THE APPLICATION OF HIGH CAPACITY ION EXCHANGE ADSORBENT MATERIAL, SYNTHESIZED FROM FLY ASH AND ACID MINE DRAINAGE, FOR THE REMOVAL OF HEAVY AND TRACE METALS FROM SECONDARY CO-DISPOSED PROCESS WATERS

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KEYWORDS

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Major and trace metals
Energy of hydration
Effective charge of zeolite surface
In South Africa, being the second largest global coal exporter, coal mining plays a pivotal role in the growth of our economy, as well as supplying our nation’s ever increasing electricity needs; while also accounting for more than 10% of the $20 \times 10^9$ m$^3$ water used annually in the country. Coal mining may thus be classified as a large-scale water user; known to inevitably generate wastewater [acid mine drainage (AMD)] and other waste material, including fly ash (FA).

Current and conventional AMD treatment technologies include precipitation–aggregation (coagulation/flocculation) – settling as hydroxides or insoluble salts. The process stream resulting from these precipitation processes is still highly saline, therefore has to undergo secondary treatment. The best available desalination techniques include reverse osmosis (RO), electro dialysis (ED), ion exchange and evaporation. All available treatment methods associated with raw AMD and its derived process stream fall prey to numerous drawbacks. The result is that treatment is just as costly as the actual coal extraction. In addition, remediation only slows the problem down, while also having a short lifespan.

Research conducted into converting fly ash, an otherwise waste material, into a marketable commodity has shown that direct mixing of known ratios of FA with AMD to a pre-determined pH, serves a dual purpose: the two wastes (AMD and FA) could be neutralized and produced a much cleaner water (secondary co-disposal [FA/AMD]-process water), broadly comparable to the process water derived from precipitation-aggregation treated AMD. The collected post process solid residues on the other hand, could be used for production of high capacity ion exchange material (e.g. zeolite A, faujasite, zeolite P, etc.). The produced ion exchange material can subsequently be utilized for the attenuation of metal species in neutralized FA/AMD-process waters.

The aim of this research investigation was to study the potential application of high quality zeolitic adsorbents, prepared by post process synthesis of FA/AMD-solid
residues (collected at circum-neutral pH, from the neutralization reaction of South African fly ash and acid mine drainage), for the decontamination of process waters; with respect to the immobilization of metal species from solution. The zeolitization method was based on hydrothermal activation of the post process solid residues (source of aluminum and silicon) with NaOH.

Experimental design methodology was focused on identifying the influential parameters, and evaluating the interactions occurring between the active zeolite functional groups and aqua-metal cations. The overall goal was to understand the processes governing the solid/solution interface. The protocol involved the use of model solutions, consisting of selected heavy metals (Ba$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Al$^{3+}$ and Fe$^{3+}$), which was subjected to batch type experiments in a jacketed temperature controlled water bath shaker. Several influencing factors were investigated, including solid/solution ratio; agitation period; temperature variation (20 – 40°C); solute concentration variation and presence of competing ions (Ca$^{2+}$ and/or Mg$^{2+}$).

The metal uptake onto the zeolite phase was calculated. The distribution coefficients (K_D) were determined for the sorption system as a function of temperature and solute concentrations. The thermodynamic parameter, ΔG° for metal sorption on the synthesized zeolite was also determined from the temperature dependence. A considerable pH rise upon zeolite addition was anticipated – which could affect the mechanism of metal binding by changing it from ion exchange to adsorption of monovalent hydroxo-species. Thus another novel aspect of the proposed process lay in the possible application of these types of zeolites for the removal of anion forming metals (e.g. AsO$_4^{2-}$) from solution. In addition, zeolite behavior with respect to trace metal cation removal was also studied. Trace and anionic metal removal investigations were conducted in batch mode with artificially polluted model solution in which arsenic (As), mercury (Hg), selenium (Se), boron (B) and molybdenum (Mo) were chosen as target metal ions.
Aiming at substantiating the advantage of the synthesized zeolites over expensive commercially obtained ones and synthetic organic exchange resins (Lewatit TP 207- chelating resin for heavy metal removal) in terms of alternative low cost sorbent systems, experiments were conducted to compare metal removal capacity and selectivity. The prepared zeolitic material was also reacted with process waters with varying pH’s (3.00; 8.10 and 12.43), obtained directly from the collected filtrates of the reaction of FA with AMD in a ratio of 1:3.5 (FA:AMD).

The results showed that FA/AMD-related solid residues were transformed into near homoionic state Na-form zeolite, containing a high proportion of crystalline faujasite phases and a fraction of hydroxysodalite also present. Decontamination tests showed that the uptake of heavy metals with the synthesized zeolitic material consists mainly of different ion exchange processes and adsorption, accompanied by precipitation, particularly at high initial metal ion concentrations. The major parameters found to influence metal retention include metal ion hydration, solution matrix, space requirements in the zeolite micropores and the strength of metal-framework oxygen bonds. Selectivity series deduced from equilibrium isotherms and distribution coefficient is $\text{Ba}^{2+} \geq \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Cu}^{2+} \geq \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}$.

A drastic increase in acidity value (pH) upon zeolite addition was caused by simultaneous uptake of hydrogen ions by the zeolite and zeolite hydrolysis (dissolution). Optimum period for the system to reach equilibrium was shown to be 60 minutes. Temperature elevation had a consequent increase in metal uptake, the overall process being spontaneous. Sorption of $\text{Sr}^{2+}$ was severely hindered in the presence of competing ion, $\text{Ca}^{2+}$; while sorption of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ was adversely affected by the presence of both $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$. Anion forming species were immobilized through binuclear complex formation on the zeolite surface and other complex formation
mechanisms. Through such mechanisms, arsenic was removed to below the proposed MCL for potable water.

The synthesized high capacity inorganic ion exchange material proved to be more effective in terms of metal removal than selective metal binding resin; while also having similar capacity as its commercial counterpart.

The ion exchange material showed a considerable selectivity for the priority contaminant, mercury and as such this ion was removed to levels below WHO’s proposed MCL.

It was found that the operating capacity of the synthesized ion exchange material far exceeds its cation exchange capacity.
I declare that *The Application of High Capacity Ion Exchange Adsorbent Material, Synthesized from Fly Ash and Acid Mine Drainage, for the Removal of Heavy and Trace Metal from Secondary Co-Disposal Process Waters* is my own work, that it has not been submitted before for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated or acknowledged as complete references.
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Glossary of Terms

Acronyms and Abbreviations

Al     Aluminum
AMD    Acid Mine Drainage
Ba     Barium
CEC    Cation exchange capacity
DVB    Di-Vinyl-Benzene
DWAF   Department of Water Affairs and Forestry
°C     Degrees celcius
EC     Electrical conductivity
EDR    Electrodialysis Reversal
Fe     Iron (Ferric/ferrous)
HCl    Hydrochloric acid
HCIM   High capacity inorganic ion exchange material
HDPE   High density polyethylene
K_D    Distribution coefficient
C_i    Initial metal concentration
kl     kilolitre
kV     Kilovolts
LOI    Loss on ignition
mA     Milli ampere
meq g⁻¹  Milliequivalents per gram
meq kg⁻¹  Milliequivalents per kilogram
mgL⁻¹  Milligrams per Liter
μm     Micrometer
mL     Milliliter
mmol g⁻¹  Millimol per gram
Mn     Manganese
Mo     Molybdinum
mS/cm  Millisemens per centimeter
ppm    Part per million
q_e    Metal uptake
Rh     Ruthenium
RO     Reverse Osmosis
C_e    Solution phase at equilibrium
SAMD   Synthetic acid mine drainage
Sr     Strontium
TDS    Total dissolved solids.
Glossary of Terms

Acidity

The acidity is the capacity of water to give (or donate) protons ($H^+$).

Alkalinity

The capacity of water to accept protons. Solids, including minerals, contribute to the long-term acidity or alkalinity of water via such reactions as ion exchange of protons and weathering (dissolution).

Amorphous solid

It is a solid that has a disordered structure; it lacks the well defined arrangement of basic units (atoms, molecules, or ions) found in a crystal.

Amphoteric

A general term referring to a species that can act as an acid and a base. The species need not to be amhiprotic.

Coagulants

Reduce the net electrical repulsive forces at particle surfaces, thereby promoting consolidation of small particles into larger ones and a such enhances the settling process.

Crystalline solid

Is a solid composed of one or more crystals; each crystal has a well defined ordered structure.

Desalination
Glossary of Terms

The removal of dissolved inorganic solids from a solution (e.g., water) to make it free of dissolved salts.

**Electrolyte**

A substance which dissociates free ions when dissolved (or molten) to produce an electrically conductive medium. Electrolytes generally exists as acids, bases or salts.

**Flocculation**

Aids the clarification by promoting the formation of flocs which settle more rapidly. The primary purpose of flocculation is to agglomerate the finer particles and enhance settling in order to obtain a clear secondary process effluent. The agglomeration is achieved by bridging the space between particles, through a process whereby segments of a polymer chain absorb suspended particles, thus creating larger ones.

**Hardness**

A characteristic of natural water due to the presence of dissolved magnesium and calcium. Hardness is usually expressed in terms of grains per gallon, parts per million, or milligrams per litre, all as calcium carbonate equivalent. Water hardness is responsible for most scale formation in pipes and water heaters, and forms insoluble when reacted with soaps.

**Isoelectric point**

The point at which a mineral surface charge changes sign is called the zero point of charge (ZPC). If a surface charge changes its net surface charge from positive to negative solely because of adsorption of $\text{H}^+$ or $\text{OH}^-$ ions, the pH of charge reversal is called the *isoelectric point* (IEP) or also called the point of zero net proton charge (PZNPC).
Le Chatelier’s Principle

When a system in equilibrium is disturbed by a change of temperature, pressure, or concentration variable, the system shifts in equilibrium composition in the way that tends to counteract this change variable.

Mass action Law

It is a relation that states that the values of the equilibrium-constant expression $K_c$, are constant for a particular reaction at a given temperature, whatever equilibrium concentrations are substituted.

Oxidation

The process of introducing oxygen to a compound, resulting in the loss of electrons from the atoms and as such oxidizing the relevant contaminants to a less soluble state.

pH (potential of hydrogen)

An expression of the acidity of a solution; the negative logarithm of the hydrogen ion concentration. pH is a measure of intensity and not capacity, for example, one will be able to measure how acidic or basic a solution is. It is the logarithm of the reciprocal of the hydrogen ion concentration of a solution. At the neutral point, 7, the presence of equal concentrations of free hydrogen and free hydroxide ions are indicated.

Total dissolved solids

The weight of solids in true solution per unit volume of water. An electrical conductivity test only provides an estimate of the TDS since non-conductive substances cannot be measured electrically. TDS is expressed as mg/L per unit volume of water.
Zeolite Dissolution (Hydrolysis)

A chemical property of zeolites which corresponds to the detachment of framework Al─O─Si bonds according to their amphoteric behavior in the acidic or alkaline solution.
CHAPTER 1

General Introduction

Every drop of water has a message:
“Look after me and I will look after you. People that treat me well will prosper
and are healthy: civilizations that treat me poorly crumble and disappear!”

1.1 Introduction

This thesis describes the application of FA/AMD-related zeolitic material;
synthesized from post process solid residues, collected from the neutralization
reaction between fly ash and acid mine drainage; for the attenuation of heavy and
trace metals in process waters.

Chapter 1 gives a comprehensive but brief overview on all the aspects of relevance
for the significance of the proposed study. These include the water scarcity in South
Africa, the two main pollution aspects associated with coal mining, as well as major
drawbacks of all available AMD/process-water treatment methods and the importance of alternative materials for wastewater treatment (particularly fly ash).

1.2 The global water compartments

Water is a critically important resource. It is essential for human survival, agriculture and food production, as well as manufacturing, mining and industry.

It has been estimated that approximately 97.6 percent of the water at the earth’s surface is contained in oceans, with a salt concentration so high that it cannot be utilized for human consumption. The following table gives an outline of the water availability on the earth in terms of percentages:

Table 1.1: The globe’s water compartments: water availability

<table>
<thead>
<tr>
<th>Water Compartments</th>
<th>Total % Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>100</td>
</tr>
<tr>
<td>Ocean</td>
<td>97.6</td>
</tr>
<tr>
<td>Ice and Snow</td>
<td>2.07</td>
</tr>
<tr>
<td>Groundwater down to 1km</td>
<td>0.28</td>
</tr>
<tr>
<td>Lakes and Reservoirs</td>
<td>0.009</td>
</tr>
<tr>
<td>Saline Lakes</td>
<td>0.007</td>
</tr>
<tr>
<td>Soil Moisture</td>
<td>0.005</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>0.001</td>
</tr>
<tr>
<td>Swamps and Marshes</td>
<td>0.003</td>
</tr>
<tr>
<td>Rivers and Streams</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
South Africa in particular, suffer from several critical challenges with respect to water\textsuperscript{[2]}: 

The first aspect, is that our country is a water scarce continent: In 1997, for example, the water resources per capita in Zambia were 12 000 kl and 10 000 kl in the USA., while South Africa had only 1050 kl. Secondly, some areas (e.g. the east coast) receive abundant rainfall, while much of the country is arid or semi-arid. This results in an uneven spreading of the water resources across the country and as such, the nation suffers from hydrological extremes. Thirdly, the groundwater resources are not abundant, resulting in the water requirements far exceeding the natural availability of water in several catchments.

At current consumption levels the available water resources across the country will not meet projected demands within the next 30 years\textsuperscript{[2]}. One such area in South Africa, which inevitably gives rise to highly polluted waste waters, is the coal mining industry.

1.3 Coal mining in South Africa: Electricity supply

In South Africa, the mining sector contributes between 20 and 30 percent of the country’s mineral sales, and our country is the second largest coal exporter in the world\textsuperscript{[3]}.
An area, which is by and large based on coal mining in particular, is the electricity supply sector.

Supplying electricity plays a pivotal role in South Africa, in which it makes up 25 per cent of final energy demand in the country’s economy [3]. South Africa’s generating technology is by large based on coal fired power stations, with about a million tons of coal finding it’s way into South African homes. These homes are particularly those in the “Highveld” area, including regions such as the high plateau of Gauteng, the Free State and Mpumulanga, where most of the countries mining activities takes place [3].

According to the Department of Water Affairs and Forestry (DWAF), mining and power generation accounts for more than 10% of the total of $20 \times 10^9 \text{ m}^3$ water used annually in South Africa [4]. The main heavy metal-laden waste which emanates directly from coal mining operations, even decades after the decommissioning of a mine, is acid mine drainage (AMD) and since mining sites are usually close to natural streams, thousands of kilometres may be affected and as such, toxic metal pollutants are bound to enter our waterways [5].

Given the fact that the mining industry gives rise to huge amounts of waste effluents, like AMD, which causes decades of water pollution, as well knowing that our country is generally a water scarce continent with predictions of a continent wide water crisis for the year 2025 [2, 6] and adding to that, the unfortunate fact that 97.6% of our
globe’s water cannot be utilized, it becomes painfully obvious that we desperately need to preserve our water.

The other major by-product emanating from the process of coal combustion, is fly ash, which is in fact a world wide problem, with an estimated global production of 200 million tons per year \[^7\].

1.4 Fly Ash

Generally, fly ash is an agglomerate of microspheres, up to hundreds of μm in diameter. These microspheres are mainly composed of Si and Al with minor amounts of Fe, Na, K, Ca, P, Ti and S. The major mineral compounds include amorphous aluminosilicate glass and in addition, other crystalline phases such as mullite, hematite, magnetite, lime anhydride and feldspars are also present \[^8\]. Although a percentage of fly ash is constructively utilized, there is still a significant amount which needs to be disposed of and are subsequently stored in what is called “ash dams” and this type of storage has a huge land requirement \[^9\]. The other major problem is that fly ash particles are considered to be highly contaminating, since their high surface area leads to enrichment in potentially toxic trace elements which condense during the cooling of the combustion gases \[^8\].
Considering the preceding fact, as well as bearing in mind that large landscapes becomes unusable due to fly ash waste storage, it clearly spells out the urgent need for innovative technologies to promote alternative fly ash utilization.

Considering that the components in fly ash are Al and Si compounds, as well as the fact that they contain numerous mineral phases; which are known as being effective adsorbents for metal species from wastewaters\(^\text{[10]}\), scientists were prompted to utilize its properties for the attenuation of metal species in metal-laden wastewaters; which can, depending upon solution pH, be used for cation as well as anion removal, due to the change in charge of surface functional groups in relation to the change in solution pH\(^\text{[11]}\).

The use of fly ash for the synthesis and application of high capacity ion exchange materials, such as zeolites, were also quite extensively explored; based on the similarity of fly ash to certain volcanic material, which is the precursor of natural zeolites\(^\text{[12]}\).

1.5 **Acid mine drainage (AMD): A potential source of toxic metals**

Acid mine drainage is the most well documented type of water pollution associated with the mining industry, and has as yet not been solved\(^\text{[5]}\). It results from the accelerated oxidative dissolution of exposed minerals, principally sulfides, giving rise to acidic, metal-enriched waters generally referred to as AMD\(^\text{[13]}\).
The chemical environment in which AMD forms can briefly be described as follows:\textsuperscript{[13]}. Minerals such as pyrite (FeS\textsubscript{2}; the most abundant of all sulfide minerals) are chemically (and biologically) stable in oxygen and water deprived situations. However, upon exposure to both moisture and air, sulfide minerals will oxidize spontaneously, with either molecular oxygen or ferric iron [Fe(III)] acting as oxidant\textsuperscript{[13, 14]}. While sulfide mineral oxidation may be abiotic, the rate of reaction is greatly enhanced (by many orders of magnitude), in the presence of certain microorganisms (particularly Thiobacillus Ferrooxidans), especially in acidic conditions\textsuperscript{[13, 14]}. The acid produced from the oxidation processes consequently lowers the pH of the water, making it corrosive and unable to sustain normal aquatic life\textsuperscript{[13, 14, 15]}. In short, AMD can be described as a low pH, high acidity discharge which contains high levels of iron, aluminum, sulphates, and especially heavy metals, some of which are extremely toxic.

### 1.6 Treatment technologies for AMD and other metal-laden waste streams

Discharge from process and mine wastewater, including acid mine waters, typically contain pollutants, that cause harmful effects on receiving waters and adverse impacts on human health. Amongst these pollutants, are dissolved heavy metals, such as arsenic, mercury, etc. which can, depending on the chemical form and dosage, cause acute poisoning and subsequent death of humans, when exposed to them. The
fact that metals are non-biodegradable raises serious issues concerning their removal from potential sources.

To alleviate the problem of AMD, water quality standards have been implemented, which requires that mine discharges and other metal-laden waste streams be treated to meet certain requirements before it may be discharged \[4\].

Current and conventional schemes for treatment of raw AMD involve precipitation-aggregation (coagulation/flocculation) – settling as hydroxides \[5, 16\].

However, these treatment technologies fall prey to numerous disadvantages such as the following \[17 – 19\]:

- coating of reactive surfaces of the neutralizing agents (limestone/rock phosphate, etc.) with ferric hydroxide precipitates, inhibits its dissolution (armoring), consequently diminishing production of alkalinity and as such stops the neutralization reaction.
- the formation of metal hydroxides is ineffective at dilute metal-bearing effluents;
- the hydroxo precipitate tends to re-dissolve, depending on the metal, via the reaction:

\[
M(OH)_{n}^{x} + m(OH)^{-} \rightarrow M(OH)_{n+m}^{(x+m)}
\]

- the pH of minimum solubility of hydroxides is different for each of the various metals present; for example, the minimum solubility for cupric hydroxide occurs at approximately pH 9.5, while for cadmium hydroxide, it
occurs around 11, and as such to achieve maximum precipitation efficiencies of the metals, acid mine waters have to be treated in several stages, with huge concomitant capital and operating cost;

- precipitation of metals become incomplete when complexing or chelating agents are present;
- the volumes of sludge formed are too large and has a high water content; thus having to be subjected to dewatering processes and subsequent disposal into landfills, which adds to the operating cost of the overall process;
- filtration may be difficult as the result of the precipitate’s fineness;
- due to large treatment plants and huge requirement of reagents and chemicals, it becomes a very costly treatment route.

The effluent derived from the primary treatment technologies, are referred to as the secondary process effluent and is normally very saline; typically still containing quantities of sulphate (over 250 mg L⁻¹), suspended metal solids (5 mg L⁻¹), as well as total dissolved metal-related solids in the region of approximately 500 mg L⁻¹ [15], which renders it undesirable for re-circulation to be utilized for industrial application and/or domestic use, or for discharge into natural waterways, therefore secondary treatment technologies are applied at this stage; collectively referred to as desalination [16] methods.
The current technologies used to desalinate secondary process effluents are evaporation, membrane technologies (e.g. reverse osmosis, electro dialysis etc), electrochemical treatment technologies, flotation and ion exchange \[^{16, 20}\].

The drawbacks of existing desalination units include extremely high operating costs, associated with increased energy consumption and high working pressures. The limited lifespan of membranes, coupled with the high probability of fouling necessitates regular replacement of units and thus adds to the capital and operation costs. In addition, the use of pH adjustment chemicals, as well as embedded cartridge filters to alleviate source water contamination, adds to the financial burden \[^{20, 21, 22}\].

Since it is now established that conventional treatments for raw AMD and its derived secondary process effluent, are quite expensive technologies which suffer from numerous disadvantages. This led scientists to a search for cheaper adsorbents which have metal-biding capacities and are able to remove dissolved and complexed metals from such contaminated waters \[^{25}\].

Fly ash is already established to posses these qualities, and being cheap as well as locally available \[^{11, 25}\], have prompted researchers to further explore its applicability in this area \[^{23, 24}\]. In South Africa in particular, this was explored through bench scale and pilot study investigations, in which the aim was firstly, to establish the neutralization capacity of fly ash for AMD \[^{26, 27, 28}\], a process known as the co-
disposal process and secondly, the application of the collected neutral solid process precipitates for the synthesis of high capacity ion exchange materials (HCIM) \[29, 30\].

These research investigations resulted in the following achievements:

- By co-disposing fly ash with AMD, two corrosive products, AMD and fly ash could be simultaneously neutralized and produced considerably cleaner water, which may be broadly comparable to the secondary process effluents derived from primary AMD treatment technologies.

- Moreover, by collecting the post process solid residues at a pre-determined pH, the successful synthesis of zeolitic products such as faujasite, sodalite or zeolite A was possible.

These synthesized zeolitic material may then be applied for the attenuation of major and trace metals from the secondary co-disposed process waters; a fact beneficial for the coal mining industry, since these waters are essentially comparable to secondary process effluents produced at mining treatment plants.

1.7 Refinement of research and research questions:

In the preceding sections, the present study was initiated by a familiarization of the major coal mining wastes and their available treatment methods, with special reference to their drawbacks. Relevant potential applications of fly ash was also
discussed. In reference to the major aspects outlined in those sections, the following conclusions and/or questions can be formulated:

- All known conventional treatment methods for AMD and its derived process effluent fall prey to serious drawbacks.
- From an economical perspective, the costs associated with these disadvantages are not low enough to compete with the resultant decontaminated effluents.
- In terms of the water aspect of environmental impacts, corrosiveness and subsequent inability to sustain aquatic life has the resultant effect that humanity is always at risk of toxication and subsequent death.
- The other environmental issue is land requirement for fly ash storage, as well as pollution associated with leaching from ash heaps.
- Search for potentially cost effective ion exchange materials have lead to the constructive utilization of AMD and fly ash resulting in their subsequent alleviation, while also meeting stringent effluent standards in terms of the resultant process waters.

Thus considering the preceding information which includes the drawbacks exerted by conventional AMD/secondary process effluent treatment technologies, as well as the discovery of potentially cost effective ion exchange materials; the basis of the current study was thus formed.
1.8 Objectives and sub-problems

The overall objective of this study was to investigate the feasibility of the application of low cost high capacity inorganic ion exchange material (HCIM), synthesized from collected FA/AMD-solid residues (precipitates), for the decontamination of secondary co-disposal process waters; with emphasis on investigating the processes governing the solid/solution interface. The HCIM synthesized and applied in the current study was a near-homoionic Na-faujasite type zeolitic material, synthesized from the FA/AMD-solid residue (co-disposal precipitate) collected from the neutralization of AMD with fly ash, based on the methodology described by V. Somerset [29].

The sub-problems investigated in achieving the overall objective included:

- The synthesis of a crystalline faujasite zeolite, which is broadly comparable to its commercial counterpart.
- Investigation of the zeolite/solution interface to attempt to understand the processes involved between the metal ions and the active zeolite functional groups.
- Zeolite/solution ratio: the optimum mass of zeolite per volume of effluent.
- The time variable (agitation period), to determine the optimum time for the system to reach equilibrium.
- Variation of temperature, to evaluate its effect on the extent of metal retention and zeolite selectivity.
• Equilibrium investigations (by varying initial metal concentration), to evaluate selectivity as well as the dominating reaction used for metal retention.

• Comparing the metal retention ability of the synthesized zeolite to its commercial counterpart (commercial faujasite, CBV 400) to evaluate the successfulness of the zeolitization process; while also comparing this alternative sorbent system to selected commercially obtained organic resin exchangers (Lewatit TP207) in an attempt to prove the cost effectiveness of the proposed system.

• The possible effects of the presence of competing ions, to observe how it influences metal removal.

1.8.1 Other novel objectives

Based on the inherit alkalinity, induced by the hydrothermal alkaline synthesis method, a considerable pH rise upon zeolite addition was anticipated — which would affect the mechanism of binding, by influencing metal speciation. The resultant effect of which could possibly be changing the mechanism of binding from ion exchange to adsorption of monovalent hydroxo-species. It is therefore hypothesized that the removal of anion forming species can also occur through the application of the proposed sorption system.
Therefore the possibility of the removal of selected anionic metal species from solution was also investigated.

### 1.8.2 Experimental Protocol

The protocol followed to execute the proposed research outline encompassed the use of model solutions, artificially polluted with selected heavy metals. However, the application of these zeolites on FA/AMD – process waters was also investigated to determine the performance of the zeolite in terms of consistency and capacity, with respect to varying matrixes and pH’s.

### 1.8 Other Considerations

Although metal-laden effluents, such as the ones described in this chapter is known to, in addition to containing dissolved metal species, also contain numerous other constituents; however, this thesis is focused only on the immobilization of dissolved metals. The reasoning behind this, is that metal ions is known to form numerous complexing species with other contaminants, so in effect, alleviating the metal species from solution will result in the reduction of the potential presence of other contaminants.
It is hoped that this thesis will provide a contribution to the understanding of the physical, chemical, electrostatic and other interactions which occurs between the synthesized ion exchange material and metal-laden wastewaters. Moreover, it is hoped that the overall significance of this study will illustrate the importance of considering the application of these alternative sorption systems in the search for cost effective methods of water purification systems; particularly in the industrial sector.

1.9 Layout of the Thesis

The rest of the thesis is divided into the following chapters:

Chapter 2 A thorough and concise review of literature surrounding the sciences of coal minerals, coal fly ash, acid mine drainage, the neutralization of acid mine drainage, desalination of process streams, and zeolites as adsorbent material is presented. Main points are then interlinked in a brief conclusion section.

Chapter 3 This chapter provides insight on the specific variables which needs to be considered in this study. The purpose is thus to form a foundation for the experimental methods of investigation, specifically in terms of the
decontamination aspect. Moreover, it serves as an introduction to the correct interpretation of the attained results.

Chapter 4  The sample preparation procedure for the FA plus AMD(FA/AMD)-solid residues and the synthesis of high capacity inorganic ion exchange materials (HCIM) are presented. A physical and chemical characterization of the prepared HCIM are also presented, using fundamental characterization tools such as X-ray Diffraction Spectrometry (XRD), X-ray Fluorescence Spectrometry (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Cation Exchange Capacity (CEC), and Nitrogen Brunauer-Emmett-Teller (N$_2$-BET) Surface Area determination. The detailed experimental protocol for the various decontamination experiments are also concisely described, while all necessary calculations are presented.

Chapter 5  In this chapter, the results for the analysis of the FA/AMD-solid residues, to assess its suitability for zeolite synthesis are presented. In addition, the presentation of the synthesized zeolitic materials are also presented in terms of a mineralogical, physical and chemical characterization perspective.
Chapter 6  An overview of the interactions between the ion exchange material and the metal ions are presented. The results for all decontamination experiments are also shown and extensively discussed.

Chapter 7  The conclusions for the study on the metal removal capacity of the ion exchange adsorbents are discussed and directions for future work are suggested.
CHAPTER 2

Literature Review

2.1. Introduction

The current chapter provides a comprehensive literature survey surrounding the issues described in chapter one, which includes the major mining by-products, fly ash and AMD; the conventional, current treatment technologies for AMD; desalination technologies for the treatment of the secondary process effluents derived from primary AMD treatments; the process of ion exchange, including inorganic and organic ion exchangers, also including zeolites and the synthesis of high capacity ion exchangers with fly ash and fly-ash related products.
2.2. Fly ash

Fly ash is the incombustible material matter which is left after all the organic components of the coal have been consumed during the process of coal combustion and is collected by means of mechanical electrostatic precipitators. The physical, chemical and mineralogical characteristics of fly ash depend on the parent coal source, the method of combustion, as well as the efficiency and type of emission control device \[31\].

2.2.1. Physical and mineralogical morphology of fly ash

Fly ash is composed of mainly silt-sized spherical amorphous ferro-aluminosilicate minerals and is generally characterized as having low permeability, low bulk density, as well as high specific surface area \[31\]. The ash particles generally ranges in size from 0.5 to 200 microns \[8, 31\]. Fly ash particles are mainly composed of:

- Silicon as SiO\(_2\)
- Aluminium, as Al\(_2\)O\(_3\)
- Iron as Fe\(_2\)O\(_3\)
- Calcium oxide
- TiO\(_2\)
- Mn\(_2\)O\(_3\),
combined in phases such as aluminosilicate glass, quarts, mullite, hematite, magnetite, ferrite, rutile, as well as various amounts of unburned carbon and approximately 20-50 trace elements \[^{8,32}\].

An equally important factor in fly ash, are the pozzolanic characteristics of the ash. A pozzolan is defined as a siliceous or siliceous and aluminous material which, on its own, exhibits little or no cementitious properties, but in the presence of moisture, reacts chemically with calcium hydroxide (CaOH), also referred to as lime, forming compounds exhibiting cementitious properties \[^{31}\]. Two major classes of fly ash can be distinguished, on the basis of their chemical composition. They are designated Class F and Class C \[^{7,31}\].

### 2.2.2. Fly ash chemistry

As discussed earlier, these characteristics depend on the parent coal source, including the combustion temperature at which the coal was fired, the air:fuel ratio, and rate of combustion, it seems appropriate therefore, to discuss the ABC’s of coal first.

#### 2.2.2.1. Coal: The origin of fly ash

Coal is an age old fossil fuel, which is converted to energy, to produce for example electricity. The formation and subsequent mineral matter contained in the coal depends on three different sources; vegetative, dentrital and chemical. Coal contains
i. inorganic elements, present in mineral phase within the coal,

ii. carbon,

iii. hydrogen,

iv. nitrogen,

v. oxygen

vi. and sulfur.

Four of the five non-metallic elements can be found in inorganic combinations within the coal seams. Carbon occurs with carbonates (Ca[Fe,Mg]CO₃); hydrogen in water of hydration and free water; oxygen in water, oxides, carbonates, sulphates and silicates; as well as sulfur in sulfates and sulfides, which is primarily pyrite and marcasite [31].

According to Sheets and Earl [31] the constituents of coal are as follows:

A. Mineral constituents:

i) *Clay minerals*

- Kaolinite ([OH]₈Si₄Al₄O₁₀)
- Illite ([OH]₄K₂[Si₈Al₂]Al₄O₂₀)

ii) *Sulfides:*

- Pyrite (FeS₂),
- Marcasite (FeS₂)
iii) Carbonates such as:

- Ankerite \((2\text{CaCO}_3\text{MgCO}_3\text{FeCO}_3)\),
- Calcite \((\text{CaCO}_3)\) and
- Sederite \((\text{FeCO}_3)\)

B. Quarts \((\text{SiO}_2)\):

The clay minerals make up approximately 60-90% of the total mineral matter, while quarts can comprise from 1 to 20% of the inorganic components found in coal. Also present in coal deposits are trace elements such as B, Cr, Cu, Mo, V, etc, which are concentrated in the coal during and following it's formation:

2.2.2.2 Occurrence and mobility of trace elements in coal and subsequent ash

Many trace elements can be enriched in coal, depending on the geochemical environment during coalification. The organic matter and inherent minerals can act as enrichment traps for numerous trace elements. During coal combustion in power stations, various physicochemical transformations takes place, which causes further enrichment of these elements in the formed ash, and subsequent dispersion of potentially toxic elements into the environment \(^{33,34}\). The degree of emission depends on the fuel quality and combustion technology. Trace elements can have:

a. Organic affinity:

- Elements associated with the organic coal matter OR
b. Mineral affinity:

- Elements associated with sulphides, aluminosilicates, carbonates and other minerals in coal.

From the investigations on trace element mobility conducted on coal \cite{34}, it showed that the affinities of trace elements control their mobility in coal and the following observations were found:

- Trace elements with major aluminosilicate affinities show the least mobility within the coal. These elements include Rb, Sb, Sn and Ta.

- Elements showing intermediate behaviour are those associated with a mixed aluminosilicate, organic and/or sulphide and/or sulphate affinity. These elements are Ba, Cd, Co, Cr, Cu, Ga, Ge, Li, Wi, Zr, as well as light rare earth elements.

- The elements showing high mobility (>70%) are those associated with sulphides, sulphates and organic matter. They include As, B, Mo, Se, Mn, Ni, Pb, Sr, U, V, Y and Zn. Amongst these B, Mo, As were found to have mobility higher than 90%.

During coal combustion, these elements are known to concentrate in the formed fly ash and thus varying mobility of elements can also be observed within the ash itself.
Elements showing lowest mobility in fly ash are those mainly associated with high temperature aluminosilicates, including Al, K, Mg, Na, Si, Cd, Pb, Sb, Ta, Tl, Zn, Zr and those associated with iron oxides: Fe, Co, Cu, Ni, Mn.

Mobile elements (30-70%) includes As, Se, Ca, P, Ge, U, V, W. These elements have partial or total affinities for different sulfates, oxides, aluminosilicates and possibly different salts such as borates and arsenates.

Elements showing the highest mobility (> 70%) includes S, B, and Mo and these elements are probably associated with easily leachable salts and oxides.

The trace element concentrations associated with fly ash is uniquely distributed within the structure:

- Certain elements are placed in the aluminosilicate matrix, including Ti, Na, K, Mg, Hf, Th and Fe.
- Others are more concentrated on the surface, such as As, Se, Mo, Zn, Cd, W, V, U.
- While some elements are situated in an acid soluble phase, and they include, Ca, Sc, Sr, La, rare earth elements and possibly Ni.
- Elements including Mn, Be, Cu, Co, Ga, Ba and Pb, though, find themselves distributed between the matrix and non-matrix material.

The occurrence, placement and mobility of trace elements in fly ash eventually plays a pivotal role in the subsequent synthesis and utilization of high capacity ion exchange materials in decontamination of process waters, and will be discussed in subsequent sections of this thesis \(^{[12]}\).
2.3 Acid mine drainage (AMD)

Acid mine drainage is an unintended, yet un-avoidable by-product of the mining and mineral industry. Its presence results in persistent environmental problems and is associated with both active, as well as abandoned sulphide and coal mine sites. This polluting stream is an issue of international concern and recent examples have been reported from various countries including, South Africa, China, South Korea, France, England, US.A., Spain, Tasmania, Ireland, Wales, etc [35, 36].

The following sections gives an overview of AMD with respect to its chemistry, environmental impact and treatment options.

2.3.1 Occurrence and description of AMD

AMD is a severely corrosive waste stream associated with coal and other sulfide-containing ore-mining operations. The excavation of mineral deposits (coal or metal-bearing), below the natural groundwater level, exposes these sulfur containing compounds to water and atmospheric influences, including oxygen and oxidizing bacteria, such as Thiobacillus Ferooxidans, which chemically reacts with these minerals, resulting in AMD [13-15].

According to Evangelou and Zhang [13], AMD is an extremely acidic discharge (with pH as low as 2), resulting primarily from oxidation of pyrite and other iron sulfides (FeS$_2$) in coal wastes, ore tailings and overburden, associated with mining operations
and is enriched with soluble iron, manganese, aluminum, sulfate, as well as heavy metals such as lead (Pb), mercury (Hg), Boron (B), etc.

