates the effluent concentrations of TAN versus the amount of treated bed volumes using a flow rate of approximately 29 ± 2 mL/min.

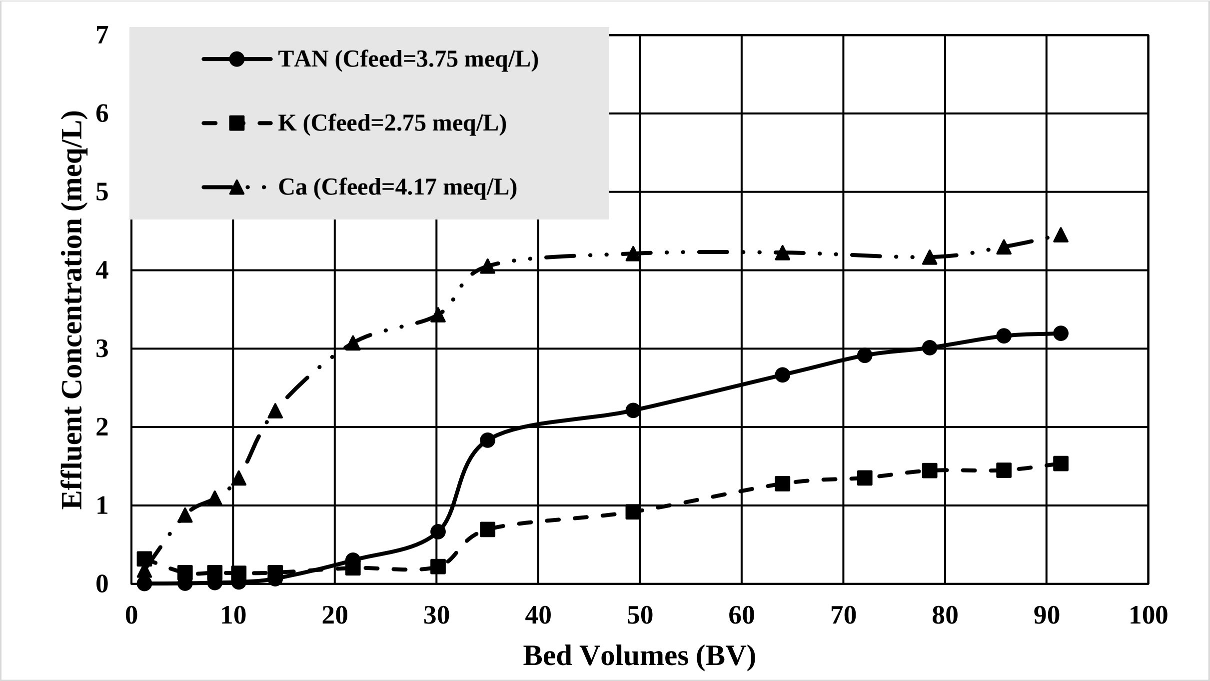

Figure 5-7. SIR-600 Column Effluent Concentrations of Calcium, Potassium and TAN for EIMWW and Unconditioned Zeolite

After treating 91 BV's, the effluent TAN concentration was 3.19 meq/L during the initial run, which was taken as near saturation. It is immediately noticeable that calcium reached saturation (i.e., $C_{eff} = C_{feed} = 4.17$ meq/L) earlier (approx. 30 BV) than the TAN, but also increased to a higher concentration than that of the feed. This was interpreted as the SIR-600 exerting a higher selectivity towards potassium and TAN than calcium and resulting in the displacement of previously exchanged calcium ions. This reinforces the previous results in Table 5-3, which demonstrated a clear preference for potassium and TAN over calcium, which reached saturation earlier than either of the other cations. Furthermore, after treating 90 BV's, the column effluent was near TAN saturation (~85 %), whereas the effluent potassium concentration was approximately 50 % of the feed concentration, suggesting a higher ultimate potassium capacity, leading to slower breakthrough. It was believed that this higher potassium capacity allowed for the

TAN adsorption front to move ahead of the potassium adsorption front, resulting in single component ion-exchange for a short duration of time. It would seem that the potassium front begun to displace previously sorbed TAN ions at 30 BV's, where the effluent of both species noted an increase of almost 2:1 TAN versus K. The batch regeneration studies indicated nearly identical capacities for TAN and potassium, therefore it would seem that at 30 bed volumes, the effects of competition became apparent, resulting in the increase for both species, and potassium removing previously sorbed TAN at a 1:1 ratio.