Although AMD is normally characterized by a distinctly acidic nature, it can however, depending on the geology of the host rock and metal sulfide content, have a near neutral or slightly alkaline pH, since the presence of calcareous minerals (calcite and dolomite) can “buffer” the pH of the mine water, but whether neutral or acidic, the drainage from most coal or other mining operations has elevated concentrations of dissolved solids, ranging from approximately 200mg L\(^{-1}\) to greater than 10 000mg L\(^{-1}\), consequently virtually in all cases of AMD, the discharge will have highly polluting effects on receiving rivers and streams\[^{36}\].

The chemical environment which results in the formation of AMD is best described in terms of two parameters, oxidation potential (Eh); and acidity (pH) in which the solid phases of iron (Fe), carbon (C), and sulfur are the most important in terms of reactions involving the generation, as well as the neutralization of acid waters\[^{15}\].

### 2.3.2 Formation and chemistry of AMD

Among the major forms of sulphide minerals found in geologic strata, are the iron disulfide minerals, pyrite and marcasite, which both have the same chemical composition (FeS\(_2\)), but differ crystallographically. Through extensive research however, it has been found that pyrite is the most prevalent form present in coals\[^{13}\].
From an environmental perspective, the potential of a coal seam to produce AMD is controlled by a host of factors – the water table, its relation to land surface, the climate pattern, the hydrology pattern, as well as the geology of the area [37]. The factors determining the rate of pyrite oxidation on the other hand, includes pH, dissolved oxygen (O₂), specific surface and morphology of pyrite, as well as the presence or absence of Thiobacillus bacteria.

Thus, during AMD formation, pyrite is oxidized in the presence of oxygen, water and bacteria, forming soluble hydrous iron (ferrous and/or ferric) sulfates – subsequent complexation of the ferrous and ferric oxidation products dissolved in water, imparts the red and yellow colour, characteristic of AMD. The process of pyrite oxidation is complex, involving chemical, biological and electrochemical reactions; however, based on extensive studies by various researchers across the globe, the process was shown to be governed by four characteristic set of reactions [13-15, 37].

\[
\text{FeS}_2 (s) + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+ \quad (2.1)
\]

\[
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \quad (2.2)
\]

\[
\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 (s) + 3 \text{H}^+ \quad (2.3)
\]

\[
\text{FeS}_2 (s) + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (2.4)
\]
Initially, pyrite in coal seams reacts with atmospheric oxygen and water, during which it is oxidized, producing $\text{H}^+$, $\text{SO}_4^{2-}$ and $\text{Fe}^{2+}$ - illustrated by equation (2.1). The $\text{Fe}^{2+}$ (ferrous iron) produced can be further oxidized by $\text{O}_2$ into $\text{Fe}^{3+}$ (ferric iron); which in turn hydrolyses into iron hydroxide and releases additional amounts of acid into the environment – shown in equations (2.2) and (2.3), respectively. The acid production causes the pH in the vicinity of the pyrite to drop and when pH drops below 3.5, the activity of free $\text{Fe}^{3+}$ in solution increases, and oxidation of pyrite by $\text{Fe}^{3+}$ becomes the main mechanism for acid production. In equation (2.4), the role of $\text{Fe}^{3+}$ in the oxidation of pyrite is illustrated.

According to Singer and Stumm, $\text{Fe}^{3+}$ is the major pyrite oxidant in the acidic pH region, while $\text{O}_2$ is expected to be the direct pyrite oxidant at neutral to alkaline pH \cite{13}. The findings of Moses et al. and Moses and Herman on the other hand, was that $\text{Fe}^{3+}$ is an effective and direct pyrite oxidant at low, as well as circum-neutral pH and the role played by dissolved oxygen is to sustain the reaction – by regenerating $\text{Fe}^{3+}$ \cite{13}.

However, it was found by various investigators that at low pH, iron oxidizing bacteria, especially thiobacillus ferrooxidans, can effectively catalyse and accelerate the oxidation of $\text{Fe}^{2+}$ by a factor of greater than $10^6$. In the presence of thiobacillus ferrooxidans and under low pH conditions, pyrite oxidation can be described by reactions (2) and (4).
2.3.2.1  Role of bacteria in pyrite oxidation

The known bacteria that have been isolated from acid mine wastes of coal mines include the following [13, 14, 31, 37]:

- Thiobacillus ferrooxidans – a iron and sulphur oxidizing bacterium;
- Thiobacillus thiooxidans – a sulphur oxidizing bacterium and
- Ferrobacillus ferooxidans – an iron oxidizing bacterium

Due to limiting factors exhibited by Thiobacillus thiooxidans and Ferrobacillus ferooxidans, the most widely studied pyrite oxidizing bacterium, is Thiobacillus ferrooxidans. Thiobacillus ferooxidans is an acidophilic organism that is ubiquitous (ever-present) in pyrite-containing geologic environments and has an unusual ability to survive environmental stress. It can tolerate extreme pH conditions (i.e. 0.8 – 6.98), temperatures between 15 – 40 °C, as well as a Fe^{2+} concentration of up to 30 g/L. Research has established that this bacterium is able to oxidize Fe^{3+}, elemental sulfur (S\textsubscript{0}) and metal sulphides, as well as other reduced inorganic sulfur compounds. The major role of these bacteria, is to regenerate Fe^{3+}, which is the major pyrite oxidant [13, 14].

2.4  Treatment technologies for acid mine drainage

AMD resulting from both active and inactive mine sites usually do not meet the water quality standards which is necessary for the safe discharge and as such, first have to be treated to meet these standards. These polluting streams are enriched with
a host of undesirable species, including soluble iron (present as Fe$^{2+}$ or Fe$^{3+}$), manganese (Mn$^{2+}$), aluminum (Al$^{3+}$), sulfates, chlorides, phosphates, as well as other heavy metals, such as lead (Pb), mercury (Hg), and oxyanions (e.g. CrO$_4^{2-}$, AsO$_3^-$ etc.), therefore conventional and current treatment technologies consist of a series of integrated steps, either used consecutively or in combination with each other, which are based on several key methods \cite{38, 39}.

AMD contains multiple combinations of acidity and metals, therefore each AMD discharge tends to be highly variable and as such requires tailored treatment. The best choice among the available treatment technologies depends on both technical as well as economic factors.

The technical factors include the following:

- acidity levels;
- effluent volume;
- type and concentration of contaminants present;
- and desired final water quality

While the economic factors are based on the following:

- prices of reagents;
- labour;
- machinery and equipment;
- the number of years needed for treatment;
- and risk factors
Current and conventional schemes for treatment of raw AMD, involve neutralization by addition of alkaline chemicals; while other chemicals used sparingly in AMD treatment includes flocculants and coagulants, as well as a process referred to as aeration (usually combined with chemical oxidants) which may also be effectively used to enhance particle settling efficiency.

2.4.1 Current active neutralization processes of acid mine drainage

Conventional, active AMD treatment schemes by and large requires the installation of actively working plants, basically consisting of agitated reactors, precipitators, clarifiers and thickeners, etc., which is quite a costly operation due to the cost of reagents, operation, maintenance, labor and disposal of metal laden sludge [5].

Among the alkaline materials used to neutralize raw AMD are:

- limestone;
- lime (including hydrated lime[Ca(OH)₂], pebble quick lime[CaO] and dolomitic lime);
- sodium hydroxide (caustic soda [NaOH]);
- sodium carbonate (soda ash [Na₂CO₃]);
- ammonia (NH₃ or NH₄OH);
- potassium hydroxide;
- and/or magnesium hydroxide (MgOH).
However traditionally, the most common method of AMD neutralization is based on limestone and/or lime treatment \[5, 13, 15\].

### 2.4.1.1 AMD treatment with limestone

Traditionally, limestone is perceived as one of the more suitable materials used for the neutralization of acid mine drainage due to a number of advantages \[39\]. These advantages include the material’s ready availability in large quantities, its considerable cost advantage over other alkaline materials, including the fact that limestone addition does not add harmful constituents to the water, as well as the fact that these carbonate-rich rocks require no preparation other than sizing – subsequently adding to its inexpensive nature.

The limestone is transported to the AMD source and added to the mine effluent in crushed form or the acid water can be pumped into nearby wells containing the carbonate rocks.

Upon contact between the limestone and the acid mine waters, \( \text{Ca}^{2+} \) ions are released and as such, alkalinity is added to the system, bringing about a subsequent pH rise. The overall effect of the added alkalinity is the neutralization of the AMD.

The limestone neutralization process is governed by three important processes, represented by the following equations:

\[
\begin{align*}
\text{H}^+ + \text{CaCO}_3 & \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}^+ & \rightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightarrow \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]  

(2.5)  

(2.6)  

(2.7)
Reactions (2.6) and (2.7) are indicative of the reactions which takes place upon contact between the acid mine waters and the limestone and these reactions only proceed at pH level of less than 6.4. Reaction (2.5), however, proceeds at all pH’s up to slightly above pH 8, where solid calcite (CaCO$_3$) is stable with the solution in equilibrium with the normal atmosphere $^{[15]}$. When the solution pH exceeds 3.75, gypsum (CaSO$_4$·2H$_2$O) is formed and precipitates, which alleviates the high sulfate concentration of the AMD $^{[39]}$.

Although limestone treatment is perceived as one of the most cost effective active precipitation treatments for AMD, it does however, portray certain disadvantages which significantly affects its neutralizing capacity $^{[13,15]}$:

- The principal disadvantage of the application of limestone is of course that the acid water is neutralized at the expense of added hardness and as such adding to the saline nature of the resulting effluent (secondary process effluent).
- When the iron rich AMD is brought into contact with the carbonate rocks, the reacting surfaces of the limestone is rapidly coated by the precipitation of insoluble ferric hydroxide, a process known as armoring. The result is that the rate of dissolution of the coated limestone is inhibited and its neutralizing capacity is subsequently diminished. The armoring problem can be minimized by fine grinding the limestone further and higher sheering rates during agitation, however this process is an expensive expedient.
• Due to the limited solubility of limestone and depending on the rate of flow of the water being treated, there may be an incomplete reaction between the acid and solid and as such, even high quality limestone requires long reaction periods, which makes the process considerably tedious and more expensive.

2.4.1.2 AMD treatment with lime

Another method, also considered one of the oldest traditional active AMD wastewater treatment methods, is lime neutralization. During the basic lime treatment process, three types of lime may be utilized \cite{40}:

i. Pebble Quick lime [also known as unslaked lime, CaO];

ii. Hydrated lime [also known as slaked lime, Ca(OH)\(_2\)] and

iii. Dolomitic lime [MgO + CaO]

However, preference is given to the use of hydrated lime and/or pebble quick lime due to the fact that dolomitic lime has the disadvantage of producing undesirable quantities of magnesium salts, specifically MgSO\(_4\) (epsom salts) dissolved in the water \cite{15}. These dissolved salts may complicate treatment of the formed effluent (secondary process waters), since magnesium is more difficult to remove than calcium.

The preparation of hydrated lime involves the addition of varying proportions of water and quicklime (CaO) – a process known as slaking, yielding a hydrated lime
slurry, which is then thoroughly mixed with the metal-bearing AMD wastewater; while pebble quicklime may also be used as treatment chemical on its own \[40\].

Upon lime dosing (Ca(OH)\(_2\) or CaO) of the acid mine waters, as in the case of limestone treatment, the derived alkalinity from the lime acts as a pH buffer and neutralizes the AMD, while simultaneously precipitating the relevant contaminants (metals, etc.).

However, metals such as iron [ferrous iron, Fe(II)] and manganese [Mn(II)] should be oxidized before being precipitated as stable compounds \[13\], which is why oxidation is combined with neutralization in treating AMD at active mine sites:

— At a typical lime treatment plant this process may either be done simply by introducing air into the wastewater, a process known as aeration; or in cases where the AMD has a high percentage ferrous iron and dissolved metals, oxidants may be used to aid the completion of the oxidation process. Among the oxidants commonly known to have been used in AMD treatment processes are the hypochlorite products, including hydrogen peroxide (H\(_2\)O\(_2\)) and potassium permanganate (KMnO\(_4\)); while calcium peroxide has been shown to oxygenate AMD, as well as to neutralize acidity.

Metals known to benefit most from the oxidation process are iron, which upon oxidation gets converted from Fe(II) to Fe(III) and manganese, which is converted from Mn(II) to Mn(IV).
After the oxidation process, the neutralizing chemical may be added to raise the pH to 6 or 7, forming ferric hydroxide as well as the precipitation of other metal hydroxides.

The most widely accepted iron oxidation reaction is as follows:

\[ \text{Fe(OH)}_2 + \frac{1}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 = \text{Fe(OH)}_3 \]

Metals such as arsenic on the other hand, which primarily exists in the trivalent [arsenite, As(III)] or pentavalent [arsenate, As(V)] form needs to be oxidized from arsenite to arsenate, since almost all the existing AMD treatment processes are effective in removing arsenate, but not arsenite\[41\].

Aeration before and after lime dosing is thus beneficial due to certain advantages, including \[38\]:

- Oxidized water will generally have the affect of the metals precipitating at lower pH values and as such aeration can be a rate limiting factor in AMD treatment systems.
- Aeration before and after lime dosing usually reduces the amount of neutralizing reagent necessary to precipitate iron and other metals, which has the overall effect of increased chemical treatment efficiency, as well as cost reduction.

There are a number of factors which have been shown to affect the efficiency of lime treatment, which include the following:
• **Slaking temperature**

Hydration of CaO at higher temperature (44-70°C) has the effect of the formation of smaller calcium hydroxide particles, resulting in the availability of larger active surface area which consequently enhances lime efficiency, as well a decrease in sludge production.

• **Control pH**

The pH during lime treatment is typically between 12 and 12.7 and this represents Ca(OH)₂ saturation – if the control pH is reached, the lime efficiency decreases sharply.

• **Mixing**

The benefits of higher agitation (mixing) rate includes better dispersion of the added lime and recycled sludge, as well as improved aeration – resulting in faster oxidation rates of ferrous iron, including sufficient mixing so larger particles remain suspended. The disadvantage is of course that this will result in increased energy consumption (electricity) and possible particle attrition (erosion) [40].

The precipitates formed from the lime neutralization process generally consists of metal hydroxides; gypsum, unreacted lime and calcite and to meet effluent targets, these precipitates must be efficiently separated from the treated water. In the industry, gravity separation is the method of choice and as such precipitates are
settled to form a treated effluent (secondary process effluent) and a sludge (metal laden sludge), in which solid/liquid separation is done in clarifiers \[40\].

Among the factors affecting the settling ability of the formed lime sludge, the final pH, as well as the surface areas and charges of the sludge particles are particularly important:

- **Final pH**
  
  This is most often controlled by the chemistry of the untreated AMD, as well as the effluent targets. This means that the major contaminants present in the raw water, will determine the final pH, for example, if zinc (Zn) is the major contaminant – the pH must be brought up to at least 9.0 (ideally, pH 9.7).

- **Surface area and particle charges**
  
  These are typically factors of the raw (untreated) water chemistry, as well as the treatment process. The efficiency of the clarifier, in which the solid/liquid separation takes place can be optimized through the controlled use of flocculants and coagulants.

- As in all known AMD treatment technologies, the efficiency of the lime process is adversely affected by certain disadvantages, which includes the following \[17 – 19, 40\]:

- The cost related to lime treatment plants are extremely high, because of the need to construct a lime treatment plant, which is accompanied by the installation of aerators, clarifiers, mixing chambers, etc.
• Since the minimum solubility for the different metals usually found in the polluted water occur at different pH values and the fact that the hydroxide precipitates are amphoteric in nature, maximum removal efficiency cannot be achieved at a single precipitation pH level and as such lime precipitation is a “limited” process.

• Since this process often needs the aid of additional chemical reagents, such as oxidants and coagulants/floculants to aid particle settling, the cost of such chemicals adds to the expenditure of the process. Another major disadvantage of lime treatment is the formation of voluminous metal hydroxide and gypsum sludge, which has large land requirements when being disposed of and can give rise to secondary wastes. It has been estimated that as much as 6.7 million m³ of lime treatment sludge is produced annually in Canada alone.

2.4.1.3 The precipitation of metals from AMD (pH at which metals attain minimum solubility)

The process of precipitation works on the basis that the pH is reached at which the metals attain their minimum solubility and as such, precipitate out. Although each metal portray its own minimum solubility at its own characteristic pH, the pH required to precipitate most metals from water ranges from pH 6 to 9 (except for ferric iron, which precipitates at approximately pH 2.0 – 3.5), thus if sufficient
alkaline material is added, such that the pH is raised up to 9, most of the metals will be hydrolyzed and precipitated\cite{13}.

### 2.4.1.3.1 Ferric precipitation

Based on the research conducted in previous investigations, it has been found that ferric hydroxide is the first metal to precipitate from AMD through the alkaline treatment process. Ferric hydroxide precipitation starts at pH 2.0 and is virtually complete by pH 3.5.

Iron precipitation from AMD may be through various phases, such as ferric hydroxide \([\text{Fe(OH)}_3]\), oxyhydroxides and/or hydroxysulfates\cite{39}.

Table 2.1 gives an overview of the phases through which iron may be precipitated:

**Table 2.1** The precipitates of iron and their representative formulas:

<table>
<thead>
<tr>
<th>Precipitate Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schwertmannite</td>
<td>(\text{Fe}_8\text{O}_6(\text{OH})_6\text{SO}_4)</td>
</tr>
<tr>
<td>2-line ferrihydrite</td>
<td>(\sim\text{Fe}_3\text{HO}_8\cdot4\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>(\text{Fe(OH)}_3)</td>
</tr>
<tr>
<td>goethite</td>
<td>(\text{FeOOH})</td>
</tr>
<tr>
<td>Hematite</td>
<td>(\text{Fe}_2\text{O}_3)</td>
</tr>
</tbody>
</table>
2.4.1.3.2 Aluminum precipitation and related phases

The next metal hydroxide to precipitate is, aluminum (Al$^{3+}$) hydroxide and this normally starts at pH 4.0 and is virtually completed by pH ±5.0. However, aluminum is a very amorphous element and as such may enter the solution again at pH 9.0 through re-solubilization of previously formed Al precipitates.

The pH at which Al removal occurs most effectively is slightly above or slightly below 5.0. As in the case of iron, aluminum removal may also occur through the formation of various phases, which may include the following:

- Gibbsite \([\text{Al(OH)}_3]\)
- Jurbaminite \([\text{AlOHSO}_4]\)
- Basaluminite \([\text{Al}_4(\text{OH})_{10}\text{SO}_4]\)

2.4.1.3.3 Calcium precipitation

The calcium concentration is primarily controlled by gypsum (CaSO$_4$·2H$_2$O) and calcite (CaCO$_3$) precipitation, while a reduction in sulfate accompanies the formation of gypsum$^{[38]}$.

In AMD situations, the formation of Fe$^{3+}$, Ca$^{2+}$ and Al$^{3+}$ ion precipitates are very important, since they subsequently act as crystallization seeds and co-precipitates for the removal of other metals by sorption or co-precipitation processes.
2.4.1.3.4 Chemical precipitation of other metals

Manganese is an extremely mobile ion and precipitation for this element is variable, due to its multiple oxidation states; however, the optimum pH for Mn precipitation is at 9.0 to 9.5 [38, 39]. Previously formed iron precipitates may play a very significant role in the removal of Mn, through co-precipitation processes, but only if the iron concentration in the water is approximately four times that of the Mn content. Mn may also be removed by the formation of the following precipitates, including:

- Rhodochrosite [MnCO₃] or
- Pyrocroite [Mn(OH)₂]

Zinc (Zn) may be precipitated as hydroxide at neutral pH values or can be adsorbed on the surface of precipitated goethite (FeOOH). However, Zn may also be removed from solution by replacing calcium in calcite, thus forming the isomorph, ZnCO₃ (smithsonite). The optimum pH for precipitation of Zn is at ± 6.6 [39].

In the case of Cadmium (Cd), the main mechanisms involved in its removal, are sorption/co-precipitation on the surface of hydrous iron and aluminum oxides. Cd removal is optimum when pH varies between 7.4 and 8.3, as well as when elevated sulfate concentration is present in solution [39].

Copper (Cu) on the other hand, may be removed by precipitation of copper hydroxide [Cu(OH)₂], or due to sorption onto previously formed iron precipitates, as
cupric ferrite \([\text{CuFe}_2\text{O}_4]\). The optimum pH for removal of this ion is between 6.0 and 7.0 \[^{38,39}\].

Ni\(^{2+}\) ions are removed by the formation of hydroxides, or, in undersaturated solutions, may be removed by adsorption on calcite (occurs at pH between 8 and 9) \[^{39}\].

At a pH of approximately 7, Co may also be removed by sorption onto the surface of calcite (\(\text{CaCO}_3\)), or at higher pH values (8.2 to 8.9) – by replacing calcium \[^{39}\].

### 2.4.2 Passive treatment systems for AMD

In view of the fact that AMD will continue to contaminate sites for decades after the decommissioning of the mine, alternative low-cost treatment schemes, referred to as passive systems have also been developed \[^{5}\]. These systems typically require less operation and maintenance, since the treatment scheme makes use of naturally occurring geochemical and biological processes in order to improve the quality of the influent water. Three principle types of passive technologies have been developed for the treatment of AMD \[^{5}\]:

i) Aerobic wetlands,

ii) Compost wetlands and

iii) Anaerobic limestone drains
In aerobic wetlands, oxidation reactions result in the precipitation of metals as hydroxides and oxyhydroxides. Compost wetlands, on the other hand, promote anaerobic bacterial activity, resulting in sulfate reduction and the subsequent precipitation of metal sulfides, as well as the generation of alkalinity. In the case of anoxic limestone drains, alkalinity is generated for the pretreatment of the acidic mine waters.

In short, the main processes encountered in passive treatment schemes for the removal of metals from AMD include metal removal by plants, algae and organic substances; reduction and limestone addition.

However, like all other AMD treatment methods, numerous drawbacks adversely influence the effectiveness of this technology [13].

- From all the treatment processes, only precipitation as either oxides or sulfides have long-term metal removal potential.
- Constructed wetlands are known to only treat the symptoms of pyrite oxidation, but not the problem itself.

Wetlands are considered a poor environment for the formation of metal oxides and oxyhydroxides, because of the typically low redox potential (Eh) associated with wetland sediments.
2.4.3 Treatment of metal-bearing waste streams, such as AMD with fly ash

Recent investigations into alternative low-cost AMD treatment materials have shown that mining by-products, such as alkaline fly ash, either on its own, or as a mixture with lime, have been found to significantly reduce AMD contaminants to within prescribed limits\(^7\).

Fly ash is characterized by having low permeability, low bulk density and an extremely high surface area. Among the two major classes of fly ash (class F \([(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 70\%]\) and class C \([(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 50\%]\)), class C fly ash portrays an appreciably increased Ca content – mainly as lime (CaO), Ca(OH)\(_2\) and calcite (CaCO\(_3\)); while in class F fly ash, Si and Al are present in dominating proportions.

The addition of high Ca-containing (class C) fly ash to aqueous solutions, results in a characteristic alkaline reaction, which brings about a pH elevation. This can be attributed to the dissolution of the highly reactive sub-micron CaO particles, contained in the mineral phases of the fly ash, of which the process is as follows\(^{42}\):

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \Leftrightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (2.8)
\]

Bearing in mind that fly ash has a very high surface area, but more specifically, due to the high Ca content of class C fly ash, it has significant neutralizing capacity and...
as such may be beneficially employed to counteract the acid potential, as well as remediation of metal-bearing waste streams \[7\].

However, the high Si content found in class F fly ashes (Al—Si—rich) on the other hand, can equally aid in its usefulness as a potential cheap adsorbent for metal-laden wastes streams. This can be attributed to the fact that the fly ash surface is spanned by charged OH—silanol groups and hydrolysis of these surface –SiOH sites, raises the resultant final pH, during the equilibration of fly ash with the aqueous phase. This is a pH dependent reaction, which leaves the active sites of the fly ash with a negative charge and as such, the fly ash can interact with potential contaminants to remove them from the aqueous phase. The hydrolysis of surface –SOH sites are portrayed in the following equation \[42\]:

\[-\text{SOH} + \text{H}_2\text{O} \Rightarrow -\text{SO}^- + \text{H}_3\text{O}^+ \] (2.9)

The efficiency of fly ash with respect to metal retention and/or metal concentration control during its application for the treatment of AMD or any other metal-bearing wastewater, is governed by certain parameters, which includes the following \[24\]:

- contact time;
- pH;
- temperature and
- ash origin

The mechanisms of interactions between the particular metal and solid (fly ash) on the other hand, is by and large, a function of pH and these mechanisms are found to be:
precipitation (including surface precipitation or bulk solution precipitation);

- adsorption (specific or non-specific, through the formation of outer-sphere complexes on the charged fly ash surface) or

- competitive adsorption with H$_3$O$^+$ (in acidic solutions)

Fly ash has also been applied for the removal of anionic species, including arsenate [As(V)], during which the following findings were made$^{[11]}$:

- As(V) removal with fly ash was largely pH dependent and the adsorption mechanisms were electrostatic attraction (resulting in ion exchange with the counter-ions in the diffuse layer) and specific adsorption (surface complexation) and these mechanistic interactions were made possible through the interaction of the arsenate ion with the hydrous oxides existing in the solid phase. At pH 4.0, the dominant hydrous oxides on the fly ash surface were ferric- and aluminum oxides; while at pH 10.0 adsorption was brought about due to calcium- and magnesium oxides. However, adsorption at pH 7.0 proved not to be as efficient and this can be attributed to the fact that at this particular pH, none of the two classes of oxides are efficient enough to interact with the arsenate ion.

The attraction for the utilization of fly ash as an alternative low-cost adsorbent was further exemplified by the successful removal of the inorganic constituent, boron, for
which standard wastewater treatment technologies, as well as desalination methods to date, proved to be unsuccessful \[43\].

2.4.3.1 The use of silica in fly ash for metal immobilization

The metal adsorption properties of silica are well known, particularly due to their amphoteric nature. Silica products can be synthesized through different methods of preparation and examples of such sorbent materials are silica gel, etc. However, in fly ash, particularly South African fly ash, silica can be found in the mineral phases which form part of the constituents of the fly ash and as such can be used in the immobilization of metal ions due to adsorption on the silica.

In the fly ash, the silica ions are connected to each other through oxygen bridging and an ordered structure is formed in which OH—silanol groups spans the fly ash surface \[44\]. Figure 2.1 gives a schematic illustration of the oxygen-bridged silica ions, as well as the OH—silanol groups on the surface, found in fly ash:

![Figure 2.1 Schematic presentation of bridged oxygen groups and surface OH—silanol groups found in silica-containing sorbent compounds, such as fly ash](image-url)
The sorption behavior of the hydrous silica compound is strongly influenced by its specific surface, which is in turn controlled by the solution pH – since pH affects the surface charge of inorganic sorbent materials. The hydrous silica are strong hydrogen-bond donors and thus, may be used in exchange reactions for metal removal from wastewater effluents and being amphoteric, may undergo dissociation reactions as follows \[44\]:

\[
\text{Si—OH} \rightleftharpoons \text{Si}^+ + \text{OH}^- \quad (2.10)
\]

\[
\text{Si—OH} \rightleftharpoons \text{Si} – \text{O}^- + \text{H}^+ \quad (2.11)
\]

**Scheme (2.10)** is acid catalyzed and thus takes place in acid solutions, leaving a resultant positively charged Si$^+$ on the fly ash surface and thus the removal of anionic species can take place. **Scheme (2.11)** on the other hand is hydroxyl catalyzed and thus takes place in basic solutions from which the negatively charged silanol may be used for the immobilization of cations. Dissociation, near the isoelectric point of the oxide, occurs in both directions, enabling the simultaneous development of both ion exchange processes.

The mechanism of adsorption for cations onto silica normally involves surface complex formation between “free” metal ions and deprotonated surface functional groups and can be illustrated by the following equation \[10\]:

\[
→\text{SiOH} + M^{Z+} \rightleftharpoons (→\text{SiO})M^{(Z-1)+} + H^+ \quad (2.12)
\]

Where

- M represents the metal ion
- Z indicates the oxidation state of the metal ion
- SiOH represents the surface groups of the silica compound
Overall, fly ash has through extensive investigations by various researchers, been classified as a very efficient, low cost adsorbent material \[23\], for the immobilization of heavy metals, and it has been proposed and proven to be used for the precipitation of metallic ions by analogy with lime treatment for the remediation of different industrial metal-bearing waste streams, such as acid mine drainage (AMD) \[7, 10, 23, 24\].

2.4.3.2 The neutralization (co-disposal) of AMD with fly ash

This reaction which have been labeled, the co-disposal process, is fairly new; however, a number of bench scale, as well as pilot studies to explore the chemistry surrounding it have been pursued by various researchers \[26 – 28\]. These experiments were based on the utilization of South African fly ash and AMD, collected from various coal mining areas, while in certain cases, synthetic acid mine drainage (SAMD) were also used.

The incentive for the co-disposal process is mainly due to the highly neutralizing capacity of fly ash, brought about mainly by its free sub-micron CaO particles which upon contact with the AMD, induced considerable pH rise in the AMD, through hydration and as such, functioned as a pH buffer, with the overall result being the precipitation of various mineral and metal species.

The initial investigations around this area was done in an attempt to show that South African fly ash may be used as a potential liming agent for the neutralization of AMD, as well as to determine the possible mineral phase formation brought about by
the FA/AMD interaction. From these investigations the following findings were made\cite{26, 28}:

- The formation of ettringite (calcium-aluminum-sulfate-hydrate) at pH 10-12, which is known to be a potentially very important hydrous oxide adsorbent material.
- Gypsum (hydrated calcium) formation occurred at pH 5.6 and this compound is known ability to serve as solid precipitant for sulfate.
- Other minerals also observed included 2-line ferrihydrate at pH between 5 and 8.
- Fly ash addition increased solution pH within the first 30 minutes due to the hydration of the free lime (provided by the sub-micron CaO particles).

Geochemical modeling confirmed the formation of ettringite and gypsum.

Further studies were also conducted, during which the fly ash/AMD ratio was varied, as well as the pH at which the solid precipitates were collected; in some cases the use of fly ash leachates as liming agents were also explored\cite{45}.

Based on the findings from these investigations it was determined that, the direct mixing of various ratios of fly ash and AMD to a predetermined pH and the neutralization (co-disposal) process between fly ash and AMD served a dual purpose; on the one side the water quality of the AMD was considerably improved through the precipitation of various solid phases, while on the other hand, some of the volatile species contained within the fly ash itself was removed with the solid precipitates formed through the process.
The quality of the water, collected from the neutralization process was found to be broadly comparable to the secondary process effluents derived from active physico-chemical treatment technologies of AMD; while characterization of solid precipitates showed that formation of valuable materials such as, aluminosilicate and/or aluminocalcium sulfate or ferrihydrite precipitates could be used as starting materials for the synthesis of high capacity adsorbent material, such as faujasite, zeolite A and soldalite, which could be used for the reduction of metal-bearing waste streams \[^{[29, 30]}\].

- Since the neutralized process water, produced from this process were significantly purified and as such contained only residual low concentrations of some dissolved metals, secondary treatment, such as desalination techniques may be applied at this stage. Thus, the application of synthesized high capacity adsorbent material for the purification of these waters were explored at this point; however, being a fairly new process, not much about the chemistry surrounding the adsorbent/process water is known yet.

### 2.5 Secondary process effluent

Conventional AMD treatment methods, which usually involves the addition of alkaline chemicals, have the effect of pH elevation which is followed by the precipitation of metals. The function of the precipitation process is thus to remove as much of the heavy metals as possible, but it yields a highly saline effluent which can be referred to as the _secondary process effluent_ \[^{[16]}\].
2.5.1 Formation and description of secondary process effluent

The secondary process effluent, produced from the primary treatment of raw acid mine waters (AMD), which includes physico-chemical treatment technologies; precipitation-aggregation (coagulation/flocculation)—settling, in most cases still has a highly saline nature \(^{[16]}\). These treated waters may typically contain quantities of sulfate (over 250 mg L\(^{-1}\)), suspended solids (5 mg L\(^{-1}\)), including hardness of more than 200 mg L\(^{-1}\) as CaCO\(_3\), as well as total dissolved solids in the region of approximately 500 mg L\(^{-1}\) which renders it undesirable for re-circulation to be utilized for industrial application and/or domestic use, or for discharge into natural waterways \(^{[15]}\), subsequently secondary treatment technologies are applied at this stage.

Existing technologies for desalination of secondary process effluents include among others evaporation, membrane technologies \([\text{e.g.} \text{electro dialysis (ED), reverse osmosis (RO), nanofiltration (NF), etc.}]^{[16, 20]}\) and ion exchange. On industrial scale, membrane technology and/or ion exchange are the more popular applied treatment processes, thus a detailed overview of these technologies, together with their associated drawbacks are discussed below.

2.6 Secondary process effluent treatment with membrane processes

A membrane can be defined as a semi-permeable barrier through which only selected species may diffuse.
The process of membrane technology is based on the application of semi-permeable membranes that are selectively permeable to aqueous solutions, as well as certain solutes and as such separates selected contaminants from water [20]. Currently on industrial scale, the more universal membrane alternatives utilized for desalination processes, includes reverse osmosis (RO), nanofiltration (NF), electro dialysis (ED) and/or electro dialysis reversal (EDR) techniques.

2.6.1 Reverse osmosis (RO)

RO is considered a physical process. It is a pressure driven membrane process in which the solution is transferred through a semi-permeable membrane barrier customized for retention of salts and low molecular weight inorganic solutes. During this process a substantially high pressure difference across the membrane is necessary to overcome the osmotic pressure difference between the salt free permeate and the saline reject (“brine”) solution. The smaller water molecules are literally pushed through the semi-permeable membrane, while the larger solute species are retained. In view of the latter statements, one can thus conclusively deduce that this process is the “reverse” of natural osmosis, which involves water diffusion from a dilute to concentrated region through a semi-permeable membrane to equalize ion concentration.

The principle by which these membranes choose or reject ions, are based on size and electrical charge. The most common membrane materials include cellulose acetate,
or polyamide thin film composite; while construction of these membranes may include either spiral wound, hollow fiber, tubular or plate-and-frame configuration [20, 22, 46]. Each type of membrane material and construction method has specific benefits and limitations depending upon feed water characteristics, as well as pre-treatment [22].

Although perceived as an economically feasible desalination process for specialized applications; however, as with all other water treatment options, is yet to overcome certain drawbacks which includes the following [21]:

- Extremely high operating pressures are required to overcome osmotic pressure gradients leading to substantial increase in energy consumption, and the fact that such plant installations and operation are relatively costly, makes this an exceedingly expensive treatment option.

- Another major problem with RO desalination facilities is the membrane susceptibility to fouling by suspended solids, colloidal material, or certain dissolved ions in the feed water. The implications of fouling are irreversible membrane damage, reduced flux rates and increased capital and operating costs.

- One critical issue for the successful application of RO, is pre-treatment. Pre-treatment has to ensure that the quality of the effluent fed to the RO membranes is consistently high to avoid variability in the feed water quality and needless to say, pre-treatment on its own has high costs attached to it.
• The basic principle on which RO operates is size exclusion and selectivity for specific metal ions is restricted and as such limits the scope of the process.

2.6.2 Nanofiltration (NF)

Nanofiltration (NF) operates according to the same basic principles as RO and can thus be considered as two faces of the same coin. The major difference between the two processes is that in the case of NF, the membrane has a much more open structure as compared to RO membranes, leading to increased membrane permeability. The “enlarged treatment area” consequently has the effect that the higher molecular weight divalent ions are easier retained, while retention of monovalent salts decreases[20]. Based on the increased permeability, capital operating costs associated with NF are generally lower than in the case of RO, however scaling and membrane fouling also significantly contributes to the expenditure of the process.

The other membrane assisted treatment options mentioned above are ED/EDR; however, since their application are based on the use of an electric current, they form part of the electro-assisted waste water treatment options and as such will be discussed in the subsequent section which elaborates on such techniques.
2.6.3 Electro-assisted technologies

Electrochemistry deals with the charge transfer at the interface between an electrochemically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as reactions within the electrolytes and the resulting equilibrium [47].

Application of electrochemical methods to remove impurities, especially with respect to the purification of dilute heavy metal process liquids, has been exhaustively investigated, since many heavy metals are very toxic and cause great environmental damage [48].

Among the different approaches, the following electrochemical treatment options may be distinguished:

- indirect electrochemical oxidation of inorganic or organic contaminants;
- direct electrochemical oxidation of the contaminants;
- cathodic removal of metal-cations (mostly heavy metals);
- separation through membranes using electric field.

To give a better perception of the various electro-assisted treatment options mentioned above, a short descriptional overview is given:
2.6.3.1 Anodic oxidation (AO)

AO has found considerable application, mainly for the treatment of organics in water; with specification to its powerful ability in the removal of organic wastes from industrial effluents; however, methods has been explored in an attempt to remove inorganic constituents from contaminated waters. One such study was done by the US EPA, using a synthetic AMD solution (FeSO₄ + H₂SO₄). During this investigation a one-compartment electrochemical cell was used to reduce H⁺ to H₂ at the cathode (made from platinum, copper, graphite and carbon felt), while oxidizing Fe²⁺ to Fe³⁺ at the anode (consisted of Ti coated with iridium oxide). After the anodic oxidation of the iron ions, it was subsequently precipitated[47].

2.6.3.2 Electrochemically activated adsorption methods

Electrochemically activated sorption, also termed electro-sorption, can be described as the adsorption of species from solution, in which the amount of material sorbed depends on the electrochemical potential applied to the adsorbent[49]. An electrochemical system consists of two electrodes, anode and cathode and a porous medium which is permeable to water (e.g. an ion exchange resin or membranes), which can be incorporated in one of the electrodes. The polluted water acts as the electrolyte in the system. A direct current (DC) voltage is applied between the two electrodes, which are immersed in the electrolyte and the resultant effect is electrolysis reactions at the two electrodes.
These electrolysis reactions, which dominates the chemistry at the phase boundaries, involves oxidation at the anode and reduction at the cathode and as such generates protons and hydroxyl ions respectively. Indicative of the preceding reactions are also the resultant pH change, of which an acid front is evident at the anode, while a base front resides at the cathode where reduction takes place [47, 50].

Oxidation and reduction reactions can be described by equations (2.13) and (2.14):

\[
\begin{align*}
\text{Anode (oxidation)} & : & 2H_2O - 4e^- & \Rightarrow & O_2 \uparrow + 4H^+ & (2.13) \\
\text{Cathode (reduction)} & : & 2H_2O + 2e^- & \Rightarrow & H_2 \uparrow + 2OH^- & (2.14)
\end{align*}
\]

In many fields of applied electrochemistry, membranes may serve as semi-permeable separators and solid electrolytes.

For the treatment of polluted water, the two main routes are:

- Electro dialysis/Electro dialysis Reversal (ED/EDR) processes
- Solid-Polymer-Electrolyte (SPE) applications

Electro dialysis (ED) is an electrochemical separation process which involves the selective migration of aqueous ions through ion selective membranes as a result of an applied electrical potential difference [51].

An ED system consists of two oppositely charged electrodes, a cathode and anode, with a number of compartments in-between. These compartments are separated by alternative cation and anion exchange membranes in a stacked configuration, filled
with polluted water (e.g. secondary process waters). The advent of an electrical potential difference, combined with electrochemical reactions, which includes reduction of water at the cathode and oxidation at the anode impel the ions through the membranes. The transport rate and direction of each ion depends on its charge and mobility, solution conductivity, relative concentrations, applied voltage, etc.

 Appropriately then, under the influence of an applied DC field, ions are forced to migrate to the appropriate electrode, which involves anions migrating through the anion exchange membrane into the adjacent compartment toward the anode, while movement of the cations will be toward the cathode. The ions that are transported out of the feed stream are collected in a brine stream and as such in ED systems, two main streams flowing in parallel to the membrane stack can be observed; one being progressively desalted and is referred to as the product stream, while the other main stream is the salt rich stream (brine).

A schematic representation of the ED process, which gives a graphical perception of the principles described in the preceding section, can be observed in figure 2.2.
Quite recently, in a quest to enhance the efficiency of ED systems, the polarity reversal process referred to as electro dialysis reversal (EDR) was developed. This involves the periodic reversal of the polarity of the electrodes, resulting in the reversal of the direction of ion movement within the membrane stack. The dilute stream then becomes the concentrate stream and vice versa.
Overall, EDR uses the technique of regularly reversing the polarity of the electrodes, thereby freeing accumulated ions in the membrane surface and as such aids in breaking up and flushing out scale and other deposits from the cells \(^{21}\), which could shorten membrane life by fouling; consequently the EDR treatment system portrays reduced sensitivity to scaling, as compared to normal ED treatment systems. The result is more durable membranes, which are able to tolerate pH from 1 to 10, as well as substantially high temperatures (up to 115).

The ED/EDR plant operation efficiency increases with an increase in feed water temperature and consequently at a typical plant, a preheating stage, which raises the temperature of the feed water to approximately 35°C immediately prior to the ED/EDR is included \(^{52}\). The increased electricity arising from the heating process evidently adds to the capital and process costs, therefore in the interest of thermal efficiency and reduced costs, heat is recovered from the streams exiting the EDR — plate heat exchangers are used to heat the inlet and cool the outlet streams. To compensate for any heat losses and to maintain a constant feed temperature, a boiler plant generates steam, which is injected into the feed water after the plate exchangers and before the ED/EDR. This steam injection ensures that the constant feed water temperature of approximately 35°C is maintained \(^{52}\).

The presence of contaminants including suspended solids, high molecular weight dissolved solids, organic compounds and colloids in the feed water may give rise to membrane fouling resulting in irreversible membrane damage and as such feed water
pre-treatment also exerts a pivotal role in ED/EDR process treatment performance, by trying to ensure that the quality of the water fed to the ED/EDR membranes are consistently high.

In order to maintain optimum performance of ED/EDR systems, membrane stacks needs to be cleaned intermittently to remove scale and other surface foulants \[21\]. Normal cleaning is usually done by a cleaning-in-place (CIP) system, which utilizes special cleaning solutions that are circulated through the membrane stack; however, the membrane stack needs to be periodically disassembled, perfunctorily cleansed and reassembled at regular intervals for effective removal of scalants and other potential surface foulants \[52\].

Disadvantages of the ED/EDR treatment system

- The major disadvantage of ED/EDR systems, as is the case in all other membrane systems, is fact that membranes have a limited lifetime before fouling or failure of adhesive bonds necessitates replacement. The costs of periodic replacement is an expensive expedient and needs to be included in any analysis of their economic viability \[20\].

- Generally, the more contaminated the feed water and the higher the desired quality of product water, the greater the likelihood of membrane fouling caused by particulate matter, scaling and bio-fouling. Since traditional primary physico-chemical treatment options have serious limitations regarding the
variable quality of the treated water they produce, the success of secondary treatment by ED/EDR processes cannot always be guaranteed.

- The constant electricity supply ensuring the maintenance of a preheated feed water evidently adds to the already expensive energy driven process.

- Although the development of the EDR process was to improve on the conventional ED treatment systems, its complexity due to additional plumbing and electrical control leads to increased capital and operating costs \cite{22}.

- These treatment systems are not suitable for secondary process waters with high levels of Fe and Mn, H₂S, chlorine or hardness.

- Since only approximately only 50% of the total dissolved solids (TDS) can be removed per pass, the ED/EDR process is limited to feed water with an maximum of 3000 mg L⁻¹.

- Since the secondary effluent fed to the ED/EDR needs to adhere to specific guidelines pertaining its pH, organic constituents, turbidity and other characteristics; in addition the system is equipped with pH adjustment chemicals (normally acid, e.g. H₂SO₄), as well as imbedded cartridge filters to alleviate source water contamination and as such, adds to the financial burden of increased operating costs.
2.7 Ion exchange

Ion exchange has been labeled as one of the best available treatment (BAT) methods for the secondary process effluent; derived from raw AMD treatment.

The process of ion exchange can be defined as the reversible interchange of a charged ion (cation or anion) for a similarly charged ion, between a solid material (the ion exchanger) and the surrounding liquid, in which there is no permanent change in the structure of the solid \[53\].

Ion exchange resembles sorption, in that in both cases, a dissolved species is taken up by a solid; however, the characteristic difference between the two phenomena is that ion exchange, unlike sorption, is a stoichiometric process where every ion which is removed from the solution is replaced by an equivalent amount of another species of the same sign. In sorption, on the other hand, a solute is taken up without being replaced by another species.

Although the distinction between the two phenomena seems clear-cut, in practice however, virtually every ion-exchange process is accompanied by electrolyte sorption or desorption and most of the common sorbents such as activated carbon, alumina, etc. can act, in turn, as ion exchangers.

The unique characteristic properties of ion exchangers can be attributed to a distinctive feature in their structure. They consist of a framework, held together by chemical bonds or lattice energy and the framework carries a positive or negative electric surplus charge, which is compensated by ions of opposite sign, also referred
to as *counter-ions* \cite{54}. The counter-ions are mobile thus able to move within the framework and can be replaced by other ions of the same sign (*counter ions*). However, electro-neutrality must be preserved, i.e., the electric surplus charge of the ion exchanger must be compensated at any time by a stoichiometrically equivalent number of counter-ions within the pores. A counter-ion can subsequently leave the framework, only when, simultaneously, another ion enters and takes over the task of contributing its share to the compensation of the framework charge\cite{54}.

A schematic representation of the process of ion exchange is illustrated by *figure 2.3*:

*Figure 2.3*: Ion exchange with a solution. A cation exchanger containing counter ions A is placed in a solution containing counter-ions B (*left*). The counter ions are redistributed by diffusion until equilibrium is attained (*right*) \cite{54}
Figure 2.3 describes a cation exchanger in the A form which is placed in a solution of electrolyte BY. Counter-ions A, migrates from the exchanger into the solution, while counter ions B migrates from the solution into the ion exchanger. In short, the exchange of counter ions takes place, which is largely a diffusion process. Within a certain time span, ion-exchange equilibrium is attained, in which both the ion exchanger, as well as the solution contains both counter-ion species A and B. However, the pores of the ion exchanger are occupied not only by charge compensating ions (counter-ions), but also by solvent and ions (solutes) which may enter the pores when the ion exchanger is in contact with the solution. Solvent uptake may result in “swelling” of the ion exchanger; while ion uptake is usually referred to as sorption.

The important properties of such exchange processes as previously mentioned are:

- there is an exchange of ions, therefore no one way uptake;
- the exchange is strictly stoichiometric;
- the exchange is reversible;
- the ion exchange capacity do not depend on the nature of the counter ion;
- the process is essentially a redistribution of counter ions between the pore liquid of the ion exchanger and the external solution;
- ion exchange is a diffusion process;
- the rate of ion exchange depends on the mobility of the counter ions.
The process of ion exchange can be carried out in a variety of different ways with different main objectives:

- **Substitution**: A valuable ion can be recovered from solution and replaced by a valueless one. Similarly, a toxic ion (e.g., mercury) can be removed from solution and replaced by a nontoxic ion.

- **Separation**: A solution containing a number of different ions passes through a column with beads of ion exchange resin. The ions are separated and emerge in order of increasing affinity for the resin.

- **Removal**: By using a combination of cation (in the H\(^+\) form) and anion resin (in the OH\(^-\) form), all ions are removed and replaced by water (H\(^+\) OH\(^-\)), the solution is thus demineralized.

### 2.7.1 Structure and properties of ion exchangers

By definition, ion exchangers are insoluble solid materials carrying exchangeable cations or anions, which can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution.

Although ion exchangers comprise a very heterogeneous group of materials, their general structure all have one common feature — a framework with electric surplus charge which can bind oppositely charged ions, as well as mobile (charge compensating) counter-ions which can be exchanged for a stoichoimetric amount of...
similarly charged ions. Exchangers carrying exchangeable cations (mobile) are called cation exchangers, while carriers of exchangeable anions are referred to as anion exchangers. Certain materials possess the ability to exchange both cations and anions and these are called amphoteric ion exchangers [54].

There are various natural and synthetic products exhibiting ion-exchange properties, however, ion exchange materials comprise two main groups: **organic** and **inorganic** exchangers.

### 2.7.1.1 **Organic Ion exchange resins**

Generally, modern organic resins should meet the following requirements [53]:

- stability in hot water;
- stability to common chemicals in solution, such as chlorine;
- only one type of functional group present;
- obtainable in a bead form of any desired size range;
- range of weak- and strong- acidic- and basic- types available;
- degree of cross- linking controllable, for special purposes.

The backbone of an organic resin, also referred to as the matrix, basically consists of irregular, macromolecular, three dimensional network of hydrocarbon chains and as such is normally known as a polystyrene matrix. Ordinarily such linear polystyrene chains (matrixes) would be soluble in water, due to dissolution of the matrix upon
exposure to the aqueous environment. However, the introduction of crosslinks, which interconnects the various hydrocarbon chains leads to an insoluble matrix with the overall expectancy being a stable resin, which is insoluble in most solvents and thus cannot be easily destroyed, other than by rupture of the carbon-carbon bonds. To date, Di-Vinyl-Benzene (DVB) is the crosslinker of choice and is applied during resin synthesis, as a technical mixture of different DVB isomers (about 40-55%). Therefore the structure of modern commercial resins are based on the styrene-divinylbenzene structure because of its superior resistance against chemical and physical stress — the structure as a whole, generally being stable at relatively high temperatures (up to and beyond 100°C) and pertains stability over a wide pH range.

In **figure 2.4 (a) and (b)**, the structure of DVB, as well as the produced resin matrix which have been crosslinked with the incorporation of DVB are illustrated, respectively:

---

**Figure 2.4**  Structure of DVB (a), which is used to crosslink the hydrocarbon chains of the ion exchange resin matrix, yielding an insoluble crosslinked polystyrene matrix (b)

X = ionogenic/functional group
Crosslinked matrices, formed by the incorporation of DVB are not only insoluble in most solvents, but also possess other characteristic features, i.e., they are elastic and can be expanded. Hence, the resin swells when in contact with an electrolyte solution, however, the swelling ability of the resin is determined by the degree of crosslinking, which is in turn determined by the DVB content \[^{[54]}\]. Resins with low DVB contents are soft and very elastic, while resins with a high DVB content appear to be harder and more mechanically stable and can hardly swell in aqueous environment.

Also observed from figure 2.4 (b), are “x”, which illustrates the ionogenic groups. The ion-exchange behavior of organic resins are mainly determined by these fixed ionic groups, which can be attached to virtually all the styrene rings in the styrene-divinylbenzene co-polymer.

Ionogenic groups must have the ability to dissociate or to be protonated in order to generate positive or negative charges. Depending on the chemical nature of the group, differentiation can be made between cation and anion exchangers.

The following table gives an overview of the ionogenic groups that may be attached to standard ion exchangers:
Table 2.2: Table of fixed ionic groups (functional groups) that may be attached to the matrices of standard ion exchange resins:

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly acidic</td>
<td>—SO₃⁻</td>
</tr>
<tr>
<td>Weakly acidic</td>
<td>—COOH</td>
</tr>
<tr>
<td>Strongly basic</td>
<td>—[N(CH₃)₃]+ (type 1), —[N(CH₃)₂ C₂H₄OH]⁺ (type 2)</td>
</tr>
<tr>
<td>Weakly basic</td>
<td>—NH₂ • H₂O, —NRH • H₂O, —NR₁R₂ • H₂O</td>
</tr>
</tbody>
</table>

An important factor of the ionic groups, tabulated in table 2.2, are their acid and base strengths, which ultimately determines the acid/base strengths of the resin types, i.e. standard resins may be either strongly acidic cation exchangers; weakly acidic cation exchangers; strongly basic anion exchangers; or weakly basic anion exchangers. In solutions, decreasing or increasing pH has the effect of progressive neutralization of fixed charges, particularly observable in weak-acid and weak-base resins, and as such, the operative capacity of such kind of organic resins are by and large pH dependent. Strongly-basic and strongly-acidic resins, on the other hand remains ionized, even at extreme pH’s (i.e. highly acidic or highly basic).

The constant need to develop and improve ion exchange based separation techniques has also given rise to the development of synthetic organic exchangers, with a very refined selectivity, with respect to the removal of specified target ions.

Thus, by using polymerization and activation methods analogous to conventional resin synthesis, a wide variety of ionogenic groups can be grafted onto a given
polymer and as such, depending on the type of group, it can be used for selective uptake of ions, principally metals.

Materials synthesized for the purpose of selective ion removal are known as chelating or complexing resins, while the ionogenic, chelating and complex forming active groups may be referred to as functional groups.

- **Chelating ion exchangers**

Chelating ion exchangers have functional groups, which can form coordination bonds with metals, in which these donor atoms are principally constituted by nitrogen, oxygen, sulfur, or a combination of these elements in the same functional group. The affinity of such resins with respect to a given metal are determined by the following criteria \[^{[55]}\]:

- ionic charge,
- hydrated ionic radius and
- ligand bonding with exposed electron pairs on nitrogen and oxygen

The bonds formed through this kind of metal sorption usually have both covalent and ionic characteristics. Since they are so highly recommended in terms of specialized target removal, these resins are well known and documented.

*Table 2.3* gives examples of principal active functional groups of ion exchange resins, used for selective uptake of metals:
Table 2.3 Table of principal active functional groups of chelating ion exchangers

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Structure</th>
<th>Selectivity for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iminodiacetic acid</td>
<td><img src="image" alt="Structure" /></td>
<td>heavy metals</td>
</tr>
<tr>
<td>Aminophosphonate</td>
<td><img src="image" alt="Structure" /></td>
<td>alkaline earth ions</td>
</tr>
<tr>
<td>Amidoxin</td>
<td><img src="image" alt="Structure" /></td>
<td>heavy metals</td>
</tr>
<tr>
<td>Bispicolylamine</td>
<td><img src="image" alt="Structure" /></td>
<td>copper</td>
</tr>
<tr>
<td>N-Methylglucamine</td>
<td><img src="image" alt="Structure" /></td>
<td>Boron selective</td>
</tr>
<tr>
<td>S-containing groups</td>
<td><img src="image" alt="Structure" /></td>
<td>mercury</td>
</tr>
</tbody>
</table>

Other characteristics, invoked by attached functional groups include the following:

- The number of the groups determines the ion-exchange capacity of the resin.
• The chemical nature of the groups significantly affects the consequent ion-exchange equilibria during the sorption reaction.

• The nature of the fixed groups also affects the resin selectivity and as such, certain counter-ions, which tend to associate with the specific functional group is preferred by the resin. For example, resins with carboxylic acids prefer alkaline earth cations, while resins with sulfonic acid prefers silver ions (Ag⁺), etc.

Due to the weakly acidic nature of chelating groups, desorption of adsorbed metals by the action of acids are relatively easy, therefore enabling the subsequent regeneration of the resin with a suitable medium.

2.7.1.2 Inorganic ion exchangers

Inorganic materials can act as ion exchangers if their structure bears an electrical surplus charge. This charge can be caused by two phenomena:

i) In the lattice M²⁺ ions are replaced by M⁺, which results in the ion of minor valence acquiring a negative charge. The charge has to be balanced by mobile cations (counter-ions).

ii) Chemical groups are situated on the surface functional groups of inorganic exchangers which can be ionized due to protonation or de-protonation. The resulting electrical charges also have to be compensated by counter-ions.
Natural inorganic exchangers can be classified into three main categories:

- zeolites, with reference to those found in nature, which falls under the banner of mineral ion exchangers;
- oxides and
- clay minerals, such as smectite clays $\text{Zr(HPO}_4\text{)}_2\cdot\text{H}_2\text{O, Sn(HPO}_4\text{)}_2\cdot\text{H}_2\text{O}$

Synthetic inorganic ion exchangers may comprise the following materials:

- zeolites, usually synthesized by autocleaving methods;
- hydrous oxides, including $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$, etc;
- group IV phosphates, which has the general structure:
- acidic salts of polyvalent metals;
- salts of heteropoly acids;
- hexacyanoferrates, as well as many other compounds.

The subgroup that have enjoyed a great deal of research and industrial application, are the mineral ion exchangers; more specifically, the zeolites.

2.7.1.2.1  Zeolites

Natural zeolites have been known for almost 250 years as microporous crystalline minerals with well defined structures. They were first discovered in 1756 by Swedish mineralogist Axel Fredrick Cronstead who discovered stilbite, a natural mineral. When visibly observing these minerals losing water, upon exposure to elevated
temperatures, he named this class of materials, zeolites, stemming from the greek word meaning “boiling stones” \cite{56,57}.

Natural zeolites originates from volcanic ash — the chemical reaction of glassy volcanic ash (source of aluminum and silicon) with pervading pore water (lake-, ground-, or seawater) altered the glass fraction into various forms of zeolite crystals. Since their discovery, about fifty natural zeolite species have been accounted for, including faujasite; clinoptalolite; ferrierite; chabasite; etc.

The naturally occurring forms of these minerals are generally mixtures of a few species, consequently they contain undesired impurity phases, which limits their value, however, due to pioneering research work done by people like Richard Barrer (the father of synthetic zeolites) and Milton (1948 to 1955), the first synthetic zeolites, which had no natural counterparts were synthesized. This was done under precisely controlled laboratory conditions, using a hydrothermal autocleaving method. An example of such a zeolite is the zeolite A.

Today synthetic zeolites, possessing specific properties for specific applications, plays a major role on industrial scale, in terms of petrochemical cracking, ion exchange (water softening and purification), separation and removal of gases and solvents, as well as molecular sieving.

Generally, zeolites are three-dimensional, microporous, crystalline solids that contain aluminum, silicon and oxygen in their regular framework; water and cations are located in the pores. Basically a tetrahedron of $(TO_4)$, of four oxygen ions
surrounding a central ion of which the central ion (T) ion can either be tetravalent silica (Si$^{4+}$) or trivalent alumina (Al$^{3+}$). Adjacent tetrahedra are linked at their corners through a common oxygen ion (figure 2.5),

![Figure 2.5: Adjacent SiO$_4$ and AlO$_4$ tetrahedra: the primary building units of zeolites, joined through a common oxygen](image)

resulting in an inorganic molecule a with a structurally distinct three-dimensional framework. This arrangement reduces the oxygen/silicon ratio to 2:1 and in zeolite structures, some of the qaudrivalent silica (Si$^{4+}$) is replaced by trivalent alumina (Al$^{3+}$), resulting in a deficiency of positive charge in the aluminosilicate framework, which means that a negative surplus charge resides at each tetrahedron in the framework, having aluminum in its center and this is illustrated in Figure 2.5.
Figure 2.6: Structure of an ideal zeolite framework of tetrahedral $[\text{SiO}_4]^{4-}$ with a Si/Al substitution ($[\text{AlO}_4]^{5-}$) yielding a negative surplus charge\(^{[12]}\)

The residing excess negative charge requires the introduction of charge compensating cations (counter ions, $C^{n+}$) into the structure. These charge-compensating cations are not covalently bound to the zeolite structure, but have considerable freedom of movement and can readily be substituted with a host of other cations.

Natural, as well as synthetic zeolites have a rather rigid framework structure. Their structures are associated with certain unique features, among them being their strictly uniform pore diameters and pore widths, giving rise to a pronounced "sieving action", on molecular scale: Larger cations are partially or completely excluded by the zeolite, whereas smaller species can be exchanged or adsorbed, and as such,
zeolites have found wide scale applications as molecular sieves. This group of materials offers extremely large specific surface areas and in terms of pore size, zeolites are typical microporous materials, in which pores are classified on the basis of their diameters, according to IUPAC classification \[58\]:

- the smallest are micropores: \( 2.0 \text{ nm} \geq d_p \),
- intermediate are mesopores: \( 2.0 \text{ nm} < d_p \leq 50 \text{ nm} \) and
- and larger, are macropores \( d_p > 50 \text{ nm} \)

with \( d_p \) being the pore diameter.

Located inside the zeolite framework are channels, channel intersections and/or intersections with dimensions ranging from 0.2 to 1 nm, which connects the strictly uniform pore apertures (openings) with larger void volumes known as supercages. Inside these pore apertures are water molecules, as well as mono- and divalent cations, such as Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\). The residing negative framework, caused by the replacement of Si\(^{4+}\) with Al\(^{3+}\) within the zeolite framework, is compensated by these small cations, resulting in a strong electrostatic field on the internal surface.

The chemical composition of a zeolite can consequently be represented by the following general formula:

\[
A^{m+}[(\text{SiO}_2)_{x} \cdot (\text{AlO}_2^-)_{y} \cdot z\text{H}_2\text{O}]
\]

Where

- \( A \) is a cation with the charge \( m \) (e.g. Na\(^+\), Ca\(^{2+}\), etc.)
- \((x+y)\) is the number of tetrahedral per crystallographic unit cell
- \( x/y \) is the framework silicon/aluminum ratio \( n_{\text{Si}}/n_{\text{Al}} \)
Based on Löwentstein’s rule it is precluded that two adjacent tetrahedra contain aluminum on tetrahedral positions; i.e. $\text{Al}—\text{O}—\text{Al}$ are forbidden, or $n_{\text{Si}}/n_{\text{Al}} \geq 1$ [58].

The ready exchangeability, and relatively innocuous nature of the charge-balancing cations ($\text{Na}^+, \text{K}^+, \text{Ca}^{2+}$ and $\text{Mg}^{2+}$); used to compensate the negative surplus charge residing in the zeolite framework, renders them particularly suitable for the removal of undesirable species (particularly metal ions) from various wastewaters [59]. The process by which these exchangeable ions gets replaced by other ions from solution are referred to as ion exchange. The exchange process involves replacing one singly-charged exchangeable ion in the zeolite by one singly-charged ion from the surrounding solution, or by replacing one doubly-charged ion from the zeolite with a doubly-charged ion from solution. Thus by exchanging equivalent amounts, electroneutrality in the zeolite is maintained.

The magnitude of the cation exchange ability of a given zeolite is known as its cation exchange capacity (CEC) and it is commonly measured in terms of exchangeable cations per gram (or 100 grams) of zeolite. The CEC may thus be defined as the number of counter ions present per unit weight of zeolite and as such, represents the number of cations available for exchange, in other words, it is a function of the degree of Al substitution for Si in the zeolite framework structure; the greater the substitution, the greater the deficiency of positive charge and the greater the number
of charge-balancing (exchangeable) cations required for maintaining electrical neutrality.

This gives rise to a very important parameter of zeolites, the Si/Al ratio. This ratio has a direct effect on the hydrophobicity and organophilicity of a zeolite; which in turn, determines the zeolite’s suitability as an adsorbent \[^{60, 61}\]. In general, a zeolite with a low Si/Al ratio, in other words, a zeolite containing a relatively large proportion of aluminum atoms, will tend to be hydrophilic, while a high silica zeolite will be hydrophobic. Thus, a smaller Si/Al ratio, is indicative of the increased number of terminal Al-OH surface functional groups at the mineral-water interface; which consequently leads to a greater capacity for ligand exchange \[^{60, 61}\], the overall effect being better performance in terms of metal removal from contaminated waters – therefore for natural and synthetic inorganic zeolites, (such as the ones under discussion in the current research applications) it was found that the total exchange capacity may depend on the experimental conditions, and as such, the maximum exchange capacity may considerably differ from the theoretically determined total ion exchange capacity \[^{60}\].

The water, earlier described as being contained within the framework channels (hosting the exchangeable cations), can be removed upon exposing the zeolite to elevated temperatures, between 200- and 350°C. The process, termed dehydration, or also known as zeolite activation, is reversible, in which the zeolite re-adsorbs water at ambient temperature. Dehydrated zeolites are highly hygroscopic and can
effectively be used to remove water from solvents, with a capacity of up to twenty five percent of their dry weight in water. Similarly they can also accommodate solvent molecules on the basis of size, without change in the external volume of the crystal. On this same principle, gases can also be separated, through size exclusion, with preference given to polar solvent molecules and gases, since zeolites are polar hydrophilic materials [54].

In view of all these unique properties inherent in zeolites – based on their crystal structure; uniform pore diameters and pore widths; relatively high specific surface area; reversible dehydration; exchangeable cations; Si/Al ratio and ability to develop internal acidity, a host of functions pertaining to these mineral species can be summarized, with respect to industrial applications, as well as in terms of environmental protection:

Zeolite functions include the following:

- Chemical sieving
- Gas adsorption: removal of specific toxic gases from gaseous emissions.
- Water adsorption: reversible adsorption of water without any desorption chemical or physical change in the zeolite matrix.
- Industrial catalyst application: Use in fluid catalytic cracking (FCC) of heavy distillates, which is one of the most important chemical processes worldwide. As a whole, the cost of petroleum refining worldwide would be higher by at least 10 billion US dollars per year, without the use of
zeolites catalysts \cite{58}.

- Environmental protection applications including:
  
  — ammonia removal from urban, agricultural and industrial waste waters, subsequently reducing odor intensities.
  
  — classified as one of the best available technologies (BAT) for the treatment of secondary process effluents, produced from the active treatment of AMD, particularly with respect to salinity and metal removal.

One must however bear in mind that the selectivity, exchange capacity and dehydration rate depends on various factors including, Si/Al ratio; pore volume and pore size; size and shape of cages and channels in zeolite structure; type of adsorption sites; etc., and as will differ from one zeolite to the next.

- Secondary building units

The primary building units of zeolites, SiO$_4$ and AlO$_4$ tetrahedra, (Si$^{4+}$—O—Al$^{3+}$) may be joined in various ways to eventually form common crystalline zeolitic structures, such as zeolite X, Y, A and many others. Lining four tetrahedral, results in the formation of a square, while combining six tetrahedral units results in a hexagon \cite{56}.

Subsequently then, by combining these hexagons and squares, the cubo-octahedron, sodalite, may be formed. Sodalite, also known as a $\beta$-cage, is an important secondary building unit, which has projecting oxygen atoms, available to form bonds with other
sodalite cages, at intersections — from which various zeolite structures are derived \[^{58}\]. One example is the zeolite faujasite, which results from the junction of sodalite units via their hexagonal faces, whereas the A-type zeolite is formed through the connection of sodalite units via their square faces \[^{58, 56}\].

The connection of 24 sodalite cages (\(\beta\)-cages) via their hexagonal faces results in the formation of the mineral, faujasite also known as zeolite-Y. Figure 2.7 gives an illustration of the structure of faujasite, resulting from the binding of 24 sodalite cages. Faujasite plays a very important role, both in terms of heterogeneous catalysis, as well as environmental protection. This can be attributed to its relatively spacious pore system; consisting of what is known as supercages, with a diameter of 1.3 nm. The spaciousness of the pores will thus also allow easier access to potential constituents (e.g. metal ions), resulting in better ion retention capacity. According to UIPAC classification, it is classified as a three-dimensional 12-membered–ring pore system \[^{58}\].

Figure 2.7 The structure, micropore systems and dimensions of faujasite, derived from the binding of 24 sodalite cages \[^{58}\]
2.8 Synthesis of zeolites from fly ash

The attraction of zeolitization of pulverized fly ash (PFA) were explored when the need arose for inexpensive synthetic zeolites with built-in adsorption properties, since fly ash is a low cost, readily available raw material for such products \[12\].

Experimenting with the synthesis of zeolites from fly ash was initiated by Holler and Wirsching in 1985. Testing the potential of zeolite growth from fly ash was prompted by the similar chemical composition of fly ash and some volcanic rocks, precursor of natural zeolites, (interaction of volcanic ash with hydrothermal solutions or groundwater transforms it into natural zeolites \[12, 62\].

Due to the high content of reactive phases such as aluminosilicate glass, and to the high specific surface area of fly ash, these combustion wastes are suitable starting materials for the synthesis of zeolites \[12\].

The major components of fly ash is silicon dioxide (SiO\(_2\)) and aluminum trioxide (Al\(_2\)O\(_3\)), which are the essential reagents in the synthesis of zeolites.

Since the initial studies by Holler and Wirsching, various research articles have been published, proposing different hydrothermal activation methods for synthesizing zeolites from fly ash, including \[63, 64, 65, 66\].

All the methodologies developed for the synthesis of zeolites from fly ash are based on the dissolution of Al-Si-bearing fly ash phases with alkaline solutions.
(predominantly NaOH or KOH solutions) and the subsequent precipitation of zeolitic material \cite{12, 62}.

Zeolitization proceeds in various stages, during which the Al- and Si- bearing phases of the fly ash are sequentially dissolved, with the aluminosilicate glass phase being activated first, followed by the quartz phase and lastly, digestion of the mullite phase. Two fly ashes therefore, with similar SiO$_2$/AlO$_3$ bulk ratios, but different quarts-mullite/glass, proportions; resulting in different glass matrix composition, under the same activation conditions, will consequently produce different zeolites. One can conclude, that the SiO$_2$/Al$_2$O$_3$ ratio of the glass matrix is one of the parameters exerting a major influence on the type of zeolite produced. The other important parameters for zeolite growth from fly ash are:

- **Activation time**

  The time needed for good synthesis yield are inversely proportional to the glass content, with longer time required (24 to 48 hours) to obtain a good yield from high mullite or quarts fly ashes.

- **Activation agent concentration and temperature**

  Application of lower temperature and concentration will result in the production of zeolites with high cation exchange capacities (CEC), such as NaP, A, chabisite, etc, while increasing these parameters will consequently produce low CEC zeolites such as hydroxyl-sodalite.
• **Fly ash/activation solution ratio**

With higher-activation solution/fly ash ratio, the highest synthesis yields are obtainable, but certain disadvantages are encountered, including increased water consumption and longer activation periods. Conversely lower activation solution/fly ash ratios dramatically reduced the activation time as well as the water consumption, but total dissolution of quartz and mullite is not achieved. By varying the parameters influencing the classic alkaline conversion of fly ash, including different activation solution/fly ash ratios; temperature; pressure and reaction time, the various researchers mentioned above have proved that zeolites can be produced by the hydrothermal treatment of fly ash.

During a research investigation conducted by V. Somerset \[29\], the conventional hydrothermal activation method proposed by Rayalu et. al. \[9\] for the synthesis highly crystalline faujasite was customized and optimized for the synthesis of faujasite from co-disposal precipitates, collected at near neutral pH.

2.9 **Conclusions.**

All the conventional treatment technologies for AMD and its derived process stream fall prey to numerous drawbacks and as such alternative low cost treatment methods are explored. Fly ash can be successfully applied to treat metal-bearing waste waters. The synthesis of zeolites from fly ash has been extensively investigated. Prior
research has shown that the fly ash-related material could be successfully used for decontamination of metal-bearing effluents. Further research has shown that the neutralization reaction (co-disposal reaction) of fly ash and AMD produced a cleaner process effluent and the collected neutral solid residues may be used for the synthesis of high capacity inorganic ion exchangers. These ion exchangers may be used for decontamination of metal bearing waste waters.
CHAPTER 3

Variables for Investigation

3.1 Introduction

This chapter takes a much closer look at the specific variables which needs to be considered during the application of inorganic exchangers (zeolites) and resin exchangers, as applied in the current study. The significance of this review, is the formation of the basis of the experimental methods of investigation, specifically in terms of decontamination investigation parameters, because the experimental methods used are based on the qualitative assessment of such variables. Moreover, this review also gives an enhanced understanding of the obtained results, since it assesses and defines important aspects, as it applies to the zeolitic material produced in this study.
3.2 Total Capacity

An ion exchanger can be considered as a “reservoir” of exchangeable mobile ions (also referred to as functional groups/ionogenic groups, or exchangeable cations) and these ions are utilized in ion-exchange operations and hence, the number of ionogenic groups/exchangeable ions per specified amount of ion exchanger is one of the most important characteristics of an ion exchanger [54].

It is therefore important that the total number of exchangeable ions and as such, the total number of sites available for exchange, of an ion exchange material, should be determined prior to ion exchange application. Since every type of ion exchanger portrays a characteristic constant of exchange sites available for ion exchange, this phenomenon can be used for characterization of a particular ion exchanger, and it is usually independent of experimental conditions [54].

In the case of zeolites, evaluation of their total exchange capacity may be determined by ammonium acetate extraction, in which the amount of ion (NH₄⁺) adsorbed by the zeolite, while displacing the exchangeable cations inherent in the zeolite structure is measured and the exchange capacity subsequently determined [67].

In the case of ion exchange resins, on the other hand, the total capacity determination is normally done after converting the resin by chemical regeneration techniques to a given ionic form. The exchangeable ions are then chemically removed from a measured quantity of the resin and this process can be done by titration, as a function
of solution pH; in which the titrant used, depends on the type of exchanger; for example, in the case of a weakly acidic exchanger, sodium hydroxide may be used as titrant. A quantitative determination of the exchangeable ion; removed from the resin, can be done by conventional analytical techniques, such as atomic absorption spectroscopy (AAS), or inductively coupled plasma mass spectroscopy (ICP-MS). The total capacity of ion exchangers is usually expressed in milliequivalents per gram (meq g⁻¹) or in milliequivalents per 100 grams (meq/100g) of exchanger.