The resulting exchange capacities for calcium, potassium and TAN were all plotted to allow for direct comparison between each species and further characterize the selectivity of the SIR-600. These results are presented in Figure 5-8.

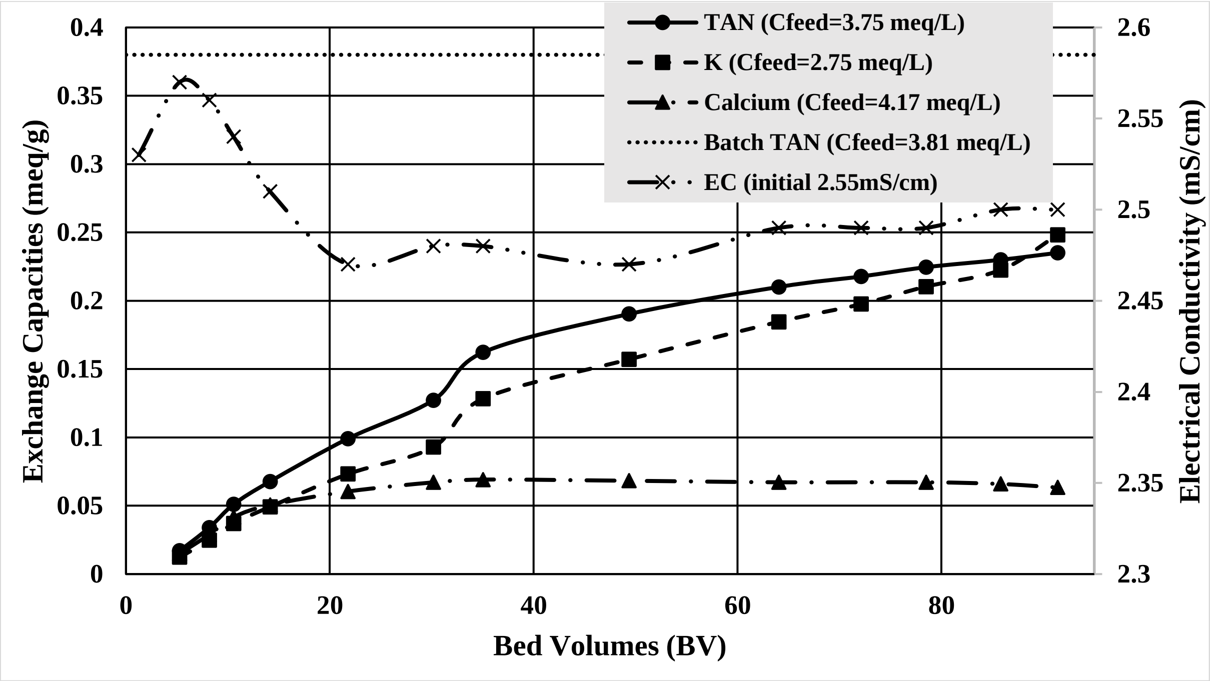

Figure 5-8. SIR-600 Un-Conditioned Column Saturation Capacities for EIMWW

The results illustrated in Figure 5-8 are of interest as the SIR-600 demonstrated a slight preference for TAN over potassium up until approximately 85 % TAN saturation or after the treatment of 90 BV. This preference for TAN may be due to the lower K^+ feed concentration (2.75 versus 3.75 meq/L). From Figure 5-7 it was noticed that after treatment of 90 BV's, potassium effluent was only 55 % of saturation. Regardless, these capacities are similar and correspond to the results found in Table 5-3, which reported similar capacities for potassium and TAN. The thick dotted line in Figure 5-8 represents the batch TAN exchange capacities obtained for batch studies treating the same source of EIMWW. This reduction in capacity, 0.38 meq TAN/g in batch tests versus 0.24 meq TAN/g in column operation is significant, approximately 0.14 meq TAN/g reduction (or 58 %) of the batch capacity. While it is common when treating complex solution for column saturation capacities to plateau and slowly increase in capacity over a large amount of time, this represents a rather substantial loss in performance comparatively to the batch exchange capacities. It is possible that this was due to a drastic reduction in contact times; the batch tests had a contact time of 24 hrs, whereas lab-scale column tests generally have a contact time ranging 1.5-7.5 minutes (Crittenden et al. 2012). The column in these experiments featured a contact time of 1.6 minutes. The differences between the two types of tests are more likely explained by the nature of the tests. During the batch tests there was a limited mass of the stronger sorbing species (i.e., K^+) which limited the extent of the reduction in the exchange capacity exhibited for TAN, while in the column system, the feed continuously introduces additional mass of the stronger sorbing species and resulted in even greater competitive exchange and ultimately a reduction in the TAN capacity.

The electrical conductivity was measured at several intervals. A fluctuation was noted between the 5 BV's and 20 BV's mark which could initially represent a loss of electrical neutrality.

When comparing to the capacities, there is no noticeable effect which seems to correlate with this fluctuation. Therefore, the spike in EC could be from the residual regenerant that was not completely eluded during the backwashing with distilled water. After treating 20 BV's the EC stabilized at approximately 2.50 mS/cm which was comparable to the influent reading of 2.55 mS/cm. This was attributed to the variability of equipment and therefore electroneutrality was maintained.

The column was regenerated several times with a 10 % NaCl solution and the experiment was repeated with EIMWW and an effluent breakthrough concentration criterion of 0.55 meq TAN/L (10 mg TAN/L). This was followed by another regeneration and repletion using a single csolute TAN synthetic wastewater solution. This breakthrough concentration was selected as it is a potential effluent discharge criterion. The results of which are presented in Figure 5-9 where the effluent TAN concentration versus treated bed volumes are compared for both wastewaters allowing to determine the extent to which competing ions affect the exchange process. It is important to note that the synthetic wastewater consisted of a single-solute TAN solution.

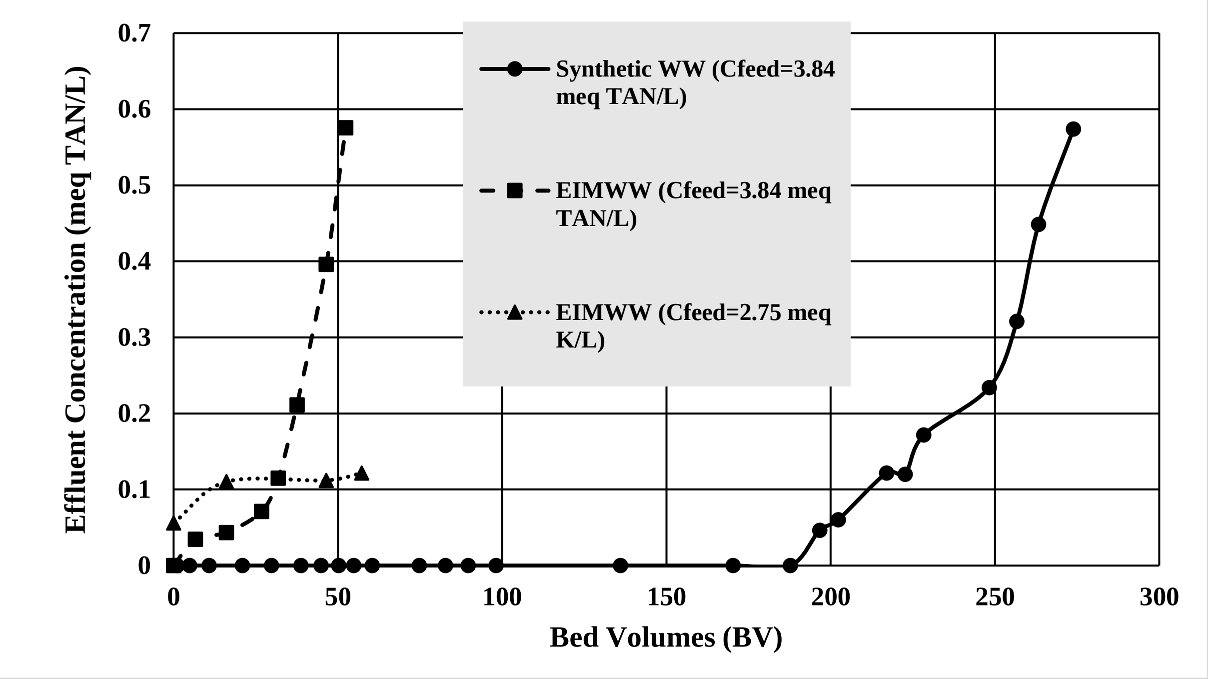

Figure 5-9. SIR-600 Column Effluent TAN Concentration Versus Treated Bed Volumes for 10 mg TAN/L Breakthrough