3.3 Ion-exchange Equilibria [54]

During ion exchange operations, the exchanger is contacted with a solution and this may be done through batch type reactions or by ion-exchange columns. In these applications, a measured amount of ion exchanger, be it zeolite or resin, are contacted with a certain volume of the solution, containing the desired impurities. Batch type experiments are usually done under agitation such as stirring or shaking, while in the case of columns, no agitation is necessary, since the predetermined amount of ion exchanger is placed in the column, while the particular solution runs through it at a certain rate and as such the selected ions are retained within the ion exchanger [54].

Thus, during the exchange process, ions from the ion exchanger, are exchanged for similarly charged ions from the solution and this process is illustrated in equation 3.1:

\[ z_B A_z^{x+} + z_A B_z^{y-} \rightleftharpoons z_B A_z^{x+} + z_A B_z^{y-} \]
Where $z_A$ and $z_B$ are valences of the in-going and out-going positively charged ions, A and B and subscripts s and z refer to solution and zeolite phases, respectively. At equilibrium, both the ion exchanger and the solution contain both counter-ion species, A and B.

As a rule, during ion exchange processes, the ion exchanger prefers one species to another and this ability of the exchanger to distinguish between various counter ion species is called selectivity $^{[54]}$.

### 3.3.1 Selectivity

Selectivity is a characteristic of an ion exchanger, which prompts the exchanger to prefer one counter-ion to another and as such, this phenomenon drives the reaction either to the left or right hand side. The overall selectivity of the exchanger may quantified in terms of the selectivity coefficient.

The selectivity coefficient for equation (3.1), above can be written as follows:

$$ K_{C/A} = \frac{[RC]^{Z_A}[A]^{Z_c}}{[C]^{Z_A}[RA]^{Z_c}} $$

(2)

The above reaction (equation 3.2) is obtained by the application of the mass-action law to the ion exchanger; however, the selectivity coefficient is not constant over a wide range of concentration ratios and surface concentrations $^{[54]}$ and as such, other methods may be applied when determining selectivity. One such method is the distribution coefficient, which is discussed later in the chapter.
According to literature findings, the preference of an ion exchanger for a particular species may have various causes, of which the most important being:

- The electrostatic interactions between the charged framework of the exchanger and the counter ions (from solution) depend on the size and, in particular, on the valence of the counter ion.
- In addition to the electrostatic forces, other interactions between the ions and their surrounding environment may effectively play a role.
- The pore structure and size of the exchanger, particularly zeolites, may have the effect that large counter ions are sterically excluded, with factors such as ionic radius and hydration shell strongly playing roles in this respect.

However, often, selectivity is a result of a combination of two or more of these factors, but from the above factors it may be safe to assume that selectivity is by and large due to the nature of the counter ion contained in the surrounding solution.
3.3.1.1 Factors influencing and contributing to selectivity

Electric interactions between the ion exchanger and the metal cation, may involve amongst others, one main interaction, electroselectivity.

- **Electroselectivity**

The valences of the counter ions have a strong effect on ion-exchange equilibria. This effect is purely electrostatic. As a rule, the ion exchanger prefers the counter ion of higher valence; the preference increases with dilution of the solution. The strength of the electrostatic attraction depends mainly on the ionic charge and the distance of closest approach between the counter ion and the functional groups.

- **Selectivity based on interaction of hydrated counter ions with functional groups**

Every metal cation, dissolved in water has a hydrated layer, in which the water molecules surrounds the metal ion and as such an aqua complex, \((\text{M(H}_2\text{O)}_x\text{)}^{n+}\), is formed \[^{68}\]. The hydrated layer surrounding the cation has a characteristic thickness and stability, which can be expressed in terms of hydration enthalpies.

In the case of zeolites, they are rigid structured ion exchangers, with uniform pore sizes and due to their sieving action, can totally exclude a counter ion if the size
exceeds the zeolite pore size, because in their case, swelling pressure is considered an infinite factor. However, for a hydrated cation (counter ion) to enter a zeolite structure, it normally needs to shed some of its hydration shell and zeolites with high exchange capacities (high charge densities) can easily strip the hydration shell of a aqua cation complex.

For zeolites, the character of selectivity changes as a function of ion exchange capacity and pore size. In a zeolite with a low exchange capacity, the dominant action for selectivity, is its sieving ability. Zeolites with pore diameters, smaller than the fully hydrated metal cation, prefers counter ions with a hydrate layer which has the lowest possible stability, since shedding part of the hydration layer will then be easier.

In zeolites with very high exchange capacities, the effect of the counter ion’s hydration shell is not very significant and as such do not play such a major role during the interaction of the ion with the zeolite structure. This latter statement is exemplified, due to the fact that high charge density zeolites can strip the hydration shell of the aqua complex, regardless of hydration energy and as such, selectivity, depends on the association of cation to the zeolite.

In the case of ion exchange resins, when a larger, fully hydrated counter ion enters an ion exchanger, they produce a pressure which tends cause swelling of the solid matrix and this phenomenon is known as swelling pressure. If the large hydrated counter ion is replaced by a smaller counter ion, the swelling pressure becomes
lower, and consequently the ion exchange resin prefers ions with smaller hydrated
diameters. Resins with increased crosslinking experiences the effect of swelling
pressure stronger.
The structural elasticity of ion exchange resins causes selectivity partly on the basis
of the hydrated ion diameter and partly on the basis the stability of the hydration
shell.

- **Other interactions between counter ions and functional groups**

Other interactions between the counter ion (metal ion) and the fixed ionic groups can
be the formation of chemical bonds, which could have an ionic or covalent bond
character; or in the case of transition metals, is referred to as a coordination bond [54]
The bond character is determined by the ability of the exchanger and the cation to
donate and accept electrons.

Generally, all inorganic exchangers forms ionic bonds with all metal ions, with very
few exceptions. The few exceptions, are, amongst others, organic complexing agents
which are immobilized in the inorganic substructure.

Resin exchangers, however, may also form a wide variety of bonds, ranging from
ionic to coordinate bonds. When the resin has chelate forming functional groups, or
donor atoms without an electric charge, such as nitrogen or sulfur, a more covalent
bond character results.
The main rule is that ion exchanger prefer counter ions which can form stronger bonds with the exchanger and this rule can be explained in terms of the Le Chatelier principle.

In conditions where the ion exchange process occurs in considerably alkaline pH ranges, the precipitation of certain solid phases on the surface of the ion exchanger may be induced and as such, they can act as crystallization seeds for the subsequent precipitation of the counter ion. The result would be the enhancement of the counter ion uptake by the ion exchanger. This occurrence has a particularly high probability during experiments with inorganic exchangers, such as the ones synthesized in this study.

However, in practice, precipitation is usually avoided because it may, in some cases, clog the pores of the ion exchanger.

The temperature dependence of equilibria in general, is related to the standard enthalpy change which accompanies the reaction.

Ion exchange is not a chemical reaction and occurs, as a rule, with little evolution or uptake of heat. However, ion exchange may be accompanied by other processes (e.g. sorption, specific adsorption, etc), with considerable enthalpy changes. Temperature fluctuation thus, may very well influence process as a whole, because temperature elevation may increase the available surface area, as well as changing pore sizes of the exchanger; or temperature elevation, may also enhance the diffusion rate of counter ions, all of which can result in the increase of the ion exchange rate. The
overall effect will then be an enhancement of metal retention capacity of the exchanger.

3.3.2 The distribution coefficient and practical capacity

The distribution coefficient \([K_D]\) is a measure of the distribution of the counter ion between the solution and the solid exchanger at equilibrium, and it is highly dependent on the selectivity of the ion exchanger. Thus in many interactions between ion exchangers and metal ions, the reaction equilibrium may be expressed in terms of the distribution coefficient.

The distribution coefficient may be defined by equation 3.3:

\[
K_D = \frac{(C_i - C_e)}{C_e} \cdot \frac{V}{m} = \frac{\%\text{Ads}}{(100 - \%\text{Ads})} \cdot \frac{V}{m}
\]

(3.3)

Where

- \(C_i\) and \(C_e\) refers to the initial and equilibrium counter ion concentrations, respectively.
- \(V\) and \(m\) refers to the volume effluent and mass solid exchanger, respectively.
- \(\%\text{Ads}\) refers to the % counter ion (metal ion) removed from solution.

\(K_D\) is expressed in ml/g.

In general, experimental conditions, such as metal concentration and pH have a considerable effect on the distribution coefficient; however, the numerical \(K_D\) value
can be used as a comparative measure in the determination of the efficiency, as well as the selectivity of ion exchangers, in terms of metal ion removal.

The sorption capacity; also known as the practical specific capacity, or the operating capacity, is also an important parameter and can be determined after the equilibration of the ion exchanger with the polluted solution. This capacity is an indication of the amount of metal ion loaded onto the solid phase (amount of solute taken up by ion exchanger, \( q_e \)) and as such, can be defined as the proportion of the total capacity of the ion exchanger, used during the ion exchange process. This parameter is highly dependent on experimental conditions and as such is influenced by quite a number of factors, including the following \(^{[53, 54]}\):

- total capacity; since an ion exchanger with a high total capacity, will subsequently have a high operating capacity;
- concentration and type of ions to be sorbed;
- site accessibility: although a particular ion exchanger may have a variety of sites available to a given ion, these sites may show different relative affinities for different ions; consequently the accessibility and hence exchange rate may be different for the different sites ;
- pH variation might not directly influence the exchange reaction, but will definitely change the metal speciation and in the process, may change the exchanger’s affinity toward a particular metal ion;
- temperature and
• the rate of agitation or, in the case of column treatment; rate of percolation, might influence operating capacity.

The operating capacity may be expressed in meq g\(^{-1}\), mg g\(^{-1}\) or mmol g\(^{-1}\).

3.4 Competing ions

In wastewater effluents, beside the exchangeable metal contaminants which is to be removed, there are other species which will interfere with the ion exchange process by competing for the available exchange sites on the ion exchanger and as such, may adversely effect the success of the process. It is thus beneficial to investigate the effect of competing ions, on the metal loading onto a given ion exchanger.

3.5 Interactions between zeolite and metal ions (counter ions)

To understand the dynamics involved in the processes taking place at the solid-solution interface, between zeolites (as the ones produced in this research investigation), one requires an appreciation of the reactions describing the transfer of metal ions between the zeolite and the aqueous solution, as well as an understanding of the structure and chemical bonding at the zeolite-water interface. Thus bearing in mind the previous statement, prior research investigations have established that
when studying the adsorption behavior of metal ions (Me$^{n+}$) on zeolite structures, the following reactions needs to be considered:\cite{69}:

- **ion exchange** of the exchangeable cations within the zeolite structure for the counter-ions from the solution;
- **surface hydrolysis** of the meal ions and their exchange for protons in the hydroxide bridges, between the surface functional groups;
- the strength of the metal ion interaction with the zeolite framework, is largely dependent on the **hydration** of the metal.
- competing exchange reactions between counter ions in solution and free hydronium ions (H$^+$), a phenomenon that normally occurs in acidic solutions.

To gain a better understanding of these reactions and the solid-solution interface as a whole, the following section gives a detailed overview of the process mechanisms.

### 3.5.1 Metal ion hydration

The first aspect to consider in an interaction between a zeolite, or any other solid exchanger and a bulk solution, is metal hydration, which is brought about by the attraction of the metal ions for the surrounding water molecules and as such, favors the dissolving of the ionic solid in the water.

The energy and attraction between an ion and water molecules are caused by interactions known as ion-dipole forces which occurs as follows:
• Water molecules are polar, so they orient themselves with respect to nearby ions. In the case of a cation, the water molecules orient with their oxygen atoms (which is the negative ends of the molecular dipoles) toward the cation. However, in the case of an anion, the water molecules orient with their hydrogen atoms (the positive end of the molecular dipoles) toward the ion.

An example of a cation, surrounded by water molecules can is illustrated in figure 3.1

Figure 3.1 Adsorption of water molecules onto a metal cation (e.g. Zn$^{2+}$), referred to as hydration$^{[70]}$.

The strength of the force between the ion and the surrounding water, is largely dependent on the charge density of the ion and as such, a smaller ion, which has a large concentrated electric charge will attract water molecules more strongly, resulting in a corresponding high energy of hydration$^{[70]}$.

Once hydrated, the metal ion is referred to as the aqua-ion, while the metal-water complex is referred to as the metal-aqua-complex. Hydration may also be followed by hydrolysis; defined as the degree to which the adsorbed H$_2$O molecules dissociates to satisfy the electronegativity, or more simply defined as the reaction of
an ion with the water molecules to produce the conjugate acid and hydroxide base, or
the conjugate base and hydrogen ion \footnote{70}. Equation 3.4 illustrates the hydrolysis
reaction of metals:

\[
[M(H_2O)_x]^n^+ + H_2O \leftrightarrow [M(H_2O)_{x-1}(OH)]^{(n-1)+} + H_3O^+ \tag{3.4}
\]

Where

\begin{align*}
M & = \text{refers to the metal ion} \\
N & = \text{the valence of the metal ion}
\end{align*}

3.5.2 Transport of the metal ion complex to the zeolite surface

The next step involves the transport of the metal-aqua-complex, from the bulk
solution to close approximation with the surface of the zeolite structure and this can
take place through convection and/or diffusion processes.

Thus, the metal-aqua-complex are brought within “critical distance” from the
charged surface functional groups; which spans the zeolite surface, and as such can
interact with these functional groups in a number of different ways which will be
subsequently discussed.

3.5.3 Zeolite-solution interface

The crystal structure of zeolites, earlier said as being are made up of SiO₄ and AlO₄
tetrahedra which are joined at their corners through a common oxygen. The overall
effect being that the net formulae of the tetrahedra are SiO$_2$ and AlO$_2^-$, i.e. one negative surplus charge resides at each tetrahedron in the framework which has aluminum at its center and this negative charge, is counter balanced by the exchangeable cations, which is used for ion exchange processes. Thus, the bridged ≡Al-O-Si≡ functional groups would form part of the surface moiety found on the zeolite surface and they represent sites which can be used for potential ion exchange or complex formation (outer and/or inner-sphere complexes) with the aqua-ions from the metal-complex $^{71, 72}$.

Amongst these sites on the zeolite surface, some have a fixed charge and thus represents the effective negative charge of the zeolite; as such they may be referred to as \textit{permanently active charged sites} and the primary action which takes place at these sites are \textit{ion exchange reactions}.

In addition to the fixed charged sites, on the zeolite surface, one also finds what is referred to as \textit{variable charge sites}, in which the functional groups (≡Al-O-Si≡) interact with the surrounding water molecules and as such can either be protonated or deprotonated. \textbf{Figure 3.2 (a) and (b)} illustrates the protonation and deprotonation reactions of the variable charged surface functional groups:
Figure 3.2 (a), (b): The protonation (a) and deprotonation (b) of hydroxyl bridges of the variable charge functional groups on the zeolite surface [73]

The overall effect of the reactions shown to occur in Figure 3.2 (a and b), results in variable charged sites on the zeolite surface, providing adsorption sites for metal ions.

Another phenomenon known to occur at the zeolite surface, which also plays an important role in the retention of metals is dissolution of the zeolite phase; a process which is highly pH dependent, since it is catalyzed by hydroxyl ions, hydronium ions and/or water. In this process, detachment of a surface unit into the aqueous phase occurs and this charged surface unit is thus the precursor for complex formation on the zeolite surface, with counter ions from solution. An example of zeolite dissolution is illustrated in equation 3.5, which is shown to be acid catalyzed and as such is expected to happen in acidic environments – a process that may potentially be beneficial for anion adsorption [71, 74].
\[ \equiv \text{Al—O—Si} \equiv + \text{H}^+ + \text{H}_2\text{O} \leftrightarrow \equiv \text{SiOH} + \equiv \text{AlOH}_2^+ \] (3.5)

In light of all the latter interactions around the zeolite surface, one can thus conclude the following:

At the zeolite-water interface there is a separation of electric charge. The distribution of ions in the neighborhood of the charged surface is idealized by what is known as the electrochemical double layer (EDL). The EDL is characterized by a fixed charge, or surface charge attached to the solid surface (permanently active charged sites); while the other layer is distributed more or less uniformly on the electrolyte (solution) or in contact with the charged solid surface, which have been described earlier as being the variable charge sites [71, 73].

Thus in general, the surface moiety of the zeolite surface may be perceived as a metal complex (Si and Al) with aqua, oxygen, hydroxo or other ligands and these functional groups can be used to remove metal ions from solution in a number of ways, which will be discussed in detail, in the decontamination results section [71].

3.5.4 Diffusion of metal ions through zeolite pores

Ideally, the aqua-ion diffuses through the zeolite pores and gets exchanged with the exchangeable cations from the zeolite structure (Na\(^+\)). However, before the metal ion can move through the pores it also has to undergo rejection of some of its
surrounding water molecules – a process which differs from one metal cation to the next, since the extent of hydration depends on the size of the bear metal ion. After water dissociation, the metal ion then proceeds to diffuse through the zeolite pores into the smaller zeolite channels, at which point it may have to loose some more water molecules if the hydrated ion is still too bulky, followed by the retention of the aqua-ion in the zeolite, with a simultaneous release of equivalent (charge based) amount of Na⁺ ions into the solution and as such, the sodium concentration in the effluent is subject to increase.

In practical applications, ion exchange is usually not the only mechanism of metal retention and can thus be accompanied by numerous other reactions; however these mechanisms are discussed in detail in the decontamination results section of this research investigation.
CHAPTER 4

Experimental Methods of Investigation

4.1 Introduction

This chapter gives a concise, yet detailed description of the sample preparation procedure followed for the FA/AMD-solid residues (co-disposal precipitates: AFA-Nav-ppts) preparation, as well as synthesis procedure of the high capacity inorganic ion exchange materials (FA/AMD-related zeolites (HCIM), ArnavZ₁, ArnavZ₂ and ArnavZ₃). In addition, all physical and chemical characterization techniques used for analysis of samples are described.

Also described in this chapter, is the experimental protocol for the various decontamination experiments (including model solutions, as well as FA/AMD-process waters). All the necessary calculations are also presented.

4.2 Preparation FA/AMD-process solids and zeolitic material

The method of zeolite synthesis follows the procedure outlined in the masters dissertation of V. Somerset [29], which involved a tailored modification of the classical alkaline hydrothermal treatment of fly ash to produce crystalline Faujasite...
zeolites\textsuperscript{[9]}. During the study, conducted by V. Somerset the conventional zeolite synthesis was customized and optimized for the synthesis of Faujasite from FA/AMD-solid residues; collected at near neutral pH from the co-disposal of predetermined fly ash/AMD ratios, as starting materials\textsuperscript{[29]}

4.2.1 Raw material sampling sites and sampling methods

The fly ash used for the present study, which includes adsorbent material preparation, as well as FA/AMD-process water (secondary co-disposal process water) preparation was collected from the ash disposal sites at Arnot Eskom coal fired power station, near Witbank, Mpumalanga, in South Africa. Fly ash was taken from the hoppers and collected in either high density polyethylene (HDPE) plastic buckets or in high density, air tight sealed plastic bags. The collection date, hopper number and sample number were recorded on the containers. The labeled containers were subsequently sent to the Bellville laboratories by courier service.

The acid mine drainage (AMD) was obtained from the Navigation coal mine near Witbank, where it was collected in plastic containers from the AMD ponds at the mining area.

The collected AMD was transferred into 5 litre HDPE plastic containers, and sampling was done in such a manner to keep air out of the containers. This was achieved by filling them up to the top, after which the containers were tightly sealed with air tight fitting lids. The collection date, sampling site, sampler and sample
number were recorded on the containers. The labeled samples were refrigerated at 4°C and couriered to the research laboratories in Bellville, where they were again refrigerated at 4°C upon receipt.

4.2.2 Preparation of near neutral fly ash plus acid mine drainage co-disposal precipitates (FA/AMD-solid residues: AFA-Nav-ppts)

This method involves the neutralization co-disposal reaction between FA and AMD. In these experiments, the volume of acid mine drainage and mass of fly ash added, was based on a pre-determined ratio. The ratio of FA:AMD was 1:3.5 and this exact ratio was used in the synthesis of all high capacity inorganic ion exchange materials, recorded in this research investigation (ArnavZ1, ArnavZ2 and ArnavZ3).

4.2.2.1 Experimental procedure

Based on the pre-determined ratio of FA:AMD (1:3.5), a specific volume of AMD was pored into a beaker, and it’s initial EC, pH and TDS measurements recorded at ambient temperature. Subsequently, a known mass of dry FA, also measured with respect to the pre-determined FA:AMD, ratio was mixed with the AMD. The fly ash used for the preparation of the co-disposal precipitate for both ArnavZ1 and ArnavZ2 were obtained from the same sample container. In the case of ArnavZ3
solid residue preparation, on the other hand, fly ash was obtained from a different sample container. The anticipated significance of the different FA sample; although obtained from the same sampling site, will be discussed later in the thesis.

The reaction mixture of FA and AMD was then stirred with an overhead stirrer, fitted with stainless steel paddle impellers. The measurements for EC and pH of the co-disposal reaction mixture was initially taken every ten minutes for the first hour, after which it was recorded between longer time intervals (e.g. 30 minutes, 1, 2 and 3 hours) until the a near-neutral pH of approximately 7 was obtained. At that stage the reaction mixture was filtered with Whatman filter paper and buchner filtration system, after which the filtrate was collected and stored in a plastic HDPE container at 4 °C, while the co-disposal precipitate was dried in an oven at 70 °C. Once dry, the FA/AMD-solid residues were stored in air tight HDPE plastic containers. This was then the starting material for the zeolite (Faujasite) synthesis.

The filtrate collected from the co-disposal of FA with AMD was referred to as or FA/AMD-process effluent (secondary co-disposal process waters).
4.2.3 Synthesis of high capacity inorganic ion exchange material (HCIM)

This is the stage that involved the utilization of the collected near neutral FA/AMD-solid residues as starting materials for the synthesis of high capacity ion exchange adsorbent material.

During this research investigation, the aim was to synthesize a highly crystalline faujasite type zeolite. The zeolite synthesis method involved a fusion step, an aging step and crystallization step:

4.2.3.1 Fusion process

The fusion step was employed for optimal extraction of alumino-silicates from the FA/AMD-solid residue starting materials.

The collected FA/AMD-solid residue (co-disposal precipitates) was fused with sodium hydroxide (NaOH) in a 1:1.2 ratio (FA:NaOH). The fusion mixture of FA:NaOH was obtained by grinding and mixing the reactants (FA/AMD-solid residue + NaOH) with mortar and pestle and once a fine, homogeneous mixture was obtained, it was heated to 600 °C.

In the case of the preparation of ArnavZ₁ and ArnavZ₂, the grinded mixture was not placed in a pre-heated furnace. After placing the mixed reactants in the furnace, the temperature was slowly raised to the pre-determined 600°C and subsequently heated
for exactly 2 hours. In the case of ArnavZ$_3$, on the other hand, the grinded reactants were placed in a pre-heated furnace and fusion was done for 2 hours at 600 °C.

At the completion of the fusion step, the products were cooled to room temperature and again ground and milled with mortar and pestle.

4.2.3.2 Aging process

Once at room temperature, the cooled fused product was subsequently mixed with deionised water, in a measurement of six times its quantity and the thoroughly mixed slurry was subject to ageing for 8 hours. The mixing and ageing process was done in a high density glass McCartney (Schott) bottle.

The aging method followed, was exactly the same for all zeolitic material synthesized.

4.2.3.3 Crystallization and collection of zeolitic product

The aluminosilicate fused mass/slurry, obtained after fusion and aging is amorphous and changes to crystalline state when subjected to hydrothermal crystallization; which occurred in this step. The method used were as follows:

The aged slurry was subjected to hydrothermal crystallization by placing it in a thermostat oven at 100 °C for a period of 24 hours. At the appointed time, the
crystallized product was removed from the oven and allowed to cool to room temperature for approximately 30 minutes to 1 hour. The solid zeolitic product was recovered by filtration (Whatman filter paper) and thoroughly washed with copious amounts of deionised water until a filtrate pH of between 10-11 was obtained. The collected product was subsequently dried at 70 °C, after which it was cooled to room temperature and transferred to an airtight glass or plastic vial-type container and kept sealed until it was used in the decontamination experiments.

In summary, thus:

By alkaline fusion of FA/AMD-related starting materials with NaOH, the aim was to produce as far as possible, a highly crystalline, homoionic Na-form faujasite type zeolite and its subsequent application in decontamination experiments.

In the quest to synthesize a faujasite type zeolitic material, three fly ash-related zeolitic material were produced and they were labeled:

- ArnazZ₁;
- ArnazZ₂ and
- ArnazZ₃
4.3 pH, electrical conductivity (EC) and total dissolved solids (TDS) measurements

All pH measurements were taken using an Orion 420 A+ pH/ORP/ meter, with an automatic internal temperature sensor. Calibration of the instrument was done using a three point calibration at pH 7, pH 4 and pH 10. The EC and TDS was measured with a portable, Hanna HI 991301 pH/EC/TDS/Temperature meter instrument. Calibration of the instrument was done prior to sample measurements, with a standard HI 70030P 12.88 mS/cm (set at 25 °C) calibration solution.

4.4 Mineralogical characterization

4.4.1 X-ray Diffraction Spectrometry (XRD) analysis

The FA/AMD-solid residue and zeolite sample mineralogy was evaluated by conducting XRD spectrometry. X-ray diffraction spectrometry (XRD) analysis was also employed to monitor the success of zeolitization of the various synthesized zeolitic material. The instrument used in this case was a Philips Analytical graphite monochromator with copper Kα radiation, and 2θ values ranging from 5 to 70°, using a 0.1 interval with 2 second counts, were used. The mineral phases present in the adsorbent material, were searched and identified with the internal JCPDS reference
library, while the graphical presentation were done with the application of X’Pert Graphics \cite{75, 76}.

### 4.4.1.1 Sample preparation for XRD analysis

Particle size should be fairly uniform and small, preferable less than 10\(\mu\), as well as well dried. The newly synthesized zeolite material was therefore milled and ground with mortar and pestle, into a fine powder form and dried overnight in an oven at about 70 °C.

Approximately 3g of the dried specimen was transferred into the holding area of the sample holder, which should be of sufficient size, so that the beam can irradiate the actual sample and not the holder, which may give rise to spurious peaks. To prevent orientation of the grains within the holding area, as well as to ensure a flat sample surface area, the sample was flattened with filter paper or a small, square glass plate. The specimen was subsequently transferred to the aluminum analysis port, where the analysis took place.
4.5 Physical characterization

4.5.1 Nitrogen Brunauer-Emmett-Teller (N$_2$-BET) surface area determination

The BET technique has the ability to provide information on the specific surface area, total pore volume, pore size and pore volume distribution of the specified specimen, and as such, is used to determine the surface morphology of the sample.

a) In BET analysis, characterization is done with gas adsorption, and of all readily available gases, nitrogen proved to be the superior adsorptive and is thus universally pre-eminent. The physical adsorption reactions applied in this technique, are weak Van der Waals forces. Here use is made of a Nitrogen adsorption porosimeter\cite{77, 78}.

4.5.1.1 Method and sample preparation\cite{77, 78}

The specific surface area and volume of the micropores of the zeolite samples were determined with a Micromeritics, Tristar 3000, Micropore analyzer. Sample characterization was based on the physical adsorption of nitrogen at liquid nitrogen temperature, 77K.

- Sample preparation

Approximately 3g of the zeolite sample were milled and ground to obtain an even particle sized powder. The sample was dried for 24 hours at approximately 70 °C.
prior to analysis. Approximately 1g of the sample was weighed out for the actual BET analysis.

The specimen was degassed at 120 °C in flowing He, to remove all moisture and then at 350 °C under vacuum, in order to free all the pores of any gas particles. The weighed specimen was then inserted into the analysis port and analyzed at liquid nitrogen temperature (-196 °C), followed by the admission of the adsorbing gas in incremental doses and its equilibration in a static volumetric system until atmospheric pressure was obtained.

The accumulated gas quantity adsorbed, versus the pressure at a particular temperature, was graphed to generate an adsorption isotherm. The information obtained from the adsorption isotherm allowed the characterization of pore size distribution, as well as total surface area and micropore volume.

4.6 Chemical characterization

4.6.1 X-ray Fluorescence Spectrometry (XRF) analysis

The elemental composition, measured as major oxides, including the major and minor heavy metals contained in the FA/AMD-solid residue samples, as well as for selected high capacity ion exchange zeolitic material (HCIM) was measured by XRF analysis. The instrument used, was a Philips 1404 XRF Wavelength Dispersive Spectrometer, utilizing 6 analyzing crystals and a Rh X-ray tube target. To prevent
interaction of the X-rays with air particles, a vacuum was used as the medium of analysis.

4.6.1.1 Method and sample preparation

The sample (FA/AMD-solid residue and/or HCIM) were dried at 70 °C for 24 hours, and then milled and ground with mortar and pestle, to obtain a homogeneous powder. Prior to analysis, the sample was further crushed in a Zibb mill to reach a grain size of approximately 5 µm and then 1 g of the sample was heated for 5 hrs at 110 °C. It was again weighed after heating to determine any adhesive water present. Subsequently, the sample was then heated for 5 hours at 900 °C, after which it was weighed to determine any other volatiles present (e.g. S, C, N compounds) and presented in analysis as LOI (Loss on Ignition). This figure may be positive in the event of any oxidation, taking place during the time in the furnace at 900 °C.

Approximately 0.28g of the sample was weighed out of the 110 °C H2O - and LOI-determined sample into a platinum crucible and thoroughly mixed with 1.5g Norrish Spectroflux no. 105 (a mixture of 47% Li2B4O7, 36.7% Li2CO3 and 16.3% La2O3 to enhance the fluxing process). The next step involved heating it at 1000 °C for 5 hrs to start the melting process. Individual samples were then heated over a flame to melt completely and poured onto a carbon disc where they were pressed to produce a flat penny-shaped disc. Care was taken not to leave the sample over the flame for too
long as the alkali elements (Na, K) may vaporize over direct heat. The disc was then ready for analyses by XRF.

The spectrometer was fitted with a Rh tube with six analysing crystals, namely: LIF200, LIF220, LIF420, PE, TLAP and PX1 and the detectors – a gas-flow proportional counter, scintillation detector or a combination of the two. The gas-flow proportional counter uses P10 gas, which is a mixture of 90% Argon and 10% Methane. Major elements were analysed on a fused glass bead at 50 kV and 50 mA tube-operating conditions. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured.

4.6.2 Exchangeable cations and cation exchange capacity (CEC) [67]

4.6.2.1 Materials

- 250 ml round-bottom flask with splash head condenser;
- A 1M ammonium acetate solution, adjusted to pH 7, with the addition of glacial acetic acid;
- A potassium chloride (KCl) solution with a resultant pH of 2.5 (made by dissolving 100g of KCl to 800 ml water in a 1L flask and the subsequent addition of 3.0 ml 1M HCl, then made up to the mark);
- A 40% sodium hydroxide solution;
- Boric acid (H₃BO₃), prepared by dissolving 20g H₃BO₃ in a 1L flask with deionised water;
• 95% ethanol;
• A 0.01M hydrochloric acid (HCl) solution;
• Mixed indicator, prepared by dissolving 0.1g methyl red and 0.1g bromocresol green in 250 ml ethanol;
• A borate buffer solution, made up by dissolving 9.5g Na₂B₄O₇·10H₂O in 1L deionised water and subsequently mixing 500 ml of this solution with 88ml sodium hydroxide and made up to the mark with deionised water in a 1L volumetric flask;
• A mechanical shaker;
• Whatman no. 44 filter paper;
• Filter funnels

4.6.2.2 Exchangeable cations (Ca²⁺, Mg²⁺, K⁺, Na⁺)

The procedure to determine the amount of exchangeable cations held in the “exchange sites” of the zeolite, involved replacing the exchangeable cations in the zeolite by a added cation (NH₄⁺) and measuring their concentration [67].

Approximately 5g of zeolite sample was weighed out and placed in a 100 ml polyethylene bottle, after which, 25 ml ammonium acetate solution was added and the mixture shaken in a mechanical wrist shaker, for 1 hour. The supernatant was then filtered directly into a 100 ml volumetric flask through a filter paper held in a
funnel inserted in the neck of the flask, but care was taken not to pour any solid material into the funnel. Then, 20 ml ethanol was added to the bottle and shaken, and, after allowing the solid material to settle, the supernatant was filtered into the same 100 ml volumetric flask as before. The washing, shaking and filtering procedure was repeated twice more, each time letting the solid sample remain in the bottle. The extract was subsequently made up to the 100 ml mark with deionised water and concentrations of exchangeable cations (Na⁺, Mg²⁺, Ca²⁺ and K⁺) determined with ICP-MS analysis.

The concentrations were converted to milliequivalents (meq) per 100 g of sample as follows:

- \( \text{mg Ca g}^{-1} \text{ solid} = 0.1 \times \frac{C_{Ca}}{5} \)
- where \( C_{Ca} \) is the concentration of Ca in the sample extract in mg L⁻¹
- therefore,
  \[
  \text{mg Ca (100g) }^{-1} \text{ sample} = 100 \times \frac{C_{Ca}}{5} = 20 \times 0.1 \times C_{Ca}
  \]
- and
  \[
  \text{meq Ca (100 g) }^{-1} \text{ sample} = 2 \times \frac{C_{Ca}}{20.0}
  \]
- Similarly:
  \[
  \text{meq Mg (100 g) }^{-1} \text{ sample} = 2 \times \frac{C_{Mg}}{12.2}
  \]
  \[
  \text{meq Na (100 g) }^{-1} \text{ sample} = 2 \times \frac{C_{Na}}{23.0}
  \]
  \[
  \text{meq K (100 g) }^{-1} = 2 \times \frac{C_{K}}{39.1}
  \]

Finally, the sum (∑) of the exchangeable cations can be calculated:
Sum of exchangeable cations:

\[
\sum (\text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+) \text{ in meq (100g)}^{-1} \text{ or meq g}^{-1}
\]

4.6.2.3 Cation exchange capacity (CEC) determination [67]

The CEC of the zeolites samples were determined by measuring the amount of NH₄⁺ retained by the solid material while replacing the exchangeable cations in the previous procedure:

The extracted solid sample from the previous procedure was mixed with 25 ml KCl (pH 2.5) solution. The mixture was then shaken for 30 minutes and filtered into a 100 ml volumetric flask, during which the solid material was leached onto the filter paper with successive small portions of the KCl solution into the flask and made up to the mark with deionised water. Subsequently, 50 ml of the filtrate was transferred into a 250 ml round-bottom flask, and diluted with 50 ml deionised water. The borate buffer was then added and the resultant solution was distilled:

- **Distillation process**

To the 100 ml solution contained in the round-bottom flask (50 ml filtrate + 50 ml water), 5 ml of the borate buffer solution was added. The flask was connected to the condenser and a flow of cooling water turned on. The tip of the condenser was immersed in a receiving flask, which contained 10 ml boric acid solution and 5 drops of the mixed indicator. The distillation was then slowly proceeded, but care was
taken not to boil the flask to dryness, since it could have caused distillation of interfering substances. The distillation process was continued until approximately 50-60 ml of the distillate was collected in the receiving flask.

After the distillation process, the collected distillate was titrated with 0.01 M HCl until the color at the end point changed from green to pink.

The $\text{NH}_4^+$ in the extracted sample was calculated from:

$$\text{mg NH}_4^+ - \text{N kg} = 140 \times F \times V/M$$

- Where:
  - $V$ = the volume of titrant used up (ml)
  - $M$ = the weight of the sample (g)
  - $F$ = the inverse fraction of the extract taken for distillation

This was expressed as meq kg$^{-1}$ by dividing by the atomic mass of Nitrogen (N), and subsequently converted to meq (100 g)$^{-1}$ to give the CEC:

$$\text{CEC [meq (100 g)$^{-1}$]} = \text{NH}_4^+ - \text{N [meq (100 g)$^{-1}$]} = F \times V/M$$

### 4.6.3 Inductively Coupled Plasma Spectrometry (ICP-MS) analysis

Initial and equilibrium concentrations of major and trace elements in the filtrates and effluents were determined by application of ICP-MS analysis. The instrument used for the analysis, was a Perkin Elmer Elan ICP-MS unit.
4.6.3.1 Sample preparation for ICP-MS determination

Prior to dilution for ICP-MS analysis, all samples were filtered through a 0.45 µm membrane filter. The conductivity (EC) and pH readings were then recorded, after which the sample was diluted with deionised water until the EC reading was less than 1.5 mS/cm. The diluted sample was then acidified with the addition of 50% nitric acid \[^{[80]}\].