The presence of competing ions resulted in a large impact on the TAN uptake capacity. TAN breakthrough when treating the EIMWW occurred after 50 BV's, whereas the synthetic single component wastewater breakthrough was observed after 274 BV's. When treating the EIMWW the column's IE material was only able to treat 18 % of the volume of wastewater treated for the single solute TAN solution. This would incur the necessity for more frequent regenerations. The implications of such include increase in chemical costs, loss of treatment time due to regeneration and higher water consumption from regeneration processes. These results demonstrate that the feasibility of TAN ion exchange applications need to be assessed with the wastewater in question and not a single solute TAN solution.

Furthermore, during the breakthrough column experiment treating the EIMWW the 0.55 meq TAN/L breakthrough occurred later than in the initial run, approximately 20 BV (Figure 5-7) as opposed to the 50 BV's shown in Figure 5-9. The lower quantity of BV's treated prior to breakthrough is attributed to the lack of several regeneration cycles performed in between these two experiments which resulted in a conditioning effect on the IE material, thus increasing the effective exchange capacity. There were no noticeable changes in conductivity for the 0.55 meq TAN/L breakthrough runs. Figure 5-10 compares the capacities obtained for both the single component synthetic wastewater and the second EIMWW run during the 0.55 meq TAN/L breakthrough experiments. When the TAN capacities were considered during the first 50 BV's, the synthetic wastewaters capacities were nearly identical to the EIMWW TAN capacities.

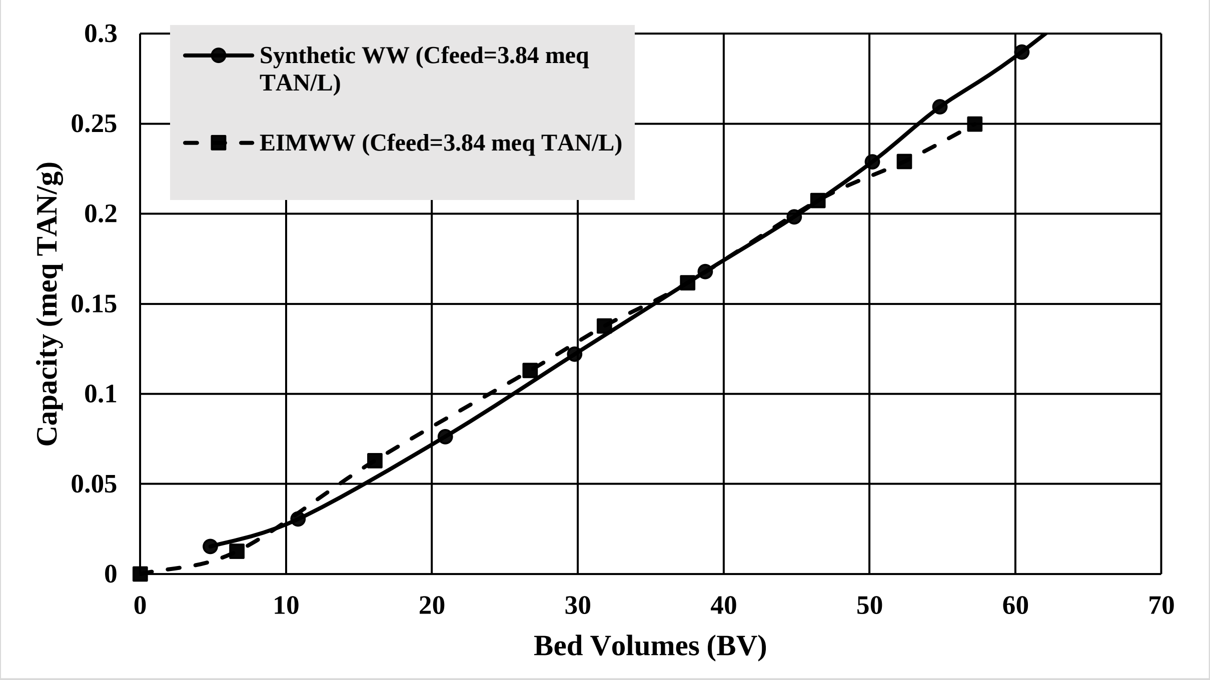

Figure 5-10. SIR-600 Column Breakthrough Capacities for 0.55meq TAN/L Breakthrough

Referring to Figure 5-10, in the treatment of the synthetic solution, TAN was undetectable until approximately 187 BV's whereas when treating the EIMWW breakthrough concentration was attained after 50 BV's. This reduction was, as previously mentioned attributed to competition, but as the TAN exchange capacities are identical up until 50 BV's, this indicated that the impact of competition had not yet taken effect. It was believed that exchange capacity for potassium was higher than that of TAN, resulting in the potassium adsorption front within the IE bed to trail behind the TAN adsorption front. This could be due to the lower influent K^+ concentration (~26 %) which resulted slower relative loading rates. The effluent potassium concentration demonstrated in Figure 5-9 remained minimal at approximately 0.1 meq K^+/L indicating effective potassium adsorption. Furthermore, referring to Figure 5-7, it would seem that the potassium adsorption front reached the same point in the column as the TAN front at approximately 30 BV's. At this point an increase in potassium and TAN effluent concentration was observed, where the potassium begun competing with TAN for exchange sites and TAN was desorbed. This increase in concentration presented in Figure 5-7 was 1.17 meq/L for TAN whereas the potassium increase was 0.47 meq/L, slightly less than half of the TAN increase, further indicating that the potassium front had reached the TAN front and begun removing TAN from exchange sites at a nearly 1:1 ratio thus beginning the effects of competitive adsorption. Following this increase both concentrations increased at a similar pace.

The TAN exchange capacity of the SIR-600 when treating the synthetic TAN wastewater reached 1.19 meq TAN/g at a breakthrough concentration of 0.55 meq TAN/L. This was 81 % higher than the 0.24 meq TAN/g breakthrough capacity measured for the EIMWW. The potassium and calcium capacities were respectively 0.21 meq K^+/g and 0.17 meq Ca^{2+}/g for the final loading run. Thus, the column's K^+ capacity at the breakthrough (i.e., non-saturation) was 23 % higher than that of TAN, while for the batch tests for the same sorbent-regenerant combination the K^+ capacity was only 11.3 % higher. This suggests that the dynamic conditions in the column further favour the exchange of K over TAN. The summation of all three species was a total of 0.62 meq /g, approximately half of the total measured capacity for the synthetic wastewater, however the higher value for the synthetic wastewater was likely due to the significantly longer column run which permitted greater degree of saturation. Finally, once the EIMWW reached breakthrough, the effluent pH was 6.14 and thus the concentration of unionized ammonia was 0.007 mg TAN/L, which is lower than the required effluent required by the CCME (Environment Canada 2010).

5.4 Conclusion

Two zeolites, a natural clinoptilolite and a modified clinoptilolite (SIR-600) were evaluated for their regenerative abilities and long-term performance when removing TAN from an explosive impacted mining wastewater using batch adsorption/regeneration/adsorption experiments. Both regenerants containing KCl featured lower TAN uptake capacities compared to the NaCl regenerants for both zeolites. The 5 % NaCl and 10 % NaCl regenerants had higher TAN exchange capacities than the 2.5 % NaCl regenerant for both IE media. The natural clinoptilolite's TAN exchange capacities for these regenerants were 0.33±0.03 and 0.36±0.05 meq TAN/g respectively, while for the SIR-600 regenerated with 5 % NaCl and 10 % NaCl solutions had higher TAN capacities (0.42 ± 0.02 and 0.47 ± 0.02 meq TAN/g, respectively).

The SIR-600 media was used in continuous flow bench-scale column tests to compare the impact of competitive adsorption in a dynamic system. In all the tests TAN broke through before potassium indicating that the media had a higher selectivity for potassium, and the TAN and K^+

loadings at the selected breakthrough level indicate a higher preference for K^+ over TAN than indicated in initial batch experiments. When the column treated EIMWW, TAN exhaustion occurred after approximately 90 BV's with an ultimate capacity of 0.24 meq TAN/g, which is less than the 0.38 meq TAN/g obtained in batch tests using the same wastewater. For the EIMWW, the column effluent reached TAN breakthrough after approximately 50 bed volumes whereas the synthetic wastewater did not reach breakthrough until 274 bed volumes. Prior to breakthrough the SIR-600 had nearly identical TAN exchange capacities for both wastewaters, which suggests that competition from various ions, namely potassium and calcium had not taken effect and would only become prominent if the column was operated for a longer duration. This indicated that potassium exchange is higher than TAN resulting in a slower adsorption front and the increase in concentration around breakthrough was caused by the adsorption front catching up. Finally, it was determined that an IE system can successfully treat the EIMWW to meet the effluent NH_3 concentration set by the CCME