4.7 Use of the prepared zeolites (HCIM) in decontamination experiments

Based on the results obtained from the characterization techniques, the zeolite with the superior characteristics was chosen for application in the decontamination experiments. In these experiments, the fly ash-related zeolitic material was contacted with both model solutions consisting of selected heavy metals, as well as FA/AMD-process waters, by means of a structured series of experiments.

4.7.1 Experiments with model solutions

To understand the removal mechanism involved during the application of any type of adsorbent material, as well as to optimize the overall removal efficiency of the remediation system for best performance, one needs to investigate certain important parameters. Subsequently certain parameters were studied, including:
i. solid/liquid ratio (g/100ml),
ii. contact time,
iii. presence of competing ions,
iv. metal concentration and equilibrium,
v. temperature variation

The results obtained from these investigations were used to evaluate which parameters could enhance or adversely affect the remediation process.

### 4.7.1.1 Materials and chemicals

- nitrate salts of selected metals, purchased from E. Merck and Sigma Aldrich;
- buchner filtration systems;
- jacketed temperature controlled water bath shaker;
- 0.45 µm membrane filters;
- commercial faujasite (CBV 400), purchased from Zeolist International;
- commercial chelating ion exchanger (Lewatit TP 207), purchased from Bayer Hispania Industrial;
- stopwatch;
- deionised water;
- 150 ml Capacity HDPE containers
All commercially purchased chemicals used in this study were analytical reagent grade.

4.7.1.2 Calculations and preparation of stock and working solutions

Nitrate salts of the required metals were used to formulate multi-metal stock solutions, containing the selected metals for which the concentration for each metal was 1000 mg L\(^{-1}\). These stock solutions were prepared by dissolving the appropriate mass of the nitrate salts, which was calculated by the following sequential steps:

i) The mass percentage (%) of the particular element (A) contained in the nitrate salt was determined as follows:

\[
\text{Mass % A} = \left( \frac{\text{Mass of A in whole compound}}{\text{Mass of whole compound}} \right) \times 100\%
\]

ii) The calculated mass percentage of A was used to determine the mass of the nitrate salt needed to formulate a solution of 1000 mg L\(^{-1}\), with respect to the particular element (A).

The correct mass of the nitrate salts were then weighed out and dissolved in deionised water and nitric acid (HNO\(_3\)) to formulate the artificially polluted stock solutions containing the selected metals.
To conduct the actual decontamination experiments, the working solutions were prepared by appropriate dilution of stock solutions immediately prior to their use.

All sorption studies with the model solutions were carried out in high density plastic polyethylene containers with a volume capacity of 150 ml, by subjecting a given dose of zeolite (ArnavZ₃) to a period of shaking with 100 ml of the synthetically prepared effluent and the suspension periodically shaken in a jacketed temperature controlled, thermostat water bath shaker. Each zeolite/effluent sample was individually placed in separate containers and at the designated times, the container was removed from the shaker and the filtrate collected by filtering the suspension with a 0.45 µm membrane filter, after which initial and equilibrium metal concentrations were determined with ICP-MS analysis.

4.7.1.3 Effect of Solid/Liquid ratio (g/100ml)

These experiments involved variation of the liquid-solid ratio (V/m) of zeolite-solution mixture, to investigate the effects of zeolite dosage on the retention of the selected metals during the decontamination experiments. Thus zeolite dosages were varied from 1.0- to 2.0- to 3.0- to 5.0 g and equilibrated with 100ml aliquots of the model solution for 60 minutes. The working solution for this series of experiments was a model solution consisting of Mn²⁺, Fe³⁺, Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺, Sr²⁺, Ba³⁺, and Pb²⁺ at an initial concentration of 4 mg L⁻¹, which was prepared by the
appropriate dilution of the 1000 mg L\(^{-1}\) stock solution immediately prior to conduction of the experiments. The experiments were conducted in batch mode at constant temperature (20 °C) and the suspension agitated by periodical shaking in the temperature controlled thermostat water bath shaker. At the designated time, the suspensions were filtered and the metal concentrations of the untreated and treated effluents were determined by ICP-MS analysis \cite{59}.

4.7.1.4 **Effect of contact time variation**

The effect of contact time on the sorption of selected metals onto ArnavZ\(_3\) was investigated and as such, the optimum time for the metal-zeolite system to reach equilibrium was determined.

The working solution in these experiments was a model solution consisting of Ba\(^{2+}\), Pb\(^{2+}\), Sr\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Mn\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\) ions, with an initial concentration of 5mg L\(^{-1}\) (\(\pm\) 10% error deviation) with respect to each metal, which was prepared by the appropriate dilution of the 1000 mg L\(^{-1}\) stock solution immediately prior to conduction of the experiments. The concentration of each metal contained in the untreated sample was analyzed with ICP-MS analysis.

These experiments involved varying the equilibration time, while keeping the other parameters constant. The zeolite/effluent ratio; as determined from the solid/liquid variation experiments, used, was 5g zeolite per 100ml of effluent. The experiments
were conducted in batch mode and suspension agitated by periodical shaking in the temperature controlled thermostat water bath shaker.

The contact time was varied from 60, 120, 180, 240, 300, 360, 420, 540, 660 up to 1440 minutes and at each designated time interval, the particular sample was removed, filtered and the filtrate was analyzed through ICP-MS analysis. The temperature was kept constant (20 °C) throughout the experiments by circulating the thermostat controlled water.

4.7.1.5 Effect of temperature variation

The effect of temperature variation on the metal retention capacity of the zeolite was determined by elevating the temperature up to 30 and 40 °C (303 and 313 K), while keeping the other parameters constant.

The working solution in these experiments was a model solution consisting of Ba$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Al$^{3+}$ and Fe$^{3+}$ ions, with an initial concentration of 5mg L$^{-1}$ (+/- 10% error deviation) with respect to each metal, which was prepared by the appropriate dilution of the 1000 mg L$^{-1}$ stock solution immediately prior to conduction of the experiments. The concentration of each metal contained in the untreated sample was analyzed with ICP-MS analysis.

Thus 5.0 g zeolite was equilibrated with 100ml of the model solution for a period of 60 minutes; as determined through the time variation investigations and the suspension agitated in batch mode by periodical shaking in a temperature controlled
water bath shaker. After one hour of contact, the suspensions were filtered and ICP-MS analysis was done to evaluate the quantity of metal reduction from the contaminated solutions.

4.7.1.6 Concentration variation experiments and equilibrium investigations

In these experiments the effect of variation of metal concentration on equilibrium was determined by varying the concentration from 5-, 10-, 15- and up to 20 mg L\(^{-1}\), while keeping all the other parameters constant.

The working solution in each case; consisting of Ba\(^{2+}\), Pb\(^{2+}\), Sr\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Mn\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\), was prepared by appropriate dilution of stock solution immediately prior to commencement of the experiment. The solid-solution suspension (5g zeolite per 100 ml effluent) was equilibrated for a period of 60 minutes, after which samples were taken out, filtered and metal concentration was evaluated by means of ICP-MS analysis.

4.7.1.7 Effect of the presence of competing ions

The effect of ionic strength on metal cation retention capacity of the zeolite was studied by using Ca(NO\(_3\))\(_2\)\(\cdot\)4H\(_2\)O and Mg(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O as electrolytes. These investigations were done by varying the electrolyte concentration in terms of Ca\(^{2+}\), which were as follows:
Samples containing only \( \text{Ca}^{2+} \), in addition to the selected metals were equilibrated for a period of 60 minutes; while samples containing both competing ions, \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) were equilibrated for 60 minutes after which filtration was done, to collect the filtrate for ICP-MS analysis.

Appropriately then, the working solutions for samples containing no additional competing ions consisted of an initial metal concentration of 5 mg L\(^{-1}\), taking into account the error variation with respect to the initial concentration in terms of each metal ions (caused by moisture in salts, dilution of stock solutions, etc.). The working solution for the samples containing only \( \text{Ca}^{2+} \) as competing ion, consisted of an initial 295 mg L\(^{-1}\) \( \text{Ca}^{2+} \), in addition to the selected metal ions initially present (5 mg L\(^{-1}\) initial concentrations). The other sample, contained both \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \), in addition to the initial metal ion concentration of 5 mg L\(^{-1}\). The initial concentrations of the competing ions for the latter sample were 262 mg L\(^{-1}\) \( \text{Ca}^{2+} \) and 75 mg L\(^{-1}\) \( \text{Mg}^{2+} \), in addition to the initial 5 mg L\(^{-1}\) in terms of the selected metals contained in the sample.

In these experiments, the error variations with respect to initial concentration in terms of each of the selected metals was higher than in the case of the other experiments, for which a +/- 10% initial concentration deviation was usually taken into account.

The concentrations of all ions in solution was measured before and after contact with the zeolite.
4.7.1.8 Experiments comparing the FA/AMD-related zeolite (HCIM) with commercial faujasite (commFau) and with commercially obtained chelating ion exchanger (Lewatit TP207)

These experiments were conducted to observe the capacity and selectivity of the (selected) synthesized zeolite with the commercially obtained faujasite zeolite, as well as with the commercially obtained selective organic exchange resin.

Before utilization of the weakly acidic, macroporous cation exchange resin, an initial conditioning of the resin was carried out. The conditioning treatment consisted of its washing with deionised water and conversion into its acidic form by treatment with 0.1 M HCl in a glass column. Once in its H⁺ form, the resin was again washed with deionised water until a pH of the residual water was close to approximately 5.0, after which further treatment with HCl solution was done to a pH of 2.5. The treated resin was dried at 20 °C and stored in an airtight sealed container until it was used in the experiments [81, 82].

No additional conditioning was necessary for the commercial faujasite zeolite, and as such, the dried zeolite was used in its obtained form.

The working solutions for these experiments consisted 5 mg L⁻¹ Ba²⁺, Pb²⁺, Sr²⁺, Cu²⁺, Co²⁺, Zn²⁺, Mn²⁺, Al³⁺ and Fe³⁺, which was prepared by appropriate dilution of stock solution immediately prior to commencement of the experiments. The usual
10% error deviation with respect to initial metal ion concentration was taken into account.

The experiments were conducted in exactly the same manner as the time investigations. Thus the contact time was varied from 60, 120, 180, 240, 300, 360, 420, 540, 660 up to 1440 minutes and at each designated time interval, the particular sample was removed, filtered, and the filtrate was analyzed through ICP-MS analysis. The temperature was kept constant (20 °C) throughout the experiments by circulating the thermostat controlled water.

### 4.7.2 Decontamination experiments with FA/AMD-process effluents

These experiments involved the equilibration of the (selected) synthesized zeolite, with actual FA/AMD-process effluents (secondary co-disposed process waters), for a period of 60 minutes while keeping all parameters constant.

The secondary co-disposed process waters used for these experiments were collected at predetermined pH’s from the co-disposal reaction of Amot fly ash with Navigation AMD, in a ratio of 1:3.5. The waters were collected at three different pH’s, 12.43; 8.10 and 3.00.

The aim of these experiments were to evaluate the consistency in terms of zeolite performance with real co-disposed waters, as apposed to its performance with the model solutions, as well as to observe the matrix effect on removal performance,
since the ion concentration of each collected FA/AMD-process effluent sample was considerably different from the next.

 Appropriately then, 5g zeolite was equilibrated with 100ml effluent for a period of 60 minutes at a constant temperature (20°C) in the jacketed thermostat controlled periodical water bath shaker. Suspensions were filtered after 60 minutes of contact and ICP-MS analysis was done to observe the decrease in metal ion concentration.
CHAPTER 5

Characterization Results

5.1 Introduction

One major aspect which this chapter focuses on is to evaluate and discuss the success of hydrothermal activation of the FA/AMD- solid residues into Faujasite formation.

Based on the fact that on industrial scale millions of dollars are spent daily in terms of wastewater treatment and the acknowledgement that ion exchange is one of the major water purification techniques — the application of zeolites in this area has become a well explored phenomenon, since these minerals possess specific properties based on their crystal structure, uniform pore diameter and pore widths, high specific surface area and innocuous exchangeable cations (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)). However, since water purification is an expensive process, the need for inexpensive synthetic zeolites with built-in adsorption properties, led to the exploration of zeolitization of pulverized fly ash (PFA); since fly ash is a low cost, readily available raw material, with a high glass content \(^{23,24}\).

Additionally discussed in this chapter are the results in terms of mineralogical, chemical and physical characterization of the synthesized high capacity inorganic ion exchange material.
The characterization techniques include X-ray Diffraction (XRD) Spectrometry, Inductively Coupled Mass Spectrometry (ICP-MS), Cation Exchange Capacity (CEC), X-ray Fluorescence (XRF) spectrometry and Nitrogen Brunauer-Emmett—Teller (N$_2$-BET) surface area determination.

5.2 Characterization results for FA/AMD-solid residues (zeolite starting material)

Zeolitization of FA/AMD-solid residue (co-disposal precipitate) proceeds via various stages, during which the Al- and Si-bearing phases of the starting material are sequentially dissolved, with the aluminosilicate glass phase being activated first, followed by the quartz phase and lastly, dissolution of the mullite phase. Another essential aspect to bear in mind is that according to previous research investigations, it has been determined that a [SiO$_2$]/[Al$_2$O$_3$] ratio of more than 1.5 is necessary for the successful zeolitization of fly ash and fly ash-related starting materials [9]. The characterization techniques which can be employed to determine how successful a particular zeolite synthesis process would be, are X-ray diffraction (XRD) spectroscopy and X-ray fluorescence (XRF) spectroscopy and as such, was used to evaluate these parameters.
5.2.1 Results for mineralogical characterisation of the FA/AMD-solid residues

The mineralogical characterisation of the FA/AMD-solid residues (obtained through the neutralization co-disposal reaction of fly ash and AMD), was determined by x-ray diffraction (XRD) spectrometry.

XRD analysis, for all the FA/AMD-solid residues (co-disposal precipitates) produced in this study, showed a direct parallelism in terms of characteristic peaks observed, and as such, all the produced precipitates was shown to have similar mineralogical composition.

The result of the XRD analysis for the solid residues collected from the co-disposal reaction of Arnot fly ash and Navigation AMD is shown in Figure 5.1. This graph can be perceived as a representative XRD pattern for all the FA/AMD-solid residues produced in this study, since they were all shown to be similar. Previous investigations have revealed similar trends, in terms of peak similarity for solid residues produced from reaction of FA with AMD. [29]
Figure 5.1  XRD pattern of FA/AMD solid residue for Arnot FA plus Navigation AMD; which is the starting material for zeolite synthesis. Q = quartz (SiO₂); M = mullite (Al₆Si₂O₁₃)  
[Refer to: Appendix D 1.1]  

The XRD pattern in figure 5.1 show characteristic peaks observable in all FA/AMD-solid residues produced in the study. Quartz (SiO₂) and mullite (Al₆Si₂O₁₃) are the major phases shown in the XRD pattern, present in all the co-disposal precipitates (FA/AMD-solid residues). The presence of these phases (mullite and quartz) in the FA/AMD-solid residues were very significant for the zeolite synthesis process in this study, as prior research has shown that the dissolution of SiO₂ and Al₂O₃ from quartz, mullite and alluminosilicate glass during hydrothermal activation, will result in the nucleation and crystal growth of highly crystalline zeolites as new mineral phases or as an overgrowth of previous activation products [79].
5.2.2 Chemical characterization results of the FA/AMD-solid residues

The elemental composition of the FA/AMD-solid residues was determined by X-ray fluorescence (XRF) spectrometry analysis, in order to obtain a chemical analysis of the precipitates. The information obtained through these analysis are fundamental, since it provides data on the major oxides found in these precipitates, particularly the Si and Al contents, as well as the element concentrations. These two aspects are important information, because the Si/Al ratio is a major factor on the prediction of the success rate of zeolite conversion from FA/AMD-related material; while the comparison of element concentration between the solid residue starting material and the synthesized zeolite will give an indication of the reduction in the concentrations of potentially toxic elements (major and minor heavy metals and/or trace metal elements).

The results showing the major oxides found in FA/AMD-related solid residue starting materials, particularly the SiO$_2$/Al$_2$O$_3$ ratio, is presented in Table 5.1.

The sample used to present the major oxides in FA/AMD-solid residues, was the solid residue used for the synthesis of ArnavZ$_3$; since, as shown later in the chapter – ArnavZ$_3$ was the better of the three zeolites produced in the study.

The results for XRF analysis of the major oxides found in the FA/AMD-solid residue (co-disposal precipitate) are shown in Appendix A.
Table 5.1  XRF analysis results of major oxides found in the FA/AMD-solid residue (AFA-Nav-ppt)

<table>
<thead>
<tr>
<th></th>
<th>All concentrations in weight percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.69</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.62</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.27</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.53</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.32</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.24</td>
</tr>
<tr>
<td>CaO</td>
<td>5.49</td>
</tr>
<tr>
<td>MgO</td>
<td>1.77</td>
</tr>
<tr>
<td>MnO</td>
<td>0.11</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.22</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.47</td>
</tr>
<tr>
<td>NiO</td>
<td>0.01</td>
</tr>
<tr>
<td>H₂O⁻</td>
<td>1.41</td>
</tr>
<tr>
<td>LOI</td>
<td>6.50</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃</td>
<td>2.09</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.65</td>
</tr>
</tbody>
</table>

From table 5.1 one obtains a clear indication of the oxide concentrations of SiO₂ and Al₂O₃ and as such the ratio of [SiO₂]/[Al₂O₃] can be determined, which is shown to be 2.09. A qualitative estimation can therefore be made that, since the [SiO₂]/[Al₂O₃] is more than the required 1.5, faujasite synthesis of the fly ash-related precipitates will be successful. However, one must also bear in mind that the [SiO₂]/[Al₂O₃] is a major, but not the only factor determining the success rate of conversion of fly ash-related materials into zeolites, as mineralogical composition also plays a lesser but significant role [63, 64].

It has been previously established that, since most FA-related zeolites are made from direct conversion starting materials, the occurrence and mobility of major and minor heavy metal elements in fly ash and fly ash-related precipitates plays a pivotal role in the subsequent synthesis and utilization of high capacity ion exchange material (e.g. zeolites, etc.) in the decontamination process [33, 34, 12]. This can be attributed to, depending on the placement and mobility of certain ions, the probability of their
leaching into the zeolite structure and subsequent leaching into solution during sorption, which could adversely affect the decontamination process \[12\]. One must therefore have an indication of the elemental concentrations contained within the fly ash-related precipitate, which was done through XRF analysis of the dried specimen (the same precipitate used as for analysis of the major oxides). Table 5.2 gives an overview of the elements and their concentrations.

Table 5.2  XRF analysis results of element concentrations in the FA/AMD solid residue (AFA-Nav-ppt)

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Mn</th>
<th>Cr</th>
<th>V</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>44.67</td>
<td>672.54</td>
<td>189.38</td>
<td>150.33</td>
<td>135.65</td>
<td>51.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Mo</th>
<th>Nb</th>
<th>Zr</th>
<th>Y</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30.57</td>
<td>6.27</td>
<td>30.59</td>
<td>382.79</td>
<td>73.55</td>
<td>1170.91</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Ba</th>
<th>U</th>
<th>Th</th>
<th>Rb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>95.08</td>
<td>983.68</td>
<td>10.80</td>
<td>38.55</td>
<td>25.92</td>
<td>67.68</td>
</tr>
</tbody>
</table>

| S     | 27747.00 | |

An assessment of the contents in table 5.2 shows that amongst the dominant species present in the solid precipitate were Sr, Ba and Mn with concentrations of 1170.91 mg kg\(^{-1}\), 983.68 mg kg\(^{-1}\) and 672.54 mg kg\(^{-1}\), respectively. Sulfur however, also proved to be present in exceeding concentrations, 27747 mg kg\(^{-1}\), which might possibly be present as sulfides. As for the other elements, Cr and V were present in concentrations less
than 200 mg kg\(^{-1}\), while concentrations for all other elements, including Co, Cu, Sc, Mo, U, Th, Pb etc. were less than 100 mg kg\(^{-1}\). This raises an alarming expectancy in terms of the probability of preferential leaching of certain elements into the formed zeolite and subsequently the polluted effluent – however other factors such as placement in the zeolite structure, solution pH and matrix effect also contributes to leaching and as such, this phenomenon will differ from one experiment to the next. The phenomenon of potential leaching of elements from zeolite matrix during decontamination experiments, can be attributed to using waste material as direct conversion products (fly ash and AMD) during the hydrothermal activation synthesis\[^{12}\].

5.3 Characterization results of synthesized zeolites

Several analytical techniques were employed in the characterization and analysis of the synthesized zeolites. The mineralogical and physical analysis of the zeolitic material produced (HCIM) was performed by employing X-ray Diffraction (XRD) Spectrometry and nitrogen Brunauer-Emmett-Teller (N\(_2\) BET) surface analysis respectively. X-ray Fluorescence Spectrometry (XRF), Inductively Coupled Mass Spectrometry (ICP-MS), and Cation Exchange Capacity (CEC) techniques were used for chemical characterisation.
5.3.1 Mineralogical characterization results

5.3.1.1 Results for X-Ray Diffraction (XRD) Spectroscopy

The XRD analysis results for the synthesized zeolites are shown in Appendix D.

X-ray diffraction (XRD) techniques were employed to study the changes in the mineralogy of the synthesized zeolites and as such, a semi-quantitative estimate of the faujasite contents in the synthesized material could be made. The diffraction patterns of the samples were identified by the JCPDS reference library.

The XRD diffraction patterns of the synthesized material are shown in figures 5.2 (a) and (b), in which figure (a) illustrates the patterns of ArnavZ₁ and ArnavZ₂; while the XRD diffraction pattern for ArnavZ₃ can be seen in figure (b).

Figure 5.2 (a) XRD pattern for zeolitic material (ArnavZ₁, ArnavZ₂) synthesized from co-disposal precipitate. S = Sodalite [Na₈(AlSiO₄)₆(NO₂)₂]; H = Hematite [Fe₂O₃]; F = Faujasite [NaₓAlₓSiₓO₁₀·xH₂O]; Q = Quartz [SiO₂] [Refer to: Appendix D 1.2, 1.3]
Figure 5.2 (b) XRD pattern for zeolite (ArnavZ₃), also synthesized from FA/AMD-solid residue: F = Faujasite; Sₐ = Sodium aluminum boron silicate hydroxide sodalite

[Refer to: Appendix D 1.4]

From the evaluation of the XRD patterns the following observations were made:

- It can be observed that the characteristic “zeolite peak”, expected to be present at d-spacing below 10, are not present in the case of ArnavZ₁ and ArnavZ₂, while ArnavZ₃ shows a very well developed characteristic peak at below 10 2deg theta, corresponding to a relative intensity of 2319.

- Faujasite formation for both ArnavZ₁ and ArnavZ₂ were assessed to be fairly unsuccessful, as they contain a substantial percentage of sodalite, with some quartz and hematite also present, while only a very small fraction of faujasite can be observed. ArnavZ₃ on the other hand, contains a high degree of well developed crystalline faujasite phases, with some hydroxysodalite also present.
In light of the information obtained from the XRD patterns of the various synthesized zeolitic material, one can conclude that in the case of ArnavZ₁ and ArnavZ₂, the crystalline process was underdeveloped and as such, the products were not the aimed faujasite (zeolites-Y), but actually a fairly amorphous sodalite, which is the building block of faujasite \[^{[58]}\]. In the case of ArnavZ₃ a fairly well developed crystalline product was observed, indicating that faujasite crystallization was indeed successful in this case, however some of the formed zeolite-Y phases were transformed to hydroxysodalite as can be seen in figure 5.2 (b). The transformation of some phases to hydroxysodalite can be attributed to excessive enrichment of the FA/AMD-based zeolite system with the alkaline activator (NaOH) \[^{[9]}\]. A comparison of the synthesized ArnavZ₃ with commercial faujasite presented in figure 5.2 (c), reveals that the XRD-pattern of the FA/AMD-related zeolite fairly matches with commercial grade zeolite-Y pattern, confirming the highly crystalline phase formation of ArnavZ₃.

Figure 5.2 (c) Comparative overlapping XRD patterns for commercial faujasite and synthesized ArnavZ₃ [Refer to: Appendix D 1.5]
On further assessment of the XRD-patterns one observes that the peak intensity of ArnavZ₃ actually exceeds peak intensity of the commercial faujasite – a very significant quality, which corroborate the conclusion that a highly crystalline zeolite was produced. A slight shift in certain peaks on the theta scale, shows the positions at which some of the formed faujasite phases were transformed into hydroxysodalite, but peak shifts are quite minimal which means that ArnavZ₃ is largely single phased, with a high percentage of faujasite contained in the product [⁹].

A possible explanation for the difference between the produced ArnavZ₃ and the other two produced zeolitic material (ArnavZ₁ and ArnavZ₂) may be explained as follows:

Prior research has established that, given the fact that Al- and Si-bearing phases are dissolved during zeolitization (glass>quartz>mullite), different synthesis behavior using the same activation conditions for a similar bulk SiO₂/Al₂O₃ ratio, might be obtained. In other words, although the starting materials showed similar mineralogical patterns, slight variations in quartz-mullite glass proportions may have resulted in different glass matrixes, subsequently resulting in different zeolites [¹²].
5.3.2 Results of chemical characterization analysis

Cation Exchange Capacity (CEC) and X-Ray Fluorescence (XRF) spectroscopy techniques were used for the chemical characterisation of the prepared zeolites. The results of these analyses are discussed in the following paragraphs.

5.3.2.1 Exchangeable cations

The ICP-MS results for exchangeable cations and CEC determination are shown in Appendix B1.9

The first step in the process of determination of the CEC of an ion exchanger, is to determine the amount of cations contained in the zeolite structure, which are available for exchange (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\)). These exchangeable cations are held electrostatically within the zeolite framework structure and can be replaced by ions from the surrounding solution; the process is referred to as ion exchange. In sodium form zeolites, such as the ones synthesized in this study, higher Na\(^+\) concentration can be expected [63].

Table 5.3 presents the results for the exchangeable cations available for exchange, in the different synthesized zeolitic material, in terms of their concentrations (ppm: mg kg\(^{-1}\)) and milliequivalents per 100g of zeolite (meq./100g).
Table 5.3 Table of the extracted (exchangeable) cations ($\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$) from the synthesized zeolitic material in terms of concentrations (ppm) and meq./100g

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Concentrations in ppm (mg kg$^{-1}$)</th>
<th>(meq./100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Na}^+$ $\text{Ca}^{2+}$ $\text{Mg}^{2+}$ $\text{K}^+$</td>
<td>$\text{Na}^+$ $\text{Ca}^{2+}$ $\text{Mg}^{2+}$ $\text{K}^+$</td>
</tr>
<tr>
<td>ArnavZ$_1$</td>
<td>786.74 133.18 1.70 113.96</td>
<td>68.41 13.32 0.28 0.01</td>
</tr>
<tr>
<td>ArnavZ$_2$</td>
<td>690.32 194.24 4.64 0.00</td>
<td>60.03 19.42 0.76 0.00</td>
</tr>
<tr>
<td>ArnavZ$_3$</td>
<td>1234.96 19.462 1.517 0.00</td>
<td>107.388 1.946 0.249 0.00</td>
</tr>
</tbody>
</table>

From table 5.3 it is shown that although the idea was to synthesize a fairly homoionic Na-form Y-zeolite, the formed zeolitic material still had a small amount of exchangeable $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and in some cases $\text{K}^+$. However, ArnavZ$_3$, is observed to have the highest concentration of exchangeable $\text{Na}^+$, with much lesser of the other exchangeable cations present in its structure and as such, zeolite formation with respect to the aimed homoionic Na-form Y-zeolite was more successful in comparison with the other synthesized zeolites.

5.3.2.2 Cation Exchange Capacity (CEC) results

The magnitude of the cation exchange process in a given zeolite is measured in terms of its cation exchange capacity (CEC) and is commonly measured in terms of exchangeable cation per gram (or 100 grams) of zeolite$^{[54]}$. 


The CEC (also referred to as total exchange capacity) is a measure of the counter-ions present (charge compensating cations) per unit weight or volume of the zeolite and represent the number of cations available for exchange, in other words, it is a function of the Al substitution for Si in the zeolite framework structure – the greater the substitution, the greater the deficiency of positive charge and thus the greater the number of alkali or alkaline earth cations required for electrical neutrality, which is signified by a bigger exchange capacity [60, 61].

- The cation exchange capacity of an ion exchanger can thus be perceived as a very distinct characteristic quality, which portrays its importance in environmental protection at an industrial level for its application in the removal of undesired species from polluted effluents.

The results for CEC determination of the different synthesized zeolites are tabulated in **Table 5.4**.

**Table 5.4** Theoretically determined total exchange capacity (CEC) for the synthesized zeolites

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>CEC (meq./100g)</th>
<th>CEC (meq./g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArnavZ1</td>
<td>96.00</td>
<td>0.96</td>
</tr>
<tr>
<td>ArnavZ2</td>
<td>84.00</td>
<td>0.84</td>
</tr>
<tr>
<td>ArnavZ3</td>
<td>200</td>
<td>2.00</td>
</tr>
</tbody>
</table>

From the CEC results, tabulated in **Table 5.4**, one can observe that CEC values for ArnavZ1 and ArnavZ2 corresponded to 0.90 and 0.20 meq./g, respectively, which is...
characteristically expected values for small pore diameter sodalite zeolites (2.3 Å), as found in previous literature investigations. ArnavZ$_3$ on the other hand, has a much higher CEC value (2.0); however, it is still lower than the expected CEC for fly ash-based Y-zeolites (≈ 3.3) [12], but the reduced CEC can be attributed to the transformation of some of the faujasite (Y-zeolite) phases to hydroxysodalite, as explained earlier [9].

Although the determined cation exchange capacity gives is a significant measure of the expectant ability of the synthesized zeolitic materials in terms of metal ion removal capacity; from a practical point of view, however, the number of ions which can be sorbed or exchanged under specified experimental conditions may very well differ from the determined CEC values. The latter statement is based on previous research findings, which have established that in inorganic exchangers obtained from natural products, such as the ones produced in this study, the ion exchange capacity may depend on experimental conditions. However, not all exchangeable cations are always available for ion exchange. This can be attributed to several reasons:

- Depending on the pore size of the zeolite, some of the incoming ions which may be too large to fit into the channels of the aluminosilicate framework, may be excluded and this is made possible by the effective sieving function of zeolites.
• Another factor to bear in mind, is that some of these exchangeable cations may be components of impurities, such as feldspar, quartz and salts; which during the zeolitization process, was not completely crystallized.

Since the structure of zeolites, and faujasite in particular, is made up of sodalite cages, combined in specific manner, some of the ionogenic groups may be located in inaccessible sites of the mineral structure.

Thus, in conclusion one can say, that, although the cation exchange capacity of a zeolite can be perceived as a very distinct characteristic quality, which portrays its importance in environmental protection at an industrial level, for its application in the removal of undesired species from polluted effluents; it is not the deciding factor in determination of the zeolite’s performance during ion exchange processes, since numerous other factors also needs to be considered.

5.3.2.3 X-Ray Fluorescence (XRF) spectroscopy analysis results

The data for XRF analysis for ArnavZ3 are shown in Appendix A.

Since zeolite formation was found to be more successful in the case of ArnavZ3, XRF analysis for determination of the elemental composition contained in the synthesized zeolitic materials was only applied to ArnavZ3. The results for this investigation is presented in table 5.5.
Table 5.5  XRF analysis results of major oxides in the synthesized zeolite, ArnavZ₃

| Compound | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | P₂O₅ | Cr₂O₃ | Na₂O | CaO | MgO | MnO | SO₃ | K₂O | NiO | H₂O- | LOI | SiO₂/Al₂O₃ |
|----------|------|------|-------|-------|------|-------|------|-----|-----|-----|-----|-----|-----|------|------|-----|---------|
| Concentration (wt%) | 33.75 | 0.56 | 20.46 | 6.73 | 0.01 | 0.01 | 10.93 | 5.12 |
| SiO₂/Al₂O₃ | 1.48 | 0.07 | 0.99 | 0.13 | 0.00 | 8.71 | 10.78 | 1.65 |
| TOTAL | 99.74 |

Assessment of the results presented in table 5.5 shows that the weight percent of all the major oxides have been reduced during zeolite synthesis, which was expected, since zeolite formation from fly ash-related precipitates occurs through the sequential dissolution of the reactive and non-reactive mineral phases – glass>quartz>mullite. One particularly important aspect is the SiO₂/Al₂O₃ ratio in the formed zeolite, which is shown to be 1.65. This value has a very significant impact on the zeolite performance in the decontamination process, since according to previous literature investigations – generally, a zeolite with a low Si:Al ratio, will tend to be hydrophilic, while a high silica zeolite (>2.0) will tend to be hydrophobic and organophilic [60, 61]. In light of the latter statement and based on the low Si:Al ratio determined in ArnavZ₃, the expected results would be a higher concentration of terminal Al-OH species at the zeolite-water interface during decontamination, as well as increased hydrophilic nature of the zeolite and this could lead to an enhanced metal exchange capacity.
It was expected that a reduction in elemental concentrations of major and minor heavy metals will occur during zeolite synthesis and as such, concentrations for heavy metals were also determined by application of XRF analysis, which is presented in table 5.6. An assessment of the results tabulated in table 5.6 reveal that concentrations for all elements, (except Cu) was reduced in the formed zeolite, as compared to their concentrations in the FA/AMD-solid residue (presented in table 5.2). The highest reduction was observed for S, which was reduced by 23 493 mg kg\(^{-1}\) during zeolite synthesis, however Ba and Sr, although also slightly reduced during zeolite synthesis, were still the dominant species in the synthesized zeolite (ArnavZ\(_3\)) with concentrations of 865.81- and 1000.25 mg kg\(^{-1}\), respectively. Although these values gives some estimation of the element concentrations found in the zeolite structure, to make a conclusive quantitative estimation on the expected leaching behavior of certain elements during the decontamination experiments, the fly ash itself must be subjected to standard leaching procedures, since occurrence and mobility of elements are largely dependent on the coal source and the subsequent formed fly ash. These results are presented in chapter 6.
Table 5.6  XRF analysis results of element concentrations in synthesized zeolite, ArnavZ$_3$

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Mn</th>
<th>Cr</th>
<th>V</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>36.40</td>
<td>437.90</td>
<td>45.83</td>
<td>2.02</td>
<td>133.89</td>
<td>69.57</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
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<td></td>
<td></td>
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<tr>
<td>V</td>
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<td>Zn</td>
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<td></td>
</tr>
<tr>
<td>Cu</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Mo</th>
<th>Nb</th>
<th>Zr</th>
<th>Y</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>28.58</td>
<td>0.77</td>
<td>24.53</td>
<td>324.26</td>
<td>60.33</td>
<td>1000.25</td>
</tr>
<tr>
<td>Mo</td>
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<td></td>
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</tr>
<tr>
<td>Nb</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Zr</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Ba</th>
<th>U</th>
<th>Th</th>
<th>Rb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>88.74</td>
<td>865.81</td>
<td>8.87</td>
<td>31.33</td>
<td>6.06</td>
<td>48.91</td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>U</td>
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<td>Rb</td>
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<td>Pb</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>4254.00</td>
</tr>
</tbody>
</table>

5.3.3 Physical Characterization results of synthesized zeolites

The data for BET results of the synthesized zeolites are shown in Appendix C.

The physical analysis of the synthesized zeolitic material was conducted by the application of gravimetric nitrogen Brunauer-Emmett-Teller (N$_2$ BET) surface analysis technique.

BET has the ability to provide information on the specific surface area, total pore volume and pore size of a particular specimen, consequently these parameters for the synthesized zeolites were obtained through BET analysis. The results are presented in table 5.7.
Table 5.7  

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>BET surface area m²/g</th>
<th>Pore volume cm³/g</th>
<th>Pore size Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArnavZ₁</td>
<td>173.296</td>
<td>0.269</td>
<td>62.093</td>
</tr>
<tr>
<td>ArnavZ₂</td>
<td>230.7319</td>
<td>0.248</td>
<td>42.935</td>
</tr>
<tr>
<td>ArnavZ₃</td>
<td>327.341</td>
<td>0.310</td>
<td>54.497</td>
</tr>
</tbody>
</table>

From table 5.7, one can observe that the surface area, pore volume and pore size of ArnavZ₃ proves to be considerably better than for the other two zeolites, which signifies that this zeolite would be better suitable for application in the decontamination experiments.
CHAPTER 6

Results for decontamination experiments

6.1 Introduction

The main objective of this chapter is to study the sorption behavior of the synthesized FA/AMD-related zeolitic material; ArnavZ3, with respect to the immobilization of heavy and trace metals commonly present in secondary process effluents and to explore the applicability of these low cost ion exchange minerals for the decontamination of actual secondary process effluents.

At a typical active mining wastewater treatment plant, the effluent produced from the primary physico-chemical treatment technologies; precipitation-aggregation coagulation/flocculation)-settling, are referred to as the secondary process effluent. However, in this research investigation, the secondary process effluent was collected from the co-disposal process between raw AMD and fly ash. It has already been established in previous investigations that fly ash can successfully be used as a “liming agent” for the precipitation of metals from AMD [26, 29].

The effluent collected from the co-disposal reactions, are referred to as secondary co-disposed process waters (or FA/AMD- process effluent).
These waters typically still contain a host of undesirable species including, major, minor and trace metals, as well as nitrates, sulfates and chlorides.

Thus adsorption is usually quite a complex process; often involving much more than simple ion exchange into the pore openings of the ion exchanger. Factors such as the pH, nature and concentration of the counter ion (metal ion), ion hydration, varying metal solubilities, the presence of competing, and complexing ions all effect the amount of metal ion that will adsorb \[72\] and as such, zeolite selectivity. To study these parameters; including the physical, chemical and electrostatic interactions between the sorbent (FA/AMD-related zeolitic material) and the sorbate (selected metal ions), decontamination experiments were conducted with model solutions consisting of selected metals.

Based on the insight gained from the experiments conducted with the model solutions, the system was then optimized and customized for the purification of the FA/AMD- process waters.

The efficiency of these ion exchangers were also evaluated by subjecting them to experiments in which their remediation potential was compared with the commercially obtained faujasite zeolite (CBV 400, obtained from Zeolist International), as well as a commercially obtained chelating cation exchanger (Lewatit TP 207, from Bayer), which selectively removes heavy metals from wastewater, through chemical bonds between its aminodiacetic acid functional groups and the counter ion.
6.2 Potential leaching of elements from fly ash

The first step in investigations involving the utilization of high capacity sorbent (ion exchange) materials (HCIM), synthesized from fly-ash related material, usually encompass the subjection of the raw fly ash to standard leaching procedures \[62\]. This is done to obtain a quantitative estimation on the expected leaching behavior of certain elements and its significance is based on the fact that the mobility of certain elements may cause leaching into the zeolite phase and subsequent leaching into the contaminated effluent, when direct synthesis materials are used, as is the case in this study \[34\].

The results are tabulated in table 6.1, which shows the potential leaching for selected elements in mg L\(^{-1}\). Assessment of the results tabulated in table 6.1 revealed that the leaching order which seemed to present itself was as follows:

Ca (431.666 mg L\(^{-1}\)) > Sr (5.320 mg L\(^{-1}\)) > Ba (1.142 mg L\(^{-1}\)) > B (0.273 mg L\(^{-1}\)) > Mo (0.186 mg L\(^{-1}\)) > Cu (0.051 mg L\(^{-1}\)) > Zn (0.034 mg L\(^{-1}\)) > Ni (0.033 mg L\(^{-1}\)) > Se (0.031 mg L\(^{-1}\)).

However elements including As, Hg and Mn stayed below detection limit. The latter order is in fairly good agreement with literature findings with slight deviations in terms certain metals.
Table 6.1  Results for standard leaching tests conducted with Arnot fly ash

<table>
<thead>
<tr>
<th>Element</th>
<th>Leached (mg L(^{-1}))</th>
<th>Element</th>
<th>Leached (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>431.666</td>
<td>Zn</td>
<td>0.034</td>
</tr>
<tr>
<td>Mg</td>
<td>0.032</td>
<td>Ni</td>
<td>0.033</td>
</tr>
<tr>
<td>Fe</td>
<td>BDL</td>
<td>Se</td>
<td>0.031</td>
</tr>
<tr>
<td>Sr</td>
<td>5.320</td>
<td>Pb</td>
<td>0.001</td>
</tr>
<tr>
<td>Ba</td>
<td>1.142</td>
<td>Co</td>
<td>0.001</td>
</tr>
<tr>
<td>B</td>
<td>0.273</td>
<td>Hg</td>
<td>BDL</td>
</tr>
<tr>
<td>Mo</td>
<td>0.186</td>
<td>Mn</td>
<td>BDL</td>
</tr>
<tr>
<td>Cu</td>
<td>0.051</td>
<td>As</td>
<td>BDL</td>
</tr>
</tbody>
</table>

Conditions: 10g Arnot fly ash; 100 ml de-ionised water; room temperature (20\(^\circ\)C); reaction time (24 hours). BDL = below detection limit

One must however also bare in mind that these results are merely an indication of the general expectancy of the leaching behavior in terms of certain metals during the decontamination experiments, since other factors also needs to be considered. One such factor is the solution matrix of the contaminated effluent, which will vary from one sample to the next and as such have prominently different effects on the zeolite ion exchanger. Therefore, the potential leaching behavior of the elements may differ from one experiment to the next.
6.3 Results for decontamination experiments

In these types of experiments the working hypothesis is that the use of a product containing a high proportion of zeolite with a fraction of alkaline fly ash particles would raise the pH and induce a favorable environment for ion exchange.

Amongst the synthesized zeolitic materials (ArnavZ₁, ArnavZ₂ and ArnavZ₃), ArnavZ₃ was chosen to be utilized in the decontamination experiments. This decision was based on its crystalline nature which correlated well with respect to the commercial grade faujasite, its surface area, as well as its exchange capacity – based on the results from the characterization analysis, these parameters proved to be better than the other synthesized zeolitic materials.

Another very pivotal aspect of ArnavZ₃ is its low Si/Al ratio, which, through XRF analysis was shown to correspond to a value of 1.65. The implications of such a low Si/Al ratio, means that one can expect a higher concentration of terminal Al-OH groups at the mineral/solution interface, as well as a zeolite with a more hydrophilic nature; which consequently leads to a greater capacity for ligand exchange and thus better performance during decontamination experiments.⁵⁹⁶⁰⁶¹

The overall effect will thus be better performance in terms of metal removal from contaminated waters.
6.3.1 Results for the application of ArnavZ₃ for removal of selected ions from model solutions

In the following experiments, the prepared zeolite (ArnavZ₃) was investigated in terms of its potential for the decontamination of model solutions, artificially polluted with selected metals. Important parameters such as zeolite dosage (g) per effluent volume unit (100ml), reaction time, metals concentration, ionic strength and temperature was examined in order to understand the removal mechanisms involved and to optimize the overall removal efficiency of the system for optimum performance.

6.3.1.1 Results for liquid/solid variation investigations

In these experiments the liquid-solid ratio (V/m) of zeolite-solution mixture was varied to observe the effects of variation of zeolite dosage on the metal retention of selected metals (Mn²⁺, Fe³⁺, Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺, Sr²⁺, Ba²⁺, and Pb²⁺) with ArnavZ₃. As such, zeolite dosages was varied from 1.0g to 5.0g and reacted with 100ml aliquots of the model solution. The experiments were conducted in batch mode and the suspension agitated as described in chapter 4.

Nitrate salts of the required metals were used to formulate the model solutions, in which the aim was to prepare a solution containing 4mg/L with respect to each metal, however, experimental and analytical error, caused by moisture contained in the
nitrate salts; dilution of stock solution (1000 mg/L) and deviation of ICP-MS internal standard with respect to certain metals was considered and as such, the initial concentration was 4mg/L with an error deviation of +/- 10% with respect to each metal. This “error deviation”, with respect to initial metal concentration, was taken into account in all subsequent investigations.

The results and data obtained from the ICP-MS analysis of the treated water samples are tabulated in Appendix B1.1.

The results showing the solute concentration in liquid phase (mg L\(^{-1}\)) as a function of zeolite dosage (g), are tabulated in table 6.2. In assessment of the results, it is apparent that the equilibrium concentration in solution phase decreased with increasing zeolite dosage at a given initial metal concentration, since the fraction of metal removed from the aqueous phase increased with elevation of zeolite dosage. This trend was anticipated, since raising the adsorbent dosage, provided greater surface area and sorption sites of the zeolite \(^{[83]}\). From table 6.2 it can be observed that the biggest decrease in metal concentration (mg L\(^{-1}\)) was obtained by the application of a zeolite dosage of 5g per 100ml effluent.
Table 6.2: Results for zeolite dosage variation (g/100ml) on the sorption of selected metals

<table>
<thead>
<tr>
<th>mass ArnavZ3 (g)</th>
<th>0.00</th>
<th>1.00</th>
<th>2.00</th>
<th>3.00</th>
<th>5.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal ion</td>
<td>metal ion concentration variation (mg/L) with increasing zolite dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>4.39</td>
<td>0.04</td>
<td>0.021</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>3.92</td>
<td>0.84</td>
<td>0.42</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>Ni</td>
<td>3.97</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Co</td>
<td>4.35</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>4.34</td>
<td>0.11</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Zn</td>
<td>4.22</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Sr</td>
<td>4.19</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Ba</td>
<td>4.58</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb</td>
<td>4.33</td>
<td>0.08</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Conditions: initial metal concentration: 4mgL⁻¹ (+/-10% deviation); reaction time: 1 hour; room temperature (20°C); volume effluent: 100ml

In view of these results, it was concluded that a liquid-solid ratio (V/m) of 20, corresponding to an adsorbent dosage of 5.00g with an effluent volume of 100ml could be used in all subsequent sorption investigations with ArnavZ3.

6.3.1.2 Results for Contact time investigations

These experiments were conducted to investigate the sorption kinetics of selected metals onto ArnavZ3 and as such, the optimum time for the metal-zeolite system to reach equilibrium was determined.
The results and data for the ICP-MS analysis of the treated water samples are shown in Appendix: B1.2 (a – b).

The working solution in these experiments was a model solution consisting of \( \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Sr}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Al}^{3+} \) and \( \text{Fe}^{3+} \) ions, with an initial concentration of 5mg L\(^{-1}\) (\(\pm 10\%\) error deviation) with respect to each metal. The equilibration experiments were conducted for 1440 minutes (24 hours), however the results demonstrated that very low residual concentrations for almost all metal cations, was observed within 60 minutes of contact (0.003mg L\(^{-1}\) for \( \text{Ba}^{2+} \); 0.007mg L\(^{-1}\) for \( \text{Sr}^{2+} \); 0.009mg L\(^{-1}\) for \( \text{Mn}^{2+} \); 0.0195mg L\(^{-1}\) for \( \text{Pb}^{2+} \); 0.010mg L\(^{-1}\) for \( \text{Co}^{2+} \); 0.024mg L\(^{-1}\) for \( \text{Zn}^{2+} \); 0.025mg L\(^{-1}\) for \( \text{Cu}^{2+} \); 0.105 mg L\(^{-1}\) for \( \text{Fe}^{3+} \) and 0.221mg L\(^{-1}\) for \( \text{Al}^{3+} \)) and as such, sorption was virtually completed within this time period. The results showing the variation of metal concentration (mg L\(^{-1}\)) as a function of contact time with ArnavZ\(_3\) illustrated in figures 6.1(a) – (c), confirms the latter statement since from the curves one can observe a drastic decrease in solution metal concentration, within the first 60 minutes, after which residual concentrations of most metals are fairly constant for the remaining time up to 1440 minutes; except in the case of \( \text{Al}^{3+} \) and \( \text{Fe}^{3+} \), which showed fluctuations in terms of concentrations [Figure 5.3 (a) and (c)]. In terms of removal percentages, an optimum removal of between 90-99% was achieved for almost all metal cations studied.
Figure 6.1 (a – c) Results showing effect of contact time on removal of Mn$^{2+}$, Ba$^{2+}$, Fe$^{3+}$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Al$^{3+}$, Sr$^{2+}$ and Co$^{2+}$ in terms of concentration (mg L$^{-1}$)

(Conditions: Initial metal concentration = 5mg L$^{-1}$ +/- 10% error deviation; solid/liquid ratio(adsorbent/effluent): 5g zeolite/100 ml effluent; temperature: 20°C)
A closer assessment of the results shown in the graphs of figure 6.1 reveals a small, but significant increase in the Al\(^{3+}\) concentration during the time interval between 720- and 1440 minutes [figure 6.1(c)]. This phenomenon can be attributed to either of two reasons:

- Dissolution of the small fraction of the zeolitic phase may have resulted in an increase in the concentration of alumina. This is a process, which involves the change of the coordinative partner of the crystal constituents (surface functional groups) and is catalyzed through either proton (H\(^+\)) and/or water (H\(_2\)O) or hydroxyl group (OH\(^-\)) at acidic and alkaline regions, respectively \([62, 71, 84]\). Thus, since the pH during these reactions ranged between pH 10 to \(^{+}/\scriptstyle 10.60\), zeolite dissolution was catalyzed via OH\(^-\).

- Aluminum is a very amorphous element and as such can re-enter the solution at pH 9.0 due to resolubilization of previously formed aluminum precipitates; and since the sorption reaction occurred in highly alkaline pH regions (pH 10.0 – 10.6), the possibility of solid precipitation could not be excluded \([62]\).

**Figure 6.1(a)** showed a similar trend in terms of Fe\(^{3+}\) concentrations, which also occurred during the 720-1440 minute time interval and in terms of quantity, the increase corresponded to an increase of, from 0.284 mg L\(^{-1}\) to 1.289 mg L\(^{-1}\). This occurrence may possibly be attributed to clogging of the zeolite pores and/or reduction or even reversion of the zeolite’s effective negative charge. The reason for this assumption is based on the fact that ArnavZ\(_3\) shows a lower selectivity for Fe\(^{3+}\) as
compared to the other metals; as well as previous literature findings, which have established that the fixation of certain metal species on the zeolite surface (especially Cu$^{2+}$ and Al$^{3+}$), during the treatment of metal-bearing wastewaters could cause clogging of part of the zeolite pores and/or reduction of the effective negative surface charge or even charge reversion and as such, may adversely effect the removal of other metals$^{[85]}$.

The metal uptake (mg/g) versus time curves on the other hand, shows a smooth, continuous increase to saturation, for most cations within the first 60 minutes, after which plateau values are obtained, suggesting the possible coverage of the first monolayer on the zeolite surface$^{[71, 83]}$. However, in the case of Fe$^{3+}$ and Al$^{3+}$, although metal uptake was also rapid within the first 60 minutes, plateau values were not achieved, since a decrease in metal uptake can be observed, which reaches a minimum at 1440 minutes. In the case of Al$^{3+}$, as mentioned earlier, this may possibly be attributed to dissolution of a fraction of the zeolite, as well as reduction of the effective negative charge of the zeolite surface$^{[62, 85]}$. The curves for metal uptake versus time are shown in figures 6.2 (a) – (d), from which one can see an optimum uptake of 0.100 mg g$^{-1}$ for Ba$^{2+}$, 0.097 mg g$^{-1}$ obtained for Pb$^{2+}$, 0.095 mg g$^{-1}$ for Cu$^{2+}$, 0.094 mg g$^{-1}$ for Sr$^{2+}$, 0.092 mg g$^{-1}$ for Co$^{2+}$, 0.090 mg g$^{-1}$ for Mn$^{2+}$, 0.089 mg g$^{-1}$ for Zn$^{2+}$, 0.086 mg g$^{-1}$ for Al$^{3+}$ and 0.079 mg g$^{-1}$ for Fe$^{3+}$. In terms of the metal uptake, the following selectivity series could thus be obtained: Ba$^{2+}$ > Pb$^{2+}$ > Cu$^{2+}$ > Sr$^{2+}$ > Co$^{2+}$ > Mn$^{2+}$ > Zn$^{2+}$ > Al$^{3+}$ > Fe$^{3+}$.
Figure 6.2(a – d) Results showing the effect of contact time on metal uptake (mg g⁻¹)
(Conditions: Initial metal concentration: 5mg L⁻¹ +/- 10% error deviation; solid/liquid ratio(adsorbent/effluent): 5g zeolite/100 ml effluent; temperature: 20°C)
6.3.1.2.1 pH variation during contact time investigations

The addition of ArnavZ_3 to the model solutions caused a considerable pH rise. Figure 6.3 is a graphical illustration of the variation of solution pH throughout the time investigation experiments and upon assessment of the graph one can observe that solution pH was raised from an initial 3.5 for the untreated effluent to between 10-11 during and after treatment with the ArnavZ_3.

![Figure 6.3 pH variation during time investigation experiments](image)

This characteristic behavior in which zeolites influence solution acidity is indicative of their nature (particularly Na-form exchangers) and can be attributed to the exchange of proton ions (H\(^+\)) initially present in solution with the exchangeable cations (Na\(^+\)) present in their structures, with the resultant formation of free hydroxyl ions (OH\(^-\)) which is responsible for the rise in alkalinity\(^{[59]}\).
The reaction is illustrated in equation 6.2

\[
\text{Ze-Na} + \text{H}_2\text{O} \leftrightarrow \text{ZeH} + \text{Na}^+ + \text{OH}^- \quad (6.2)
\]

Since no additional pH adjustments were made during the equilibration process with ArnavZ₃, sorption occurred in considerably alkaline conditions, and as such, the solution could become supersaturated for certain solid phases which may have precipitated (through complex formation), resulting in enhancement of the decontamination process. The probability of precipitation could lead to the enhancement of metal removal. Since, the possibility of precipitation as a factor in terms of metal retention cannot be excluded, it is therefore important to determine the dominant method involved in the immobilization of the metals; cation exchange or solid precipitation. This may be determined in a number of methods, and one such method is the ion balance between the released Na⁺ and the total cation taken up from the solution, [86] which will be discussed in more detail in latter sections.

### 6.3.1.3 Results for the temperature variation investigations

The effect of temperature on metal retention, for the adsorption of Mn²⁺, Ba²⁺, Fe³⁺, Pb²⁺, Zn²⁺, Cu²⁺, Al³⁺, Sr²⁺ and Co²⁺ onto ArnavZ₃ was investigated at three different temperatures (20, 30 and 40°C). The results and data for the ICP-MS analysis of treated water samples are shown in Appendix B1.3
The results in terms of percentage adsorption, depicted in figures 6.4 (a – c), shows that % adsorption increased with each temperature increase, for all metal cations studied.

**Figure 6.4** Effect of temperature variation on Fe$^{3+}$ and Zn$^{2+}$ (a); Al$^{3+}$ and Cu$^{2+}$ (b); Sr$^{2+}$, Ba$^{2+}$ and Pb$^{2+}$ (c); Mn$^{2+}$ and Co$^{2+}$ (d) removal in terms of % adsorbed

Conditions: Initial metal concentration: 5mg L$^{-1}$ (+/- 10%); solid/liquid ratio: 5g zeolite/100 ml effluent
The equilibrium uptake (mg g\(^{-1}\)) of ArnavZ\(_3\) increased with temperature elevation for all metals studied. The results, tabulated in table 6.3 shows that uptake for Ba\(^{2+}\) increased from 0.998 to 0.100, Pb\(^{2+}\) uptake increased from 0.0961 to 0.0965, Cu\(^{2+}\) uptake increased from 0.0934 to 0.0944, Sr\(^{2+}\) uptake increased from 0.0933 to 0.0934, Co\(^{2+}\) uptake increased from 0.0912 to 0.0915, Mn\(^{2+}\) uptake increased from 0.0894 to 0.0896, Zn\(^{2+}\) uptake increased from 0.0873 to 0.0890, Al\(^{3+}\) uptake increased from 0.0804 to 0.0847, while the uptake increase for Fe\(^{3+}\) was from 0.0733 to 0.0735 mg per gram of zeolite, by increasing the temperature from 20 to 40\(^\circ\)C. The increase in adsorption with temperature observed for ArnavZ\(_3\), suggests the process to be endothermic.
Table 6.3 Effect of temperature (K) on metal uptake (mg g⁻¹)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Temperature (K)</th>
<th>293</th>
<th>303</th>
<th>313</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>10.10</td>
<td>10.16</td>
<td>10.37</td>
</tr>
<tr>
<td></td>
<td>Metal uptake, (qₑ) in mg g⁻¹,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.0804</td>
<td>0.0825</td>
<td>0.0847</td>
<td></td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.0894</td>
<td>0.0895</td>
<td>0.0896</td>
<td></td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.0733</td>
<td>0.0734</td>
<td>0.0735</td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>0.0912</td>
<td>0.0913</td>
<td>0.0915</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.0934</td>
<td>0.0939</td>
<td>0.0944</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.0873</td>
<td>0.0882</td>
<td>0.0890</td>
<td></td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>0.0933</td>
<td>0.0934</td>
<td>0.0934</td>
<td></td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>0.0998</td>
<td>0.0999</td>
<td>0.1000</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.0961</td>
<td>0.0963</td>
<td>0.0965</td>
<td></td>
</tr>
</tbody>
</table>

Conditions: Reaction time: 60 minutes; effluent volume: 100ml; mass adsorbent: 5g
The phenomena observed in the results illustrated in figure 6.4 (a – d), as well as in table 6.3; from which an increase in metal retention was evident, in terms of percent removal and mass per gram of zeolite, respectively, can be attributed to an increase in the overall affinity of the zeolite phase for entering of the metal ions. The latter statement is based on literature findings from which it was established that an increase in exchange temperature will cause progressive weakening of the ion-dipole forces between the exchanging ion (metal cations) and the solvent dipoles (water molecules); thereby reducing the solvation coating and kinetic diameter of the incoming metal ion and this leads to an increase in the extent of hidden site participation within the zeolite, of which the overall effect is an increase of the general affinity of the zeolite phase for the entering metal ions [85, 87].

These results are verified by a very significant parameter, known as is the distribution coefficient (K_D); a phenomenon which is an illustration of the ratio of exchange ions between the solid phase, and the solution phase at equilibrium and is measured in ml/g, as illustrated in chapter 3. The results in terms of K_D values are tabulated in table 6.4.
Table 6.4 Distribution coefficients ($K_D$) expressing adsorption for temperature investigations

<table>
<thead>
<tr>
<th>Elements</th>
<th>Temperature (K)</th>
<th>$K_D$ in ml g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293</td>
<td>303</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>156.294</td>
<td>203.174</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>3049.175</td>
<td>3634.885</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>182.735</td>
<td>184.312</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3391.848</td>
<td>4590.589</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1105.152</td>
<td>1577.287</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>820.495</td>
<td>1388.473</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>4081.213</td>
<td>4674.493</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>7806.045</td>
<td>10229.210</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>2450.019</td>
<td>3052.784</td>
</tr>
</tbody>
</table>

From the results tabulated in table 6.4 one can see that the distribution coefficient for all metals increase with each temperature augmentation, which confirms the results shown in both figures 6.4 (a-d) and table 6.3, as well as reflecting the explained reasoning concerning the changes to ion hydration which occur during exchange. The significance of $K_D$ in confirming these results can be explained as follows:

— The diffusion coefficient can be perceived as portraying a measure of the rate of exchange between an ion and the solid phase (zeolite) and as such expresses the ease of movement of the ion in the zeolite structure. Thus, the relative exchange rate is proportional to the diffusion coefficient, where the preferential uptake of an ion is proportional to the selectivity, expressed by the distribution coefficient of the zeolite for the ion. Therefore it can be stated
that, generally, selectivity is proportional to relative exchange rate. In other words, a high distribution coefficient means that the ion has the ability to make headway to any given direction relatively easy and consequently it is expected that the affinity of the zeolite for the ion will be proportionally high\cite{85}.

6.3.1.3.1 Thermodynamic parameters of temperature investigation

The equilibrium distribution coefficient $K_D$, the results of which have been tabulated in Table 6.4, can be used to evaluate thermodynamic parameter, $\Delta G^0$, which represents the change in free energy.

The following relationship have been used to evaluate $\Delta G^0$:

$$\Delta G^0 = -RT\ln K_D$$ (6.3)

The results in terms of the change in free energy ($\Delta G^0$) is tabulated in Table 6.5. It has been established that a negative value of $\Delta G^0$ suggests the spontaneous nature of the sorption of a particular metal ion and if the value of $\Delta G^0$ becomes more negative, with temperature elevation, it shows an increase in the feasibility of sorption at higher temperatures\cite{88}. Consequently, from the results shown in Table 6.5 it is evident that sorption appeared to be spontaneous for $\text{Ba}^{2+}$, $\text{Sr}^{2+}$, $\text{Co}^{2+}$, $\text{Mn}^{2+}$, $\text{Pb}^{2+}$,
Zn$^{2+}$ and Cu$^{2+}$, since the values obtained for $\Delta G^0$ was negative. The results also show that the change in free energy for all the above metals became more negative with increasing temperature, suggesting the favorable nature of sorption at higher temperature as mentioned earlier. However, in the case of Fe$^{3+}$ and Al$^{3+}$, sorption proved to be non spontaneous, since large positive values for $\Delta G^0$ was obtained for these two metal cations; however, from the table one observes that the positive free energy change value for both Al$^{3+}$ and Fe$^{3+}$ becomes smaller with increasing temperature, which is an indication that their adsorption becomes more favorable with each temperature increase.

Upon closer investigation, an affinity sequence was generated as follows:

$$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}.$$
Table 6.5 Change in free energy ($\Delta G^\circ$) for the sorption process of temperature investigation

<table>
<thead>
<tr>
<th>Elements</th>
<th>Temperature (K)</th>
<th>Change in free energy ($\Delta G^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>-2716.0</td>
<td>-3251.3</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>4378.8</td>
<td>4260.4</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>-2975.5</td>
<td>-3839.4</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-243.6</td>
<td>-1148.1</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>-482.0</td>
<td>-826.8</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>-3426.2</td>
<td>-3885.1</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>-5006.0</td>
<td>-5875.2</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>-2183.0</td>
<td>-2811.7</td>
</tr>
</tbody>
</table>

6.3.1.4 Results for sorption as a function of metal concentration

6.3.1.4.1 The equilibrium phase

One of the important physicochemical process aspects for the evaluation of parameters of a sorption process as a unit operation, is the equilibrium [83]. Consequently, the sorption of Ba$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Mn$^{2+}$ and Pb$^{2+}$ onto the ArnavZ$_3$, as a function of their concentrations was studied, by varying the metal concentration from 5 to 20mgL$^{-1}$, while keeping the other parameters constant. Since it was already established that equilibrium for reaction with ArnavZ$_3$
was achieved within 60 minutes, the concentration investigations was equilibrated for this time period only.

The results and data of ICP-MS analysis of the treated water samples are tabulated in Appendix B1.4 (a) – (d).

The relation between metal uptake \( (q_e, \text{mg g}^{-1}) \) of \( \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Sr}^{2+}, \text{Mn}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Al}^{3+}, \text{Co}^{2+} \) and \( \text{Fe}^{3+} \) on the solid phase and initial metal concentration \( (C_i, \text{mgL}^{-1}) \) is shown in figure 6.5 (a – f). As already previously established (section 6.3.1.3); in practical applications, equilibrium is most conveniently established in terms of the distribution coefficient \( (K_D) \) of the exchanged ions, since \( K_D \) data implicitly indicate the selectivity, capacity and affinity of an ion exchanger for a particular counter ion. Having said that, distribution coefficient values for ArnavZ3 are shown in figure 6.6 (a – c).
Figure 6.5 (a-f) Results showing metal binding of $\text{Ba}^{2+}$, $\text{Pb}^{2+}$ (a); $\text{Sr}^{2+}$ (b); $\text{Co}^{2+}$, $\text{Cu}^{2+}$ (c); $\text{Mn}^{2+}$ (d); $\text{Zn}^{2+}$, $\text{Al}^{3+}$ (e) and $\text{Fe}^{3+}$ (f) on ArnavZ$_3$ (mg g$^{-1}$) as a function of initial metal concentration (mg L$^{-1}$)

Conditions: solid/liquid ratio: 5g zeolite/100 ml mixed metal effluent; reaction time: 60 minutes; temperature: $\pm$ 20°C; initial metal concentration: 5, 10, 15 20 (+/- 10-15% error deviation) mg L$^{-1}$
Figure 6.6 (a-c) Variation of distribution coefficient ($K_D$) in terms of Ba$^{2+}$, Pb$^{2+}$ (a); Mn$^{2+}$, Al$^{3+}$, Zn$^{2+}$, Fe$^{3+}$ (b); Sr$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ (c) as a function of initial metal concentration in aqueous solution (mgL$^{-1}$)

An assessment of the results shown in figure 6.5 (a – f), reveals that the uptake Ba$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Co$^{2+}$ and Fe$^{3+}$ on ArnavZ$_3$ increases linearly with increase in initial concentration of metal ions in solution phase. In figure 6.6 (a – c)
on the other hand, the distribution coefficients for the metals studied, reveals that
selectivity and as such, metal uptake, is highest for Ba$^{2+}$ and Pb$^{2+}$; while slightly
lower in terms of Sr$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ and finally the lowest values obtained for Zn$^{2+}$,
Mn$^{2+}$, Al$^{3+}$ and Fe$^{3+}$. A very significant trend seems to present itself: Distribution
coefficients for all metal ions, except Al$^{3+}$ and Fe$^{3+}$, tends to show a minimum at x-
value (initial metal concentration) approximately equal to 10 mg L$^{-1}$; however, after
this point the $K_D$ value increases for all subsequent concentrations. The reason for
this finding; it is assumed, is that energetically less favorable sites becomes involved,
as going from initial concentration of 5 – 10 mg L$^{-1}$, which combined with surface
imperfections and mineral heterogeneity of zeolites, may lead to multilayered
sorption, consequently this phenomenon observed with $K_D$ variation can be attributed
to the saturation of the first monolayer of the zeolite surface in going from 5 to
10 mg L$^{-1}$. For the 15 mg L$^{-1}$ initial concentration, sorption then proceeds on the
subsequent monolayer on the zeolite surface, which has a consequent rise in
distribution coefficient.

Based on the findings in terms the distribution coefficient, as well as the specific
metal uptake; the selectivity series produced is as follows:

$$Ba^{2+} > Pb^{2+} > Sr^{2+} > Co^{2+} > Cu^{2+} > Mn^{2+} > Zn^{2+} > Fe^{3+} > Al^{3+}$$

until approximately $C_i$ equal to 10 mg L$^{-1}$, selectivity changed for Sr$^{2+}$ and Co$^{2+}$, as
well as for Al$^{3+}$ and Fe$^{3+}$. Similar findings in terms of $K_D$ selectivity series were
reported in previous literature$^{[85]}$. 


A detailed discussion of the above results, including selectivity trends is done in the following section.

Discussing metal uptake and selectivity results portrayed at equilibrium conditions

Generally, in the hydrated unit cell within the zeolite, the exchangeable cations interact with aluminosilicate framework and thus exchange is brought about. It has been found that sodium ions; being more polarizing, have a greater tendency to interact with the aluminosilicate framework and as such, is less resistant for exchange \[^{89}\]. Since ArnavZ\textsubscript{3} is essentially a near homoionic Na-faujasite-type zeolite, exchange with the metals is thus easier. However, the immobilization of metal ions from aqueous phase is a multifaceted process, since both selectivity order and maximum exchange rates are the result of physicochemical and stereochemical factors, including the following \[^{69,90}\]:

- hydrated radii;
- hydration enthalpy of cations;
- the strength of the metal-framework oxygen bond on the zeolite surface;
- space requirements in the micropores of the zeolite

The data, obtained from literature \[^{86}\], in terms of the bare metal ionic radii, as well as the very important hydration enthalpies for all the selected metals are tabulated in table 6.6
Table 6.6: Ionic radii and hydration energies for metals

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Bare metal ionic radius (Å)</th>
<th>Free energy of hydration (KJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co²⁺</td>
<td>0.89</td>
<td>-1996</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.71</td>
<td>-2100</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.88</td>
<td>-2046</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.91</td>
<td>-1841</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>1.27</td>
<td>-1443</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>1.49</td>
<td>-1305</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>1.33</td>
<td>-1481</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.53</td>
<td>-4430</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.68</td>
<td>-4665</td>
</tr>
</tbody>
</table>

Generally, as a rule, the ion exchanger (in this case, zeolite: ArnavZ₃) prefers the cation of higher valence; an effect that is purely from electrostatic forces, and in many cases the smaller counter ion [85]. Hydration of the cation on the other hand, also play a very significant role, since the migrating species are cation-water complexes and as such, some differences in ion exchange selectivity is bound to be attributable to necessity to reject some water molecules. From this point of view, the concept of rejection of some water molecules, which is related to the hydration enthalpies, does explain the low selectivity and equally low metal uptake in the case of Fe³⁺ and Al³⁺. Prior investigations have also established that group d⁶ to d⁹ ions are affected by ligand field stabilization, preferring octahedral configuration and as such, the rigid zeolite framework cannot compete with the solvent molecule ligands in providing the ions with their strongest coordination environments and therefore such strongly hydrated ions, remains far from the framework, hydrolyses, and then
connects to the framework through hydroxyl or oxide bridging\cite{69}. Another phenomenon, known to also adversely affect the selectivity of Al$^{3+}$ (apart from hydration energy), is its ability to induce reduction or reversion of the effective negative charge of the zeolite surface; caused by the formation of hydroxyl or other solid species on the zeolite surface, in the quest to immobilize the ion\cite{85}. While still on the aspect of ion hydration; this concept also easily explains the higher metal uptake and selectivity of the zeolite shown in figures 6.5 (a) and 6.6 (a) for the larger ions, Ba$^{2+}$, Pb$^{2+}$ and even Sr$^{2+}$ since they will tend to loose their hydration sheaths fairly easily, which will enhance their diffusion and ease of movement in the lattice, resulting in a bigger metal uptake. The biggest uptake, as expected was thus for Ba$^{2+}$, followed by Pb$^{2+}$ and then Sr$^{2+}$. As for the other ions, other parameters may have some significance in adversely affecting their selectivity. The lower selectivity exerted for Cu$^{2+}$, could be attributable to a number of reasons. One such reason may be that, unlike the other aqua-metal ion complexes; Cu$^{2+}$, having a coordination number of four, prefers to form a tetrahedral aqua-complex; rather than the usual hexaqua-octahedral complexes preferred by most other elements. It is likely then, that the movement of the hydrated Cu$^{2+}$ in the zeolite lattice is stereochemically hindered; a phenomenon which have been encountered before\cite{90}. Another very significant reason may be that in addition to exchange of Cu$^{2+}$ on ArnavZ$_3$, it may also be fixed in solid species growing from the zeolite surface and these precipitates may clog part of the zeolite.
pores, resulting in reduction of further metal uptake. Similar findings have already been made in prior research investigations \cite{85}.

Since adsorption phenomena are highly dependent on charge density of cation, and as such, the hydration energy of the ion, one would thus expect selectivity for the lesser hydrated \(\text{Mn}^{2+}\) ion (-1841 KJ mol\(^{-1}\)) to be greater than for the stronger hydrated \(\text{Co}^{2+}\) ion (-1996 KJ mol\(^{-1}\)). However the selectivity order produced from the equilibrium results shows the opposite effect and based on similar findings, this can be explained as follows: Although the lesser hydrated \(\text{Mn}^{2+}\) looses its hydration sheath easier than the more hydrated \(\text{Co}^{2+}\), at the same time its interaction with the framework oxygens of the zeolite is weaker, so there is compensation for the two counter-acting factors \cite{69}.

Other factors which may have contributed to the zeolite 'preference' include the possibility of the formation of large inorganic complexes (such as nitrato- or hydroxo complexes) during the sorption process, which may be mechanically excluded by the zeolite's sieving action. Such exclusions occur if the openings in the zeolite matrix (in terms of pore size) are too narrow to accommodate the incoming ion.

The variation in solid phase concentration of the sorbate (amount adsorbed, \(q_e\) in mg g\(^{-1}\)) as a function of the solute equilibrium concentration (\(C_e\) in mg L\(^{-1}\)) in aqueous phase is expressed as an isotherm which can be seen in figure 6.7 (a – b). The results from these sorption isotherms, which describes the equilibrium behavior
of the sorption process between ArnvZ$_3$ and the synthetic mixed metal effluent, shows that high selectivity was obtained for Ba$^{2+}$ and Pb$^{2+}$ and slightly lower values for Sr$^{2+}$, Cu$^{2+}$, Co$^{2+}$, and Mn$^{2+}$ and the lowest selectivity was observed for Al$^{3+}$ and Fe$^{3+}$. The selectivity series follows the order of:

$$\text{Ba}^{2+} \geq \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Cu}^{2+} \geq \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}$$

Figure 6.7 (a – b) Sorption isotherm of Ba$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Zn$^{2+}$: (a) and Al$^{3+}$, Fe$^{3+}$: (b) as a function of solute equilibrium concentration. $Q_e$ = amount sorbed per gram of zeolite

Conditions: +/- 25°C; 5g ArnavZ$_3$ per 100ml mixed metal effluent; reaction time: 60 minutes
Equilibrium pH and its effect on ion exchange

As already established, the immobilization of heavy metal ions from aqueous solutions is quite a complicated process; consisting of ion exchange and adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface [86]. The probability of precipitation of solid species is brought about by the drastic pH rise upon addition of the zeolite. In these types of reactions, the term ‘precipitation’ refers to the immobilization through outer-sphere complexes on the solid phase surface. By definition, inner-sphere complex formation involves the formation of direct chemical bond between the zeolite surface functional groups and the metal ion; whereas in outer-sphere complex formation, the ion is still surrounded by a solvation sheath of water molecules and sorbs in a non-specific or specific electrostatic or hydrogen-bonded manner.

The pH variation during equilibrium sorption experiments is tabulated in table 6.7, from which one can see that a considerable rise in pH occurred after addition of ArnazZ3 for all initial concentrations and as such, it is expected that in these highly alkaline conditions, dissociation of surface functional groups through dissolution of the zeolite phase will result in a more negative solid surface and as such, significantly contribute to the metal removal through the methods discussed in the preceding paragraph.
Table 6.7  
**pH variation during equilibrium phase investigations**

<table>
<thead>
<tr>
<th>Initial metal concentration (mgL⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated effluent</td>
</tr>
<tr>
<td>5</td>
<td>3.25</td>
</tr>
<tr>
<td>10</td>
<td>3.21</td>
</tr>
<tr>
<td>15</td>
<td>3.15</td>
</tr>
<tr>
<td>20</td>
<td>3.05</td>
</tr>
</tbody>
</table>

Since solution pH is one of the factors which controls the formation of aqua-metal and hydroxo-complex species, which can subsequently effect the mechanism of metal binding by changing it from ion exchange to adsorption of monovalent hydroxo-species, it is important to determine whether the dominating mechanism in the retention of metals was cation exchange or precipitation of solid species. As stated earlier, this can be determined by the balance of ionic charge (Na⁺) leaving the solid phase and the ionic charge taken up by the solid phase (½ Zn²⁺; ½ Ba²⁺; ½ Co²⁺; ½ Mn²⁺; ½ Sr²⁺; ½ Cu²⁺; ½ Pb²⁺; ½ Fe³⁺; ⅓ Al³⁺).  

Thus, the relation between the released Na⁺ ions and the ingoing exchangeable ions for the different initial metal concentrations in terms of individual metal ions are tabulated in **table 6.8 (a) and table 6.8 (b)**. On the other hand, Figure 6.8 shows the relation of ion balance between the released Na⁺ ions and the total cation charge entering the solid phase (meq g⁻¹) for the different initial concentrations.
Table 6.8 (a) Results showing the relation between the released Na\(^+\) ions and the ingoing counter ions for the different initial metal concentrations in terms of individual metal ions

<table>
<thead>
<tr>
<th>Initial metal ion concentrations (ppm)</th>
<th>Uptake charge (meq g(^{-1})) of particular metals on solid phase at individual initial concentrations</th>
<th>Charge of released Na(^+)</th>
<th>(1/2)Ba(^{2+})</th>
<th>(1/2)Pb(^{2+})</th>
<th>(1/2)Sr(^{2+})</th>
<th>(1/2)Co(^{2+})</th>
<th>(1/2)Cu(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0007 0.0005 0.0002 0.0016 0.0015</td>
<td>0.1835</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.0016 0.0011 0.0005 0.0033 0.0031</td>
<td>0.2360</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.0025 0.0016 0.0008 0.0051 0.0048</td>
<td>0.2811</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0034 0.0022 0.0011 0.0069 0.0064</td>
<td>0.2781</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.8 (b) Results showing the relation between the released Na\(^+\) ions and the ingoing counter ions for the different initial metal concentrations in terms of individual metal ions

<table>
<thead>
<tr>
<th>Initial metal ion concentrations (ppm: mg L(^{-1}))</th>
<th>Uptake charge (meq g(^{-1})) of particular metals on solid phase at individual initial concentrations</th>
<th>Charge of released Na(^+)</th>
<th>(1/2)Mn(^{2+})</th>
<th>(1/3)Zn(^{2+})</th>
<th>(1/3)Al(^{3+})</th>
<th>(1/3)Fe(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0016 0.0014 0.0032 0.0014</td>
<td>0.1835</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.0035 0.0028 0.0068 0.0029</td>
<td>0.2360</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.0053 0.0044 0.0107 0.0046</td>
<td>0.2811</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0072 0.0059 0.0141 0.0062</td>
<td>0.2781</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 6       RESULTS FOR DECONTAMINATION EXPERIMENTS

Figure 6.8  Results showing the relation of charge balance between released Na\(^+\) ions and total ingoing metal ions for different initial metal concentrations

Assessment of the results from table 6.8 (a) and (b), shows that in terms of values, for every divalent metal studied (M\(^{2+}\)), the released Na\(^+\) was in considerable excess (≥ twice more) to the charge of metal ions exchanged onto the zeolite, which is a very important finding, since to maintain the equilibrium during the ion exchange process; for every metal taken up, two equivalents of Na\(^+\) needs to be released according to the following equation:

\[
\text{Me}^{2+} + 2\text{NaZe} \leftrightarrow \text{MeZe}_2 + 2\text{Na}^+
\]

The same trend in terms of excess charge of Na\(^+\) was observed in the case of the trivalent ions, Fe\(^{3+}\) and Al\(^{3+}\). In the case of these ions, for every ion taken up, three equivalent Na\(^+\) needs to be released to maintain equilibrium in the system. Thus based on these findings, one would make some conclusive estimation that ion exchange appeared to be the dominant method of retention at all initial
concentrations. However, to get a relation between the total charges taken up and released, a plot was drawn, shown in figure 6.8. Thus figure 6.8, shows the balance of the total ionic charge released from- (Na⁺) and going into the zeolite phase (\(1/2\)Zn²⁺; \(1/2\)Ba²⁺; \(1/2\)Co²⁺; \(1/2\)Mn²⁺; \(1/2\)Sr²⁺; \(1/2\)Cu²⁺; \(1/2\)Pb²⁺; \(1/3\)Fe³⁺; \(1/3\)Al³⁺). The results shown in this graph reveals that the total charge of outgoing ions is higher than the total charge of ingoing ions for all initial metal ion concentrations; particularly in the more dilute solutions. From these results one can conclude that ion exchange was shown to be the dominant method of metal retention in the more dilute electrolyte solutions, but at the higher initial concentrations, especially 20 mgL⁻¹, the ratio between released Na⁺ and metals taken up, was too low to assume that ion exchange was the only method used to retain metals on the solid phase.

Finally, in conclusion one can say that the possibility of precipitation of solid phases as a means for enhancement of the decontamination processes with ArnavZ₃ should not be excluded.

6.3.1.5 Results of the effect of competing ions on metal removal from aqueous phase

The data and results in terms of competing ions investigations are tabulated in Appendix B1.5 (a – b)
The effect of ionic strength on metal cation retention capacity of ArnavZ₃ was studied by using Ca(NO₃)₂·4H₂O and Mg(NO₃)₂·6H₂O as electrolytes. These electrolytes were used, since the divalent cations, especially Ca²⁺ are usually found in excess concentrations in secondary co-disposed process waters and may pose a threat in terms of metal removal, by competing for sites on the sorbent. These investigations were done by varying the electrolyte concentration in terms of Ca²⁺ from 0 - 262 to 295 mg L⁻¹, and 75 mgL⁻¹ in terms of Mg²⁺, as described in chapter 3. The results are shown in figure 6.9, which is a plot of the amount metal removed per gram of zeolite (mg g⁻¹) as a function of initial competing ion concentration (mgL⁻¹).

Figure 6.9  Results showing the effect of the presence of competing ions on the capacity of AnavZ₃ for metal retention in terms of percent removal
The results show that for the metal cations, including $\text{Ba}^{2+}$, $\text{Mn}^{2+}$, $\text{Sr}^{2+}$, $\text{Pb}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$, a decrease in sorption occurred in the presence of competing divalent cation $\text{Ca}^{2+}$, as much as its concentration was increased. In light of the fact that the presence of $\text{Mg}^{2+}$ did not appear to affect sorption as much as $\text{Ca}^{2+}$, it is an indication that $\text{Ca}^{2+}$ is considered the major competing ion in this type of remediation experiments. A closer look at the results reveals that $\text{Ca}^{2+}$ competes very effectively with $\text{Sr}^{2+}$, since the decrease undergone in terms of removal capacity with respect to this ion at the highest ionic strength ($\text{Ca}^{2+} = 295 \text{ mg L}^{-1}$) was approximately 92%. As for the other metal cations, reduction in metal uptake in terms of percent adsorbed, at highest ionic strength corresponded to values of 17% for $\text{Ba}^{2+}$, 26% for $\text{Zn}^{2+}$, 30% for $\text{Co}^{2+}$, 27% for $\text{Pb}^{2+}$, 29% for $\text{Cu}^{2+}$ and 29% for $\text{Mn}^{2+}$. However, in the case of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ a slight reduction was observed at highest ionic strength ($\text{Ca}^{2+} = 295 \text{ mg L}^{-1}$), but in the presence of both $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$, decrease undergone in terms of metal retention with respect to these ions were higher, corresponding to values of 20% for $\text{Al}^{3+}$ and 69% for $\text{Fe}^{3+}$.

Taking into account, that the standard error of the mean was not considered in this set of experiments, the proposed discussion of results is merely an indication of the possible effect of certain competing ions on the selected metal ions and as such, may differ from one experiment to the next.
6.3.1.6 Results for the investigations for removal of trace and anion forming metal species with ArnavZ₃

The results and data for the ICP-MS analysis of treated water samples are shown in Appendix B1.6

ArnavZ₃ is a ‘near-homoionic’ Na-faujasite type aluminosilicate mineral cationic exchanger. However, as previously discussed, since pH is one of the factors which controls aqua-metal and hydroxo-complex species, and bearing in mind that the zeolite addition to the effluent had a consequent considerable pH rise, which could affect the mechanism of metal binding by changing it from ion exchange to adsorption of monovalent hydroxo-species, since the possibility of precipitation was not ruled out. Considering these factors; the zeolite behavior in the presence of trace and anion forming metals (e.g. AsO₄²⁻) was investigated to evaluate if the possibility of complex formation through specific and/or nonspecific adsorption could assist in the removal of anionic species from aqueous solutions with ArnavZ₃ [62].

The working solution in these experiments was a mixed metal model solution, consisting of Arsenic (As), mercury (Hg), selenium (Se), boron (B), molybdenum (Mo), indium (In) and thalium (Tl), with an initial concentration of 5 mg L⁻¹ (+/- 10% error deviation), with respect to each metal. The working solution was made up by appropriate dilutions of the 1000 mg L⁻¹ standard stock solution, which was commercially obtained.
The results for these investigations are tabulated in table 6.9, which shows metal concentrations before and after equilibration with ArnavZ₃, as well as quantity loaded per gram of zeolite; while table 6.10 illustrates the magnitude by which certain elements leached into solution during decontamination experiments. Figure 6.10, on the other hand, presents the percent metal removed from the aqueous phase.

Table 6.9 Results showing B, As, Hg, Tl, In, Se and Mo concentrations (mg L⁻¹) before and after treatment with ArnavZ₃

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (mg L⁻¹)</th>
<th>pH Initial</th>
<th>After treatment</th>
<th>Amount sorbed mg g⁻¹</th>
<th>MCL (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>4.859</td>
<td>2.5</td>
<td>9.89</td>
<td>0.007</td>
<td>0.097</td>
</tr>
<tr>
<td>As</td>
<td>4.827</td>
<td>2.505</td>
<td>0.046</td>
<td>2.505</td>
<td>0.046</td>
</tr>
<tr>
<td>B</td>
<td>4.092</td>
<td>3.495</td>
<td>0.012</td>
<td>3.495</td>
<td>0.012</td>
</tr>
<tr>
<td>Tl</td>
<td>4.61</td>
<td>0.00</td>
<td>0.092</td>
<td>0.00</td>
<td>0.092</td>
</tr>
<tr>
<td>In</td>
<td>5.123</td>
<td>0.471</td>
<td>0.091</td>
<td>0.471</td>
<td>0.091</td>
</tr>
</tbody>
</table>

Note: - refers to value not found in literature

Conditions: 25 °C; solid/liquid ratio: 5g sorbent/100 ml effluent; initial metal concentration: 5 mg L⁻¹(+/− 10% error deviation)

Table 6.10 Results for leaching of elements from solid phase into solution

<table>
<thead>
<tr>
<th>Elements</th>
<th>Initial concentration mgL⁻¹</th>
<th>Final concentration mgL⁻¹</th>
<th>Amount leached into solution</th>
<th>MCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>4.233</td>
<td>4.369</td>
<td>0.003</td>
<td>0.01</td>
</tr>
<tr>
<td>Mo</td>
<td>4.191</td>
<td>4.478</td>
<td>0.006</td>
<td>0.070</td>
</tr>
</tbody>
</table>

Conditions: 25 °C; solid/liquid ratio: 5g sorbent/100 ml effluent; initial metal concentration: 5 mg L⁻¹(+/− 10% error deviation)
6.3.1.6.1 Results for removal of cationic species

The results show that removal was quite favorable in terms of mercury, since very low residual concentrations (0.007 mg L\(^{-1}\)) was obtained after equilibration with the ArnavZ\(_3\) – a value which is slightly higher than the Environmental Protection Agency’s (EPA) proposed maximum contaminant level (MCL) for potable water (0.002 mg L\(^{-1}\)). The fraction of Hg removed from the aqueous phase in terms of percentage corresponds to a value of 99.79 %. Based on the results, one can conclude that the sorbent, ArnavZ\(_3\) has a considerable affinity in terms of selectivity for mercury; however, this affinity might not predominantly be based on its retention
through means of ion-exchange. The rational behind the latter statement can be explained as follows:

— Hg is a group IIb transition element and in aqueous environments; in the absence of strongly complexing ligands, its speciation is largely controlled by hydrolysis reactions. In aqueous solution the element usually exists in the divalent state (Hg^{2+}) – as a hexaqua-ion [Hg(H_2O)_6^{2+}] \[^{91, 92}\]. When the aqueous environment becomes more alkaline; thus increasing hydrolysis, the aqua-Hg^{2+}-complex rearranges and thus forms a distorted octahedral coordination, giving the appearance of a two-coordinated Hg, which has the tendency to form mononuclear linear 2-coordinated complexes \[^{91}\]. The hydration energy for Hg^{2+}, based on literature values was found to be -1824 KJ mol\(^{-1}\) \[^{93}\]; which is higher as compared to the other two less polarized cations, Tl\(^+\) and In\(^{3+}\), and as such, ArnavZ\(_3\) will tend to show higher selectivity for ion exchange with these ions, than for Hg\(^{2+}\). Based on the preceding facts, as well as considering prior investigations in terms of Hg\(^{2+}\) sorption onto mineral oxides \[^{91}\], it is suggested that, in addition to ion exchange, the hydrolyzed Hg\(^{2+}\) also gets sorbed onto ArnavZ\(_3\) through the formation of inner-sphere sorption complexes (i.e. a the formation of a direct chemical bond between Hg(II) and the surface functional groups).
As for Tl⁺, the results show that the ion was virtually completely removed from aqueous phase, with a residual concentration of 0.002 mg L⁻¹ and a correspondingly high removal of 99.99% after equilibration with AnavZ₃. This confirms the well known fact, that selectivity for this metal ion, is common to all zeolites [54]. The selectivity that is clearly exerted by the zeolite for this ion, is due to its very low polarity which leads to considerably weakening of the ion-dipole forces between Tl⁺ the surrounding water molecules. Therefore, Tl⁺ will not be very hydrated in solution and this is confirmed by its low hydration energy (-326KJ mol⁻¹). The result is that the ion easily looses its hydration sheath and thus can comfortably proceed to diffuse through the zeolite pores for ion exchange with its exchangeable Na⁺ ions.

Similar results was observed for In³⁺ and as such, also showed favorable removal, corresponding to 99.96 in terms of percentage, as well as very low residual concentration left at equilibrium (0.471 mg L⁻¹). These results is not surprising, considering the fact that both Tl and In are both IIIA main group elements [68]. It is thus assumed that they will tend to behave similarly in aqueous environment and as such, the zeolite will show a correspondingly high preference for these elements in terms of ion exchange.

In conclusion, ICP-MS results have confirmed that the Na⁺ ion concentration in the solution went up from 0.775 mg L⁻¹ to 380.034 mg L⁻¹ (Appendix B1.6) during the
decontamination experiments, which shows that ion exchange played a significant role in the removal of the cationic species from solution.

6.3.1.6.2 Results for removal of anionic species

The chemistry of As is rather different from the elements already discussed, since it usually forms oxoanions, in which As exist either in the pentavalent (AsV) or trivalent (As III) form and as such, cannot be removed by normal ion exchange processes \(^{[71]}\). During these experimental investigations, As was in the V state.

The results tabulated in table 6.9 and figure 6.10 show that, metal retention for As(V) in terms of percentage was 48.11% with a corresponding residual solution concentration of 2.505 mg L\(^{-1}\) after treatment – a value which is higher than the EPA’s MCL (0.05 mg L\(^{-1}\)).

Prior investigations, involving the sorption of As(V) on low cost sorbent materials, such as fly ash, goethite (iron oxihydroxides) and activated carbon, have established that the immobilization of As(V) occurs through strong interactions with the oxides in the solid phase of the sorbent and this interaction is pH controlled. Thus in more acidic conditions, As(V) is retained through interactions with ferric and aluminum oxides, while retention in alkaline regions is due to complex formation with calcium and magnesium oxides. The possible mechanism for these interactions are as follows \(^{[11, 94]}\).
In more acidic conditions, the mechanism occurs primarily by the exchange of hydroxyl groups on the sorbent surface. In the latter process, surface complexation occurs, when a proton from an undissociated arsenate anion forms a molecule of water with the hydroxyl group of the hydrous oxide on the surface of the sorbent, after which it is displaced by the arsenate ion. Therefore, when conditions are weakly acidic, arsenic is relatively immobile due to hydrolysis with iron oxihydroxides. As such, in weakly acidic pH conditions, soluble As(V) anions forms stable arsenates, such as scorodite \([\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}]\), erythrite[\text{Co,Ni(AsO}_4)_2\cdot 8\text{H}_2\text{O}], etc with elements in solution, including Fe, Co, Ni, Zn and Pb and is removed from solution through such complexes.

However, as the pH increases, the arsenic ion’s ability of displacing hydroxyl groups from the hydrous oxide is reduced, since less arsenic ions are protonated in alkaline conditions. Thus, in highly alkaline conditions, the calcium arsenates tend to be more stable; especially at pH’s above 10 and in the presence of excess lime. Therefore in highly alkaline conditions, arsenic removal is mainly due to adsorption on calcium and magnesium oxides, by the formation of alkaline arsenites \([\text{Ca(AsO}_2\cdot \text{Ca(OH)}_2]\), alkaline arsenates \([\text{Ca}_3(\text{AsO}_4)_2\cdot \text{Ca(OH)}_2]\), as well as gypsum \([\text{CaAsSO}_4\cdot 2\text{H}_2\text{O}]\).

In light of the latter knowledge of the chemistry of arsenic, as well as the fact that these sorption investigations occurred in considerably alkaline conditions (pH ≥ 9.9);
also bearing in mind that the starting material of this zeolite is fly ash based and
lastly, since fly ash is considered a liming agent for the treatment of metal-bearing
wastewaters – it can be concluded that the removal of As(V) in the current
investigation may be attributed to complex formation with calcium or magnesium
oxides. This argument is corroborated by the fact that according to XRF analysis,
CaO and MgO was determined as part of the major oxides found in the synthesized
zeolite (ArnvaZ3), as shown in chapter 5.

Removal for B was approximately 15%, with a residual concentration of
3.495 mg L\(^{-1}\) after treatment with ArnvaZ3, which is a far cry from the proposed
MCL of 0.3 mg L\(^{-1}\), recommended by the World Health Organization.
Boron is considered to be one of the inorganic constituents that are most problematic
and difficult to immobilize and as such the chemistry of this element is quite
complex. However; previous investigations has established that; by using low cost
sorbents; particularly fly ash, it is possible to immobilize boron from solution\(^{[43]}\). In
these processes, which is pH specific and as such, occurs primarily in alkaline
regions, B is taken up through formation of ion-pair borate species with the fly ash
and this occurs through co-precipitation with magnesium hydroxide and/or hydroxy-
oxides of alumina. The mechanism through which this happens is that hydroxyl
groups in the coordination sphere act as bridging ligands between the adsorbed
boron [as B(OH)\(_4\)] and the surface of Mg, Fe and Al oxides\(^{[43]}\).
Based on these findings and considering the fact that both alumina and silica concentrations went up by 0.619 mgL\(^{-1}\) and 17.174 mgL\(^{-1}\) (Appendix B1.6), respectively, during the decontamination experiments, it may be suggested that in these alkaline conditions (pH \(\geq\) 9.9); B was retained through complex formation with active surface hydroxyl functional groups; due to dissolution of part of the zeolite; catalyzed by hydroxyl attack of the surface functional groups (as illustrated in chapter 5).

6.3.1.6.3 Elements leached of from solid phase into solution

Se and Mo are also elements which have the tendency to form oxoanions in solution and as such cannot be removed by the normal ion exchange process. According to literature findings, sorption for these elements; like arsenate and borate (H\(_2\)BO\(_3\)^-) occurs by the exchange of hydroxyl groups on the sorbent surface, followed by its displacement by the ion itself\(^{[71]}\).

The results for these investigations, presented in table 6.10 show that Se and Mo leached from the solid phase to the solution during treatment with ArnavZ\(_3\). In terms of percentage, Mo leached by 6.84\%, while leaching for Se was 3.22\%, which corresponds to an increase of 0.287- and 0.136 mg L\(^{-1}\) for Mo and Se respectively. This phenomenon was not surprising, considering the fact that both Se and Mo, according to literature findings, proved to be very mobile in fly ash (> 90\%)\(^{[34]}\) and as such may leach into the zeolite phase during synthesis, with subsequent probable leaching into solution during the decontamination process. These findings were
confirmed through the results obtained from the standard leaching tests conducted on
the fly ash; from which it was shown that both Mo and Se leached from the fly ash,
while the fraction of leaching from Mo was particularly higher, 0.186 mg L\(^{-1}\) – a
value which is more than WHO’s proposed MCL (0.07 mg L\(^{-1}\)).

6.3.1.7 Mechanisms of metal retention

Based on the extensive discussions elaborating on the metal ion removal with
ArnavZ\(_3\), as well as referenced previous literature findings, the overall uptake of
metal ions from aqueous solution with FA/AMD-related Na-type zeolites may be
described as a process consisting mainly of different types of ion exchange and
adsorption processes, which is accompanied by precipitation; particularly at high
initial metal concentrations.

Surface imperfections and mineralogical heterogeneity of the zeolitic tuff promote
the solubility of surface functional groups (zeolite dissolution) at both higher and
lower pH values. It was identified by the determination of Si concentration in the
liquid phase. The surface charge remaining after the detachment of surface groups is
non-homogeneously distributed and presents newly formed active sites (variable
charge sites), suitable for ion retention. This occurrence is pH dependent and as such,
may also be used for anion immobilization\(^{[90]}\).
It may thus be proposed that binding onto these zeolite types (i.e. ArnavZ₃) can be described by “model” that assumes two kinds of binding sites; permanently charge sites and variable charge sites.

The possible mechanisms by which ions are retained are illustrated as follows:

- Adsorption of metal cations occurs via ion exchange with exchangeable Na⁺ ions at permanently charge sites. This reaction is caused by electrostatic attraction and this illustrated as follows:

  \[ 2\equiv\text{Ze} - \text{Na}^+ + \text{M}^{2+}(aq) \rightleftharpoons \text{Ze}^2 - \text{M} + 2\text{Na}^+(aq) \]

  Where (aq) refers to the solution phase, while Ze denotes the zeolite phase (≡Al-O-Si≡) and as shown, there needs to be a charge balance between the ions exchanged by the zeolite phase for ions from the aqueous phase [69, 72, 73]. The latter equation illustrates ion exchange for divalent ions.

- In the other mechanism, the hydrolysed aqua-metal-ion may interact with the hydroxyl-complexes on the zeolite surface through which inner-sphere complexes may be formed; resulting through the formation of a direct chemical bond between the ion and the zeolite surface [69, 73]. This retention process normally occurs at variable charge sites on the zeolite surface.
• The process is illustrated by as follows:

\[ \equiv \text{Ze} \rightarrow \text{Na} + \text{Me(OH)}_m (\text{H}_2\text{O})^{2m-n} \rightleftharpoons \equiv \text{Ze} \rightarrow \text{MeOH} + \text{Na}^+(\text{aq}) \]

• Hydrolysis and exchange of hydrated ions may also occur simultaneously, shown as follows:

\[ \equiv \text{Ze} \rightarrow \text{Na} + \text{H}_2\text{O} + \text{M}^{2+}(\text{aq}) \rightleftharpoons \equiv \text{Ze} \rightarrow \text{MOH} + \text{Na}^+(\text{aq}) + \text{H}^+(\text{aq}) \]

• The metal ions may also be retained as hydroxy complexes on the zeolite surface with the functional groups. This reaction is accompanied by the release of hydronium ions and is shown (for divalent metal ions) as follows:

\[ \text{M}^{2+}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{M(OH)}_{2\text{Zn}} + 2\text{H}^+(\text{aq}) \]

6.3.1.8 Results for comparison of sorption capacity of ArnavZ₃ with commercial Faujasite zeolite (commFau) and chelating ion exchange resin (Lewtit TP 207)

ICP-MS results for these experiments are shown in Appendix B1.2 (b) and Appendix B1.7 (a–d)
The aim of these experiments were:

- To compare the capacity and selectivity of the fly ash-related synthesized zeolite, ArnavZ₃, to the commercially obtained Faujasite-type zeolite (commFau).

- Another fundamental aim was to confirm that zeolites have an advantage over ion exchange resins; based on their much lower cost, as well as their ion selectivity, generated by their rigid porous structures [54].

These experiments were conducted in exactly the same manner as was done during the time investigations with ArnavZ₃ (Section 6.3.1.2).

The working solution in these experiments was a model solution consisting of Ba²⁺, Pb²⁺, Sr²⁺, Cu²⁺, Co²⁺, Zn²⁺, Mn²⁺, Al³⁺ and Fe³⁺ ions, with an initial concentration of 5mg L⁻¹ (+/- 10% error deviation) with respect to each metal. The experiments were done with batch method in a temperature controlled jacketed water bath shaker and the exchanger/solution suspension was equilibrated for 1440 minutes (24 hours), while individual samples were taken out and filtered at appointed times. The results for these investigations are shown in figure 6.11 (a – i).
Figure 6.11(a-d) Results showing sorption capacity of ArnavZ3 vs. commercially obtained faujsite (CommFau) and chelating cation resin (Lewatit TP207) in terms of solution concentration (mg L\(^{-1}\)) as a function of reaction time (minutes) for Al\(^{3+}\) (a); Mn\(^{2+}\) (b); Co\(^{2+}\) (c); Fe\(^{3+}\) (d).

Conditions: 5g zeolite/ 100 ml effluent; initial concentration: 5 mg L\(^{-1}\) (+/- 10%); temp: 20\(^{\circ}\)C.
Figure 6.11(e-h) Results showing sorption capacity of ArnavZ3 vs. commercially obtained faujsite (CommFau) and chelating cation resin (Lewatit TP207) in terms of solution concentration (mgL⁻¹) as a function of reaction time (minutes) for Cu²⁺ (e); Zn²⁺ (f); Sr²⁺ (g); Ba²⁺ (h) and Pb²⁺ (i).

Conditions: 5g zeolite/ 100 ml effluent; initial concentration: 5 mg L⁻¹ (+/- 10%); temp: 20°C
Figure 6.11 (i) Results showing sorption capacity of ArnavZ3 vs. commercially obtained faujsite (commFau) and chelating cation resin (Lewatit TP207) in terms of solution concentration (mgL⁻¹) as a function of reaction time (minutes) for Pb²⁺

Conditions: 5g zeolite/ 100 ml effluent; initial concentration: 5 mg L⁻¹ (+/- 10%); temp: 20°C

Assessment of the results shown in figure 6.11 (a-i), shows that in the case of Al³⁺ (a), a steep decrease in concentration could be observed within the first 60 minutes for all three ion exchangers, reaching very low concentration levels in the case of ArnavZ3 and commFau, while at this time interval the concentration for Fe in the case of Lewatit TP 207, is still quite high (> 1 mg L⁻¹). CommFau manages to maintain the low residual concentrations for the duration of the other time intervals (60 – 1440 minutes), with slight fluctuations in between; while for ArnavZ3 concentrations goes slightly up from the 60 minute interval onward and rises till approximately +/- 1.0 mg L⁻¹ at 1440 minutes. The reason for the rise in Al³⁺
concentration was already discussed in section 5. The results in terms of Lewatit on the other hand, shows a considerable inconsistency in concentration, which is shown as fluctuations in the plot, for the rest of the time intervals; with an initial rise at approximately 180 minutes and decreases again at between 720 and 1440 minutes. It is not clear at this stage why these fluctuations could be seen in the case of Lewatit.

As for Mn\(^{2+}\) (figure 6.11 (b)), both ArnavZ\(_3\) and its commercial counterpart showed considerably high removal; with a steep concentration decrease within the first 60 minutes of contact, after which both plots reaches plateau values with correspondingly low residual concentrations for the rest of the time intervals. However, in the case of Lewatit, removal for Mn\(^{2+}\) was not as efficient; a steep decrease was observed within the first 60 minutes, only reaching a residual concentration of approximately 1.9 mg L\(^{-1}\). From this point on slight fluctuations was observed for the rest of the time intervals; however, residual concentration was maintained at \(\sim\) 2 mg L\(^{-1}\).

In the case of Co\(^{2+}\) (figure 6.11 (c)) retention, all exchangers; both commercial and fly ash-related, showed a similar trend. A very steep concentration decrease was observed within the first 60 minutes of contact for all exchangers, after which smooth, continuous plateau values were reached, with a concomitant low residual solution concentration, maintained until the 1440 time interval. While residual Co\(^{2+}\)
concentrations in the case of Lewatit was slightly higher, it still showed a good selectivity for this element.

As for Fe$^{3+}$ (figure 6.11 (d)), both ArnavZ$_3$ and commFau plots showed a steep decrease in concentration within the first 60 minutes of contact, reaching fairly low residual concentrations, which was maintained fairly stable for the rest of the time intervals and as such, smooth continuous plateau values could be observed. In the case of Lewatit, Fe$^{3+}$ ion concentration also decreased within the first 60 minutes; however, significant fluctuations can be observed from this point on, for the rest of the time intervals; showing a considerable increase between $^\dagger$ 60 – 1440 minutes, reaching a residual concentration level of approximately 1 – 2 mgL$^{-1}$ for this time period.

In the case of Cu$^{2+}$ (figure 6.11 (e)), all three ion exchangers showed similar selectivity and thus a steep concentration decrease was observed within the first hour, after which plateau values were reached, with correspondingly low residual Cu$^{2+}$ concentrations left in solution at the various time intervals.

Both ArnavZ$_3$ and commFau showed similar high affinity for Sr$^{2+}$ (figure 6.11 (f)), for which the plots showed a steep concentration decrease within the first 60 minutes, after which plateau values were reached; corresponding to very low residual concentrations during the whole of the equilibration period, (i.e. 60 – 1440 minutes).
In the case of Lewatit, on the other hand, a steep decrease was also seen within the first 60 minutes, but residual concentration for Cu\(^{2+}\) only went as low as approximately 2.5 mg L\(^{-1}\), after which significant fluctuations could be observed for the duration of the rest of the equilibration period.

As for Ba\(^{2+}\) removal, the selectivity of both ArnavZ\(_3\) and commFau was quite evident, as seen from the initial steep concentration decrease observed during the first 60 minutes, followed by very low residual concentrations for the whole of the equilibration period (60 – 1440 minutes). In the case of Lewatit, an initial decrease during the first hour can also be observed; however at the 60 minute time interval the residual concentration was still fairly high, +/- 2.0 mg L\(^{-1}\); whereas after this time period, significant concentration fluctuations could be observed between 60 – 660 minutes, after which the curve remained fairly stable from 660 minutes to 1440 minutes. During the whole equilibration process with Lewatit the residual concentration of Cu\(^{2+}\) was maintained approximately between 1.5 – 2.0 mg L\(^{-1}\).

General conclusions

Based on the results obtained for the experiments conducted to compare the metal retention ability of ArnavZ\(_3\) with its commercial counterpart, as well as with the commercially obtained chelating resin, one can draw the following conclusions:

- The selectivity and metal retention capacity of the fly ash-related faujasite-type zeolite was comparable to that of the commercially obtained faujasite. These
results indicate that the synthesized zeolite does in fact contain a high fraction of faujasite within the zeolitic structure. One of the objectives, which was the synthesis and application of a faujasite-type FA/AMD-related zeolite for the purification of metal-bearing wastewaters (i.e. secondary process effluent) was thus successfully ‘executed’.

A possible reason for the low metal uptake shown by the chelating ion exchanger, may be due to the competition between hydronium ions and metal ions for exchange sites, since the pH remained below pH 4 for the duration of the experiments.

6.3.2 Results for decontamination experiments with FA/AMD-process effluents

The ICP-MS results for these experiments are tabulated in Appendix B1.8 (a – b).

In these experiments, the prepared zeolitic material (ArnavZ3) was reacted with FA/AMD-process waters, which was obtained from the co-disposal of Arnot fly ash with Navigation AMD in a ratio of 1:3.5 (fly ash: AMD). The filtrates were then collected at different pH’s and these waters were contacted with ArnavZ3 to observe any reduction in the concentrations of selected major, minor and trace elements. The same equilibration time (60 minutes), established through the model solution experiments, was used for these investigations. The solid/liquid ratio
(zeolite/effluent) used here was also 5g zeolite/100ml effluent, as established by the model solution investigation.

The results illustrating the concentrations of major, minor and trace elements for the three co-disposed process water samples before and after treatment with ArnavZ₃ are tabulated in table 6.11, while table 6.12 gives a comparison between the metal concentration remaining after treatment and the maximum contaminant levels (MCL) for the elements in potable water, given as proposed by the World Health Organization (WHO). The matrices for these water samples differs extensively from one sample to the next and as such, metal retention would be expected to differ accordingly. One other parameter which is expected to affect metal speciation and consequently, metal retention, is pH, which is different for each sample. Sample A had an initial pH of 12.43 which slightly decreased, to approximately 11.83 during treatment with ArnavZ₃, while the initial pH for sample B was 8.10 increasing to a value of 8.93 after decontamination. On the other hand, the untreated sample C was highly acidic (pH:3.00) and although pH increased after treatment, still had a fairly acidic environment (pH:4.35), which could result in unfavourable conditions for cation metal removal, as will be discussed later.
Table 6.11 Results of decontamination of FA/AMD-process waters (collected at varying pH's) with ArnavZ₃ with respect to selected metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Untreated Sample A</th>
<th>Treated Sample A</th>
<th>Untreated Sample B</th>
<th>Treated Sample B</th>
<th>Untreated Sample C</th>
<th>Treated Sample C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12.43</td>
<td>11.83</td>
<td>8.10</td>
<td>8.93</td>
<td>3.00</td>
<td>4.35</td>
</tr>
</tbody>
</table>

Concentrations of cationic species before and after treatment with ArnavZ₃ (mg L⁻¹)

<table>
<thead>
<tr>
<th>Element</th>
<th>93.820</th>
<th>1056.801</th>
<th>66.977</th>
<th>981.365</th>
<th>96.979</th>
<th>1503.200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.421</td>
<td>1.190</td>
<td>0.660</td>
<td>0.475</td>
<td>17.432</td>
<td>4.965</td>
</tr>
<tr>
<td>Ca</td>
<td>1008.426</td>
<td>267.179</td>
<td>279.860</td>
<td>256.174</td>
<td>361.349</td>
<td>102.804</td>
</tr>
<tr>
<td>Mg</td>
<td>0.162</td>
<td>0.270</td>
<td>1295.830</td>
<td>1260.495</td>
<td>799.834</td>
<td>868.631</td>
</tr>
<tr>
<td>Fe</td>
<td>1.463</td>
<td>1.290</td>
<td>16.286</td>
<td>1.011</td>
<td>4761.974</td>
<td>2424.384</td>
</tr>
<tr>
<td>Sr</td>
<td>14.403</td>
<td>2.657</td>
<td>12.598</td>
<td>3.934</td>
<td>10.169</td>
<td>14.767</td>
</tr>
<tr>
<td>Ba</td>
<td>0.506</td>
<td>0.081</td>
<td>0.079</td>
<td>0.036</td>
<td>0.084</td>
<td>0.319</td>
</tr>
<tr>
<td>Mn</td>
<td>0.016</td>
<td>0.014</td>
<td>13.550</td>
<td>0.100</td>
<td>100.350</td>
<td>101.124</td>
</tr>
<tr>
<td>Co</td>
<td>0.012</td>
<td>0.003</td>
<td>0.080</td>
<td>0.003</td>
<td>2.547</td>
<td>2.415</td>
</tr>
<tr>
<td>Cu</td>
<td>0.164</td>
<td>0.094</td>
<td>0.128</td>
<td>0.110</td>
<td>0.418</td>
<td>0.544</td>
</tr>
<tr>
<td>Zn</td>
<td>0.161</td>
<td>0.146</td>
<td>0.229</td>
<td>0.219</td>
<td>9.922</td>
<td>4.401</td>
</tr>
<tr>
<td>Pb</td>
<td>0.019</td>
<td>0.008</td>
<td>0.004</td>
<td>0.001</td>
<td>0.024</td>
<td>0.014</td>
</tr>
<tr>
<td>Ni</td>
<td>0.054</td>
<td>0.008</td>
<td>0.137</td>
<td>0.012</td>
<td>3.559</td>
<td>3.487</td>
</tr>
<tr>
<td>Cr</td>
<td>0.207</td>
<td>0.397</td>
<td>0.041</td>
<td>0.023</td>
<td>6.374</td>
<td>0.042</td>
</tr>
<tr>
<td>Hg</td>
<td>0.036</td>
<td>0.006</td>
<td>0.613</td>
<td>0.287</td>
<td>0.130</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Concentrations of anionic species before and after treatment with ArnavZ₃ (mg L⁻¹)

<table>
<thead>
<tr>
<th>Element</th>
<th>1.085</th>
<th>0.405</th>
<th>8.373</th>
<th>7.690</th>
<th>21.871</th>
<th>22.681</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.204</td>
<td>0.254</td>
<td>0.120</td>
<td>0.170</td>
<td>0.040</td>
<td>0.014</td>
</tr>
<tr>
<td>Mo</td>
<td>BDL</td>
<td>0.003</td>
<td>0.010</td>
<td>0.044</td>
<td>0.166</td>
<td>0.007</td>
</tr>
<tr>
<td>Se</td>
<td>0.140</td>
<td>0.093</td>
<td>0.395</td>
<td>0.424</td>
<td>0.178</td>
<td>0.062</td>
</tr>
</tbody>
</table>
Table 6.12: Comparing residual metal concentration (mgL\(^{-1}\)), after treatment of each sample with ArnavZ\(_3\), with the proposed maximum contaminant levels (MCL) for inorganic constituents for potable water proposed by the World Health Organization (WHO)\(^{[95]}\).

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample A (mgL(^{-1}))</th>
<th>Sample B (mgL(^{-1}))</th>
<th>Sample C (mgL(^{-1}))</th>
<th>MCL (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1056.801</td>
<td>981.365</td>
<td>1503.200</td>
<td>50.00</td>
</tr>
<tr>
<td>Si</td>
<td>16.124</td>
<td>14.121</td>
<td>67.661</td>
<td>−</td>
</tr>
<tr>
<td>Al</td>
<td>1.190</td>
<td>0.475</td>
<td>4.965</td>
<td>−</td>
</tr>
<tr>
<td>Ca</td>
<td>267.179</td>
<td>256.174</td>
<td>102.804</td>
<td>−</td>
</tr>
<tr>
<td>Mg</td>
<td>0.270</td>
<td>1260.495</td>
<td>868.631</td>
<td>−</td>
</tr>
<tr>
<td>Fe</td>
<td>1.290</td>
<td>1.011</td>
<td>2424.384</td>
<td>0.30</td>
</tr>
<tr>
<td>Sr</td>
<td>2.657</td>
<td>3.934</td>
<td>14.767</td>
<td>−</td>
</tr>
<tr>
<td>Ba</td>
<td>0.081</td>
<td>0.036</td>
<td>0.319</td>
<td>1.0</td>
</tr>
<tr>
<td>Mn</td>
<td>0.014</td>
<td>0.100</td>
<td>101.124</td>
<td>0.05</td>
</tr>
<tr>
<td>Co</td>
<td>0.003</td>
<td>0.003</td>
<td>2.415</td>
<td>−</td>
</tr>
<tr>
<td>Cu</td>
<td>0.094</td>
<td>0.110</td>
<td>0.544</td>
<td>1.0</td>
</tr>
<tr>
<td>Zn</td>
<td>0.146</td>
<td>0.219</td>
<td>4.401</td>
<td>5.0</td>
</tr>
<tr>
<td>Pb</td>
<td>0.008</td>
<td>0.001</td>
<td>0.014</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>0.008</td>
<td>0.012</td>
<td>3.487</td>
<td>−</td>
</tr>
<tr>
<td>Cr</td>
<td>0.397</td>
<td>0.023</td>
<td>0.042</td>
<td>0.05</td>
</tr>
<tr>
<td>Hg</td>
<td>0.006</td>
<td>0.287</td>
<td>0.033</td>
<td>0.002</td>
</tr>
<tr>
<td>B</td>
<td>0.405</td>
<td>7.690</td>
<td>22.681</td>
<td>0.07</td>
</tr>
<tr>
<td>Mo</td>
<td>0.254</td>
<td>0.170</td>
<td>0.014</td>
<td>0.07</td>
</tr>
<tr>
<td>As</td>
<td>0.003</td>
<td>0.044</td>
<td>0.007</td>
<td>0.05</td>
</tr>
<tr>
<td>Se</td>
<td>0.093</td>
<td>0.424</td>
<td>0.062</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Note: − indicates that no specific regulated MCL was found for the element
6.3.2.1 Discussion of results for Sample A

One of the major cationic species present in Sample A was found to be calcium. The initial concentration of Ca in sample A was 1008.426 mg L$^{-1}$ and after treatment considerably reduced, to a resulting residual concentration of 267.179 mg L$^{-1}$ and in terms of percentage corresponded to a removal of 74%. Based on the fact that Ca is considered to be one of the major competing ions during decontamination experiments, its high concentration may have adversely affected metal retention for the remaining elements due to reduction of the available active ion exchange sites on the zeolite. However, results showed that all cations, both major and minor species were fairly well removed, in spite of the high Ca concentration, which is obviously due to favourable conditions, which will be discussed later on. Sr, also present as one of the dominant heavy metals species in this sample, showed a considerable reduction in concentration, from an initial value of 14.403- to 2.657 mgL$^{-1}$ and the corresponding percentage removal was 82%.

As for the other cationic species, Fe showed a reduction from 1.463 to 1.290 mg L$^{-1}$ (12%), while reduction for Ba was from 0.506 to 0.081 (84%); Cu concentration was also lowered from 0.164 to 0.094 mg L$^{-1}$ (43%) and a decrease from an initial 0.164- to 0.146 mg L$^{-1}$ (10%) for Zn was observed.

Removal for chromium, on the other hand, was not as favourable as for the other cationic species and as such its concentration rose from an initial 0.207- to 0.398 mg L$^{-1}$, after treatment with ArnavZ3. This phenomenon can probably be attributed to the fact
that $d^6$ to $d^9$ ions are affected by ligand field stabilization \cite{69} and thus prefer the octahedral configuration which is provided by the surrounding water ligand molecules and consequently, the rigid zeolite will not be able to compete with the solvent molecules in providing the ion with its most stable coordination environment – the hydrated ion. Metal reduction in terms of ‘minor’ cationic species including Co, Mn, Pb and Ni was also evident.

On the other hand, removal also proved to be quite favourable for trace elements such as Hg with a reduction from an initial concentration of 0.036 to 0.006 mg L$^{-1}$ and as such had a corresponding 82% removal.

Owing to the ion exchange process, Na concentration increased by a value of 1047.419 mg L$^{-1}$. Another interesting observation, was the fact that K also increased by a magnitude of 8.456 mg L$^{-1}$, which means that, although the aim was to synthesize a homogeneous Na-faujasite zeolite, some of the framework exchangeable cations was not converted to the Na-form and as such could assist in ion exchange during the decontamination experiments, which would have the overall effect of enhancing the removal of cationic species from solution. Also evident from table 6.11, was the increase in Si by a value of 11.1411 mg L$^{-1}$, which indicates that dissolution of some of the zeolitic phase occurred and since the pH during decontamination was considerably alkaline (12.43 – 11.83), the dissolution was made possible by free hydroxyl ‘attack’ on the oxygen bridges of the surface functional groups. This will in-effect result in the activation of more surface functional groups.
and as such increase the effective charge of the zeolite surface – a process which is favourable for removal of cationic species\(^{[71]}\).

Amongst the anionic species, concentration for B was lowered from 1.085 to 0.405 mgL\(^{-1}\) and as such was removed from solution by a magnitude of 62%. In these alkaline regions, such a phenomenon is not surprising, since, as discussed earlier, B removal probably occurred through the formation of ion-pair borate species by means of co-precipitation with magnesium hydroxide and/or hydroxyl-oxides of alumina\(^{[43]}\). Similarly, Se was also reduced, from an initial 0.140 to 0.093 mg L\(^{-1}\) and this can be attributed to the fact that anions such as selenite, phosphate, arsenate, etc. are believed to sorb on hydrous oxides primarily by binuclear surface complexes and this occurs through the exchange with two surface hydroxyl ions. In such alkaline conditions, surface hydroxyls are highly prominent, so the chances for this process is quite possible\(^{[71]}\).

On the other hand, concentration of Mo rose with a value of 0.05 mg L\(^{-1}\) – a behaviour which was considered a possibility, since the standard leaching tests conducted on the fly ash showed that Mo is known to be highly mobile, as well as bearing in mind that leaching of this element occurred during experiments conducted with model solutions.
6.3.2.2 Discussion of results for sample B

In the case of sample B, solution matrix was considerably different since heavy metal concentration appeared to be much higher for this sample as opposed to sample A. However; one of the major competing ions, Ca, was present in a considerably less concentration than in sample A. Starting from an initial 279.860 mg L\(^{-1}\), Ca concentration decreased to 256.174 mg L\(^{-1}\) and as such only experienced an 8\% removal. Based on calcium’s small removal fraction and considering that in this sample, it is present in a much smaller fraction, it is expected that there will be more active exchange sites available on ArnavZ\(_3\) for interaction with other metal ion species.

Although in this sample, Sr was also one of the major ions present, other ions including Fe, Mn and B joined in sharing the rank of dominant species in solution. The order presented in this case was as such: Fe proved to be at the top of the list with an initial concentration of 16.286 mg L\(^{-1}\), followed by Mn with an initial 13.550 mg L\(^{-1}\), while Sr ranked third on the dominant species list with an initial value of 12.598 mg L\(^{-1}\). Removal for these cationic species proved to be very favourable indeed. Removal for Fe was 94\% with a residing 1.011 mg L\(^{-1}\) left after treatment, while Mn showed an astounding 99\% removal, leaving only 0.100 mg L\(^{-1}\) after decontamination. Sr showed a similar trend with an equilibrium concentration of 3.934 mg L\(^{-1}\) and as such had a 69\% removal.
Also present in an appreciable amount was B (8.373 mg L\(^{-1}\)), however, since these pH conditions were only slightly alkaline (8.10 – 8.93), removal for B was not expected to be as much as in the case of Sample A, since complex formation is not as likely in this pH range. Correspondingly, only a fraction of 8\% B was retained with ArnavZ\(_3\), leaving 7.690 mg L\(^{-1}\) in solution at equilibrium.

As for minor cations such as Ni (from 0.137- to 0.012 mg L\(^{-1}\)), Zn (from 0.229- to 0.219 mg L\(^{-1}\)), Co (from 0.080- to 0.003 mg L\(^{-1}\)), and Cr (from 0.041 to 0.023 mg L\(^{-1}\)); treatment with ArnavZ\(_3\) quite evidently also had a marked reduction in their concentrations.

Once again, a considerable rise in Na concentration was observed (from 66.977- to 981.675 mgL\(^{-1}\)), quite obviously due to the ion exchange processes. Moreover, the significant increase in Si concentration, corresponding to a value of 9.765 mg L\(^{-1}\) was indicative of dissolution of part of the zeolitic phase, which from earlier discussions, will enhance the adsorption process.

In terms of trace metals, once again Hg removal was quite favourable (from 0.613 to 0.287 mg L\(^{-1}\)) corresponding to a 53\% removal of this element; however in this case, the residual concentration was still higher than the MCL for Hg in potable water.

For the anionic ions Mo and Se on the other hand; being highly mobile ions \(^{[34]}\), an anticipated leaching behaviour was exhibited and as such increase for Se was from 0.093 to 0.395 mg L\(^{-1}\), while Mo concentration increased from 0.120 to 0.170 mg L\(^{-1}\)
after equilibration of sample B with ArnavZ$_3$. Similar results can be observed in the case of As, whose concentration in solution increased by a value of 0.033 mg L$^{-1}$; however is still lower than the MCL for potable water (0.05 mg L$^{-1}$). This phenomenon is not surprising, considering the fact that this element is also very mobile, since in fly ash fractions this element is partly placed in the aluminosilicate phase, but can also be found in certain non-matrix phases, and as such could leach into the zeolite phase during synthesis and in unfavourable conditions, consequently into the solution $^{[12]}$.

### 6.3.2.3 Discussion of results for sample C

In the case of sample C, in which the final pH reached was only 4.35, results were significantly different.

The working hypothesis in the application of FA/AMD-related zeolites have been described to be such that the zeolite addition would result in raising the pH and as such induce favourable environment for ion exchange $^{[62]}$, however the pH reached in this investigation was quite clearly still acidic.

Conditions for ion exchange were thus obviously not favourable enough to achieve optimum retention with respect to most cations. The reason for these unfavourable conditions are discussed below:

During decontamination experiments of such nature, the overall solution pH plays one of the pivotal roles in the success of metal cation retention. In acidic conditions,
the solution is supersaturated with free hydronium ions (H⁺) and zeolites; being amphoteric in nature, will try to elevate the solution pH when contacted with an effluent by exchanging some of their exchangeable cations, initially present in their structure, with the hydronium ions in the solution. The overall effect will be that the available active exchange sites on the zeolite surface is reduced, resulting in competition between the cationic species in solution and the H⁺ ions for ion exchange with the zeolite.

Prior investigations have established that the extent of proton exchange with zeolites can be calculated through the correlation between $C_{H/Al}$ and $C_{Me/Al}$, where $C_{H/Al}$ and $C_{Me/Al}$ are unidimensionles units, whereas $[Me],[Al]$ and Na refer to metal, aluminium and Na concentrations, respectively; expressed as mg g⁻¹ [69].

Where, the proton concentrations were calculated as follows:

$$C_{H/Al} = ([Al] - [Na] - n[Me])/[Al]$$

Where $n$ is the valence of the metal ion.

Such calculations were done for most of the cationic species and it was found that for most metals this sum was calculated to have a value of less than 1, which in effect mean that part of the active exchangeable sites on the zeolite is occupied by protons.

According to the results in table 6.11, the Si concentration rose with a value of 40.943 mgL⁻¹, which is indicative of zeolite dissolution; however since these were fairly acidic conditions, the dissolution of zeolite phase was acid catalyzed as follows [71].
From the above equation, one can see that acid catalyzed hydrolysis will result in an increase of terminal positive charge of the functional (aluminol) groups, on the zeolite surface; which will induce unfavorable conditions for retention of cation species.

The other factor to consider is, due to the possibility of potential leachable elements in the residual fly ash particles in the zeolite structure, acidic conditions could induce selective leaching of certain elements and from the results, it was shown that Ba, Sr and Cu leached into solution by 0.235 mg L\textsuperscript{-1}; 4.349 mg L\textsuperscript{-1} and 0.126 mg L\textsuperscript{-1}, respectively. However, in spite of the leaching of Ba, the overall concentration still stayed below WHO’s proposed MCL (1.0 mg L\textsuperscript{-1}) for potable water, as did Cu, whose proposed MCL is 1.0 mg L\textsuperscript{-1}.

In light of all the above factors, one can get a perception of the lower extent in terms of metal retention for this FA/AMD-process water sample; however, some cationic species were favorably reduced: Hg, which is one of the elements for which ArnavZ\textsubscript{3} has proven to have high preference for, was once again reduced; from an initial 0.130 mg L\textsuperscript{-1} to a final concentration of 0.033 mg L\textsuperscript{-1} and in terms of percentage was removed by a magnitude of 75%. Cr was also considerably reduced from 6.374 mg L\textsuperscript{-1} to 0.042 mg L\textsuperscript{-1} and as such enjoyed a removal of 99%. Similar findings in terms of Cr was made in earlier investigations and as such it was established that, unlike for the other metals, acidic environment probably is favorable for the retention of this element \cite{54}.
Also present in exceeding concentrations was Fe, which had an initial concentration of 4761.97 mg L\(^{-1}\), from which approximately 49% was removed, leaving a residual concentration of 2424.38 mg L\(^{-1}\). Since the metal loading factor onto the solid phase of this removal was calculated to be 46.75 mg g\(^{-1}\), it is obvious that this removal cannot only be ascribed to ion exchange alone. The motivation for the latter statement was based on the fact that firstly; ArnavZ\(_3\) does not have a high preference for this ion (which was established through the investigations with model solutions), and considering its high energy of hydration, as well from the experimental exchange capacity one can see that the value is far bigger than the total cation exchange capacity of the zeolite. Based on the latter statement and also considering the fact that these reactions occurred within a pH range of 3.00 – 4.35, while bearing in mind that during normal physicochemical treatment of metal-bearing wastewaters Fe is known to precipitate at between pH 3.5 – 5.00; one may conclude that in addition to ion exchange, solid phase precipitation on the zeolite surface, also played a major part in its removal.

However; since Fe was present in such high concentrations, the removal of anionic species through complex formation was considered a possibility; since ferric precipitation is known to serve as crystallization seeds for removal other metals from wastewaters. Also considering the fact that acid hydrolysis of part of the zeolite phase led to the increase of positive charge in the functional groups of the zeolite surface, one would expect the probability of anion species being removed through
binuclear surface complex formation on the zeolite surface a definite probability \cite{11, 94}.

As predicted, anions such as As was considerably removed from solution, from an initial 0.166 mgL$^{-1}$ to a residual concentration of 0.007 mg L$^{-1}$; a value which is lower than the proposed MCL (0.05 mg L$^{-1}$) of As for potable water. This removal can be ascribed to surface complexation, where a proton from an un-dissociated arsenate anion forms a molecule of water with the hydroxyl group of the hydrous oxide on the surface of the sorbent, after which it is displaced by the arsenic \cite{71}. Prior research have shown that in acidic conditions, arsenic is relatively immobile due to hydrolysis with iron oxihydroxides, as such, the soluble As anions forms stable arsenates, such as scorodite [FeAsO$_4$·2H$_2$O], erythrite[Co,Ni(AsO$_4$)$_2$·8H$_2$O], etc with elements in solution, including Fe, Co, Ni, Zn and Pb and is removed from solution through such complexes \cite{11, 94}.

Based on these findings and the fact that Fe was the dominant species in solution, our assumption that As removal was due to complex formation with hydrous oxides on the zeolite surface, probably as scorodite [FeAsO$_4$·2H$_2$O] and/or erythrite [Co,Ni(AsO$_4$)$_2$·8H$_2$O] is corroborated.

Both Se and Mo was also reduced by 64.9% and 64.8%, respectively. In terms of concentration, Se was reduced from an initial dissolved concentration of 0.178 mg L$^{-1}$ to 0.062 mg L$^{-1}$ and as shown in table 6.12, this value is just slightly above the MCL for Se (0.05 mg L$^{-1}$); while Mo concentration, on the other hand, reduced from
0.040 mg L\(^{-1}\) to 0.014 mgL\(^{-1}\), after treatment with ArnavZ\(_3\) and also in this case, the residual concentration in solution proved to be lower than the MCL, which is reported to be 0.070 mg L\(^{-1}\).

As for B, initially present in quite an appreciable amount, 21.871 mg L\(^{-1}\), leached into solution during the decontamination experiments, thus leaving a residual concentration of 22.681 mg L\(^{-1}\) in the aqueous phase. This can be attributed to selective leaching, brought about by acid extraction, catalyzed through the acidic surroundings.

In general, although overall metal retention for most cations was considerably less for Sample C, as compared to Samples- A and B, the net reduction of the effective negative charge on the zeolite surface, caused it to become more positive and as such, enhanced the immobilization of anionic species through complex formation which probably occurred via inner sphere and/or outer sphere complexes.

### 6.3.2.4 Overall conclusions on FA/AMD-process water experiments

From all the data shown in the results in tables 6.11 and 6.12, one can draw the following overall conclusions:

- The pH of the system plays a pivotal role in the speciation of the metal ions, as well as the effective charge of the zeolite surface functional groups and as such, changes the physicochemical reactions which takes place between the zeolite and the aqua metal ions.
Although the application of zeolites is generally based on ion exchange as the main mechanism of metal retention; in cases like these, where synthetic fly ash-related ion exchangers are applied, other mechanisms including specific and/or non-specific adsorption, inner-sphere complex formation, binuclear complex formation, etc. comes into play and thus considerably aids the decontamination process. As such, in systems like these, the removal of anionic species is also possible, as shown from the results in table 6.11.

Judging from the different results obtained as going from Sample A to Sample B to Sample C, it is obvious that the solution matrix effect plays a major role in the decontamination process; a finding which corroborates with prior investigations.

In all cases, ArnavZ$_3$ shows a fairly high selectivity for mercury and depending on the experimental conditions, it was shown that this element can be removed to levels almost as low as the proposed MCL for potable water (Sample A) — a fact which, on an industrial scale would prove to be beneficial for environmentally based treatments of water.

Although the decontamination proceeded at the expense of added salinity, shown by the high residual Na concentrations; the nature of such elements are primarily innocuous – a fact that is beneficial for the environment.

In consideration of the fact that in these decontamination systems, the mechanism of metal retention is not only ion exchange, but a host of integrate physicochemical interactions; one can thus conclude that the experimentally
determined exchange capacity (operating capacity) for the ion exchanger can exceed the theoretically determined total exchange capacity (CEC), which corroborates earlier findings stating that in the case of ion exchangers obtained from natural products, the ion exchange capacity may depend on experimental conditions \[^{60}\].
CHAPTER 7

Conclusions

In the following paragraphs the specific aims of this study are revisited to report whether the aims of this study were achieved, and to give an overview of the successes and shortcomings of the study.

7.1 Critical overview of the study

The FA/AMD-solid residues were successfully transformed into a near homoionic state Na-form zeolite (ArnavZ3), containing a high proportion of crystalline faujasite phases and a fraction of hydroxysodalite also present. The transformation process involved the extraction of the aluminosilicates from the solid residues through a fusion method with NaOH at 600°C for two hours, followed by hydrothermal crystallization of faujasite phases (24 hours at 100°C).

The total exchange capacity (CEC) of the synthesized zeolite was determined as 200 meq/100g. N2BET surface analysis was applied to determine the zeolite’s
surface area, micropore volume and pore size; from which the results showed the values as 327.341 m$^2$/g, 0.310 cm$^3$/g and 54.497 Å, respectively. XRF analysis revealed that the synthesized zeolite has a very low Si:Al ratio, corresponding to a value of 1.65, the result of which would be a higher terminal Al-OH and thus signifying the zeolite’s hydrophillicity and subsequent enhanced metal exchange capacity.

Decontamination studies with model solutions revealed the following:

The solid/liquid variation studies showed that equilibrium metal ion concentration in solution phase decreased with increasing zeolite dose, with an optimum decrease corresponding to 5g zeolite per 100ml of model solution. The contact time investigations showed that a drastic decrease in metal concentration occurred within the first 60 minutes of contact and at this stage, equilibrium between the zeolite- and solution phase was reached for almost all metals studied.

An increase in exchange temperature (20-40°C) was accompanied by an increase in the overall affinity of the zeolite phase for all metal ions (Ba$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Al$^{3+}$ and Fe$^{3+}$), resulting in a favorable shift in zeolite selectivity exerted toward the metal ions and a consequent higher metal uptake for all selected metals. The increase in selectivity exerted by the zeolite for all selected metal ions studied, was corroborated by the increasing distribution coefficient values (K$_D$) calculated for all metal ions, with each temperature augmentation. Exchange for all
ions was thus shown to be endothermic and accompanied by a large negative change in free energy ($\Delta G^\circ$) for $\text{Ba}^{2+}$, $\text{Pb}^{2+}$, $\text{Sr}^{2+}$, $\text{Mn}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, where the magnitude of the negative value increased with increasing temperature for all aforementioned metal ions; thus showing the spontaneous nature of sorption in each case. In the case of $\text{Fe}^{3+}$ and $\text{Al}^{3+}$ on the other hand, sorption appeared to be non-spontaneous, but became more favorable with each temperature increase (shown by the decrease in positive $\Delta G^\circ$ value with temperature elevation).

Competitive sorption of an inert electrolyte, i.e. $\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$, at highest ionic strength, severely hindered $\text{Sr}^{2+}$ sorption (by 92%); while sorption of $\text{Ba}^{2+}$, $\text{Mn}^{2+}$, $\text{Pb}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ were slightly, but not significantly affected (by approximately 17-30%, varying with each metal). In the case of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ on the other hand, sorption was more hindered in the presence of competing electrolyte consisting of both $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ions (20% for $\text{Al}^{3+}$ and 69% for $\text{Fe}^{3+}$).

Equilibrium investigations as a function of metal ion concentration revealed the following:

Taking into account the zeolite’s porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds and other surface imperfections, metal retention by ArnavZ$_3$ could be described by different binding mechanisms; ion exchange and adsorption, which was also accompanied by precipitation of hydroxo-complexes, particularly at high initial concentrations. An outline of these reactions are illustrated by the following equations:
a) Metal ions were retained by means of electrostatic forces to the permanently-charge exchange sites on the zeolite surface. This adsorption reaction involves the process of ion exchange. The exchange involving a divalent hydrated metal ion ($M^{2+}$) are depicted in the following equation:

$$2\equiv Ze - Na + M^{2+}_{(aq)} \rightleftharpoons Ze_m - M + 2Na^+_{(aq)}$$

b) Metal uptake could also occur through a more specific scenario involving the hydrolysed species. In this case, the hydrolysed metal ion associates with the zeolite as an inner-sphere complex via covalent bonding between the metal and the oxygen bridges of the functional groups ($\equiv$Si-O-Al$\equiv$) on the zeolite surface. These reactions occurs at variable-charge sites on the zeolite surface, forming stable complexes between metal cations and silanol and/or aluminol functional groups. In this case, several elementary reactions may be included, which is depicted by the following equations for divalent metal ions:

i) Hydrolysis of the metal ion in solution:

$$M^{2+} + nH_2O \rightleftharpoons M(OH)m(H_2O)^{n-m} + mH^+_{(aq)}$$

Being $n>m$ and subsequent exchange of hydrolysed species:

$$\equiv Ze - Na + M(OH)m(H_2O)^{n-m} \rightleftharpoons \equiv Ze - MeOH + Na^+_{(aq)}$$

ii) The other variant of this mechanism of retaining is simultaneous hydrolysis and exchange of hydrated ions:

$$\equiv Ze - Na + H_2O + M^{2+}_{(aq)} \rightleftharpoons \equiv Ze - MOH + Na^+_{(aq)} + H^+_{(aq)}$$
c) Another mode of metal retention was shown as precipitation as hydroxy complexes onto the functional groups on the zeolite surface, illustrated by the following equation (for divalent metal ion):

\[
M^{2+}_{(aq)} + H_2O \rightleftharpoons M(OH)_{2(Ze)} + 2H^+_{(aq)}
\]

Results suggest that the influencing parameters affecting sorption phenomena onto ArnavZ₃ include charge density and hydrated diameter, and thus at least some of the waters of hydration must be stripped from the solvated ions for exchange to take place. At high pH, adsorption for some metals were preceded by metal hydrolysis and precipitation, and appeared to coincide with the loss of outer hydration sheaths of the aqua-ion. Other parameters also found to influence extent of metal uptake included space requirements in the zeolite micropores (becoming more favourable with increasing temperature – especially for Fe³⁺ and Al³⁺), solution matrix, the strength of the metal-framework oxygen bond, as well as strength of the interaction of metal ion with zeolite framework oxygens.

The distribution coefficients (Kᵩ) determined for the sorption system as a function of initial sorbate concentration showed that energetically less favourable sites becomes involved as going from 5 – 10 mg L⁻¹ initial metal ion concentration, causing possible saturation of the first monolayer, which combined with surface imperfections and mineral heterogeneity of the zeolite, probably led to multilayered sorption for the 15-20 mgL⁻¹ initial concentration.
The affinity sequence shown by the equilibrium investigations were as follows:

$$\text{Ba}^{2+} \geq \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Cu}^{2+} \geq \text{Co}^{3+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}$$

No pH adjustments were made during the decontamination experiments and according to the pH variation, zeolite addition caused a drastic pH increase. Thus for each equilibrium investigation as a function of initial solute concentration, i.e. 5-, 10-, 15- and 20 mgL\(^{-1}\), solution pH changed from 3.25 – 10.09, 3.21 – 10.07, 3.15 – 9.96 and 3.05 – 9.89, respectively. According to the overall research investigation, this significant increase in acidity was due to simultaneous uptake of hydrogen ions by the zeolite and zeolite dissolution (hydrolysis). Zeolite hydrolysis was confirmed by the increase in Si concentration in the aqueous phase.

The balance of the ionic charge released from the zeolite phase (Na\(^+\)) and the ingoing ionic charge (½Ba\(^{2+}\), ½Pb\(^{2+}\), ½Sr\(^{2+}\), ½Cu\(^{2+}\), ½Zn\(^{2+}\), ½Co\(^{3+}\), ½Mn\(^{2+}\), ½Fe\(^{3+}\), ⅓Al\(^{3+}\)) showed that the total quantity of ingoing exchangeable ions is lower than the total quantity of outgoing exchangeable ions for all initial concentrations, particularly in the more dilute solutions, for all initial concentrations. It was thus shown that ion exchange was the dominant mechanism of metal retention, while its dominance diminishes at higher initial concentrations.

In terms of trace metals, ArnavZ\(_3\) showed high affinity for Hg(II) and it was suggested that, in addition to ion exchange, the hydrolyzed Hg\(^{2+}\) also gets adsorbed onto the zeolite through the formation of inner-sphere complexes with the active
functional groups. Considerably high affinity was also shown for Tl\(^+\) and In\(^{3+}\), due to the ion’s extremely low polarizing nature and consequent low hydration.

The considerable increase in acidity value (pH) upon zeolite addition, giving rise to adsorption of monovalent hydroxo – complexes was explored for the possible immobilization of anionic species and the following findings were made:

In these highly alkaline conditions, the results suggested that As(V) was retained (±50%) through specific adsorption (surface complexation) at hydrous oxides of aluminol sites (variable charge sites) on the zeolite surface, as well as through precipitation of calcium (alkaline arsenites \([\text{Ca(AsO}_2\text{)}\cdot\text{Ca(OH)}_2]\), alkaline arsenates \([\text{Ca}_3(\text{AsO}_4)_2\cdot\text{Ca(OH)}_2]\), gypsum \([\text{CaSO}_4\cdot2\text{H}_2\text{O}]\)) or magnesium oxides on the surface moiety of the zeolite. Boron was also retained; suggested to have occurred through formation of ion-pair species, via complex formation with active surface hydroxyl functional groups (hydrous oxides of alumina) and/or complex formation with magnesium hydroxide.

The results also showed that there was preferential leaching of selenium and molybdenum from the solid phase by 0.136- and 0.287 mgL\(^-1\), respectively. This was attributed to the leaching of these elements from the zeolite matrix; a consequence of using waste product (FA/AMD-solid residues) for direct zeolite synthesis.

Studies conducted to compare the synthesized zeolite with its commercial counterpart (commFau) showed similar trends in terms of selectivity, metal retention, as well as equilibration time. Both ArnavZ\(_3\) and commercial faujasite showed the
highest selectivity in terms of Ba\(^{2+}\) and Sr\(^{2+}\), whereas the lowest affinity was shown toward Fe\(^{3+}\) and Al\(^{3+}\). These results confirm the findings observed by the characterization analysis, in terms of the successful zeolitization of the solid residues. Metal uptake however, were slightly higher in the case of commercial faujasite, in accord with its higher proton exchange capacity and higher cation exchange capacity. Comparison studies with the chelating ion exchanger (Lewatit TP207), on the other hand, showed quite a different trend, and metal retention for this ion exchanger was not as effective as compared to the findings for ArnavZ3 and commFau. These results effectively prove one of the major aims of the research investigation, that zeolites have an advantage over ion exchange resins; based on their much lower cost, as well as their ion selectivity, generated by their rigid porous structures.

The studies conducted for decontamination of FA/AMD-process waters, collected at different pH’s, showed the following findings:

The results for these investigations showed trends similar to model solution experiments:

- The pH of the system plays a pivotal role in the speciation of the metal ions, as well as the effective charge of the zeolite surface functional groups and as such changes the physicochemical reactions which takes place between the zeolite and the effluent.
Apart from ion exchange, other mechanisms including specific and/or non-specific adsorption, outer-sphere complex formation, binuclear complex formation, were also suggested to occur, thus considerably aiding the decontamination process. As such, the removal of anionic species is also possible; as shown from the results.

Matrix effect was shown to play a major role in the decontamination process.

As in model solution studies, in all contaminated samples, mercury was effectively removed and in some cases to levels lower than the proposed MCL for potable water (Sample A) — a fact which, on an industrial scale would prove to be beneficial for environmentally based treatments of water.

Results showed that the operating capacity for the ion exchanger exceeded the theoretically determined total exchange capacity.

7.2 Overall significance of the study

Results from the study have found that fly ash (FA) and acid mine drainage (AMD) can be successfully reacted for the collection of precipitates at a near neutral pH. The addition of FA to the AMD therefore serves a dual purpose: Firstly, the reaction of FA with AMD provides an alternative method for the neutralisation of AMD, other than the conventional methods; which are known to all fall prey to extensive drawbacks. Secondly, the collected solid residues provided a rich source of Al and Si
and other aluminosilicates, for the synthesis of highly crystalline, low silica zeolitic material. This was done through hydrothermal alkaline conversion methods.

Moreover, the synthesized zeolite could effectively be used as ion exchanger and sorbent for the decontamination of process waters.

A very promising factor is that, mercury, which is considered a priority contaminant, could in some cases be removed to levels below the proposed maximum contaminant level.

A very significant finding was that, through mechanisms other than ion exchange, anion forming species was also removed from solution and based on such mechanisms, it was also possible to in some cases remove arsenic to below WHO’s proposed MCL for potable water.

7.3 Possible recommendations for future work

When aspiring to future recommendations, based on this sorption system, it would be of interest to initially answer certain questions which could give a better perspective in terms of possible applications.

1. *When would you anticipate the commercialization of this technology?*

   Due to current problems associated with the potential leaching of selected elements from the solid phase into solution, which would magnify when applied on a bigger scale, commercialization is not recommended at this stage.
2. Where and how will this technology see industrial application?

Taking into account the similtude of neutralisation processes shown during starting material preparation to industrial AMD neutralization processes, this technology could be implemented as the first step in the purification of metal bearing waste waters at an active or decomissioned mining site.

Since the overall application of this technology is based on ion exchange, it could also be implemented as part of the desalination steps at a treatment plant for AMD and its derived process stream. Since desalination techniques usually involves electrochemical methods, this option could also involve what may be referred to as “zeolite modified electrodes”, which would entail electrochemically induced charge transfer involving electroactive species in the FA/AMD-related zeolites.

3. From a financial perspective, will this technology be an economically viable?

Considering the fact that it is based on the use of waste materials, it would be classed as an alternative low cost waste water treatment method. However, the hydrothermal activation methods would, on an industrial scale prove to add to operating costs, due to increased energy consumption.

An average mining plant treats approximately 80Ml of wastewater