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Chapter 6: General Summary, Synthesis and Integration of Results

The feasibility of selective ion-exchange (IE) removal of total ammonia nitrogen (TAN) in a complex blend of real explosive impacted mining wastewater (EIMWW) was investigated. The main competing cations were potassium and calcium. This was accomplished through three main phases. The first phase investigated the batch TAN exchange capacities of five materials (three synthetic resins, one natural clinoptilolite and one modified clinoptilolite) using both a single-solute (synthetic) TAN solution and the real EIMWW. The second phase focused on the regeneration of the natural clinoptilolite and the modified clinoptilolite (SIR-600) with solutions containing various concentrations of KCl and NaCl salts acting as regenerants. Finally, the third phase consisted of continuous flow column tests with the SIR-600 modified zeolite and compared the TAN exchange capacities for a single-solute TAN solution and the EIMWW. The main conclusions are broken down by relevant article and are as follows:

6.1 Assessment of Ion-Exchange Process and Impact of Competing Ions on Removal of Ammonia from Explosive Impacted Mining Wastewater

a) The batch loading tests showed that the two zeolites (clinoptilolite natural zeolite and Resintech SIR-600 modified clinoptilolite) were superior to the synthetic ion exchange resins as they had higher capacities for TAN removal. For an equilibrium concentration of approximately 3.5 meq TAN/L the natural and modified clinoptilolite had respective TAN capacities of 0.32 meq TAN/g and 0.42 meq TAN/g versus ~0.24 meq TAN/g for the Purolite, Amberlite and Bojie synthetic resins. Furthermore, the TAN IE capacity of both zeolites was less impacted by the presence of the competing ions.

b) The Freundlich and Langmuir isotherms were used in an effort to model the experimental data and in all cases the Freundlich isotherms provided better fits (all R^2 values above 0.97).

c) Relative separation factors were calculated to compare separation of TAN versus K^+ as well as TAN versus Ca^{2+}. In all cases, for the synthetic resins the α_K^{TAN} were well below 1 (0.45, 0.53 and 0.42 for Purolite, Amberlite and Bojie respectively), indicating a larger preference for potassium. The α_K^{TAN} for both natural and modified clinoptilolite were strongly dosage dependent. The SIR-600 had a α_K^{TAN} of 1.63 and 2.95 for dosages of 0.1 g and 1.5 g respectively showing a preference for TAN.

6.2 Competitive Ion-Exchange of Ammonia from Mining Wastewater in the Presence of Ca and K: Implications of Batch Regeneration and Column Performance on Zeolite

a) The multiple cycles of loadings and regeneration tests for both natural and modified clinoptilolite showed that the multiple cycles led to the conditioning of the zeolites and resulted in larger TAN loadings than the initial batch loading tests that used IE media with no preconditioning.

b) The regeneration with the KCl solutions were not as effective as those with NaCl solutions. The best regenerations were obtained with a 10 % NaCl solution

c) The batch tests showed that in the treatment of EIMWW the zeolites had a slight preference for potassium over TAN, however in some cases the differences of the TAN and potassium loadings was not statistically significant.

d) The bench-scale continuous flow column tests with pre-conditioned SIR-600 media showed that under dynamic conditions of the tests and a 0.55 meq TAN/L effluent concentration, there was significant competition between potassium and TAN. In the treatment of EIMWW the column reached the TAN breakthrough concentration after approximately 50 bed volumes of EIMWW treated, while without competition, i.e. for the single-solute synthetic wastewater the column was able to treat 274 bed volumes. The level of competition was greater under dynamic conditions than that observed under batch tests.

6.3 Recommendations

Based on the research in this thesis, the following recommendations are made:

1. That all future experiments use preconditioned media.

2. Due to the greater degree of competition, future research focus on column experiments.

3. This research should focus of running more loading and regeneration cycles to better study the long-term performances of the process.

4. In some of the batch loading/regeneration/reloading tests some media/regeneration solutions combinations showed slightly lower preference for potassium. Column tests showed be performed for these media/regeneration solutions.

5. Other synthetic zeolites such as zeolite X and Y or Faujasite should be evaluated for TAN removal in the EIMWW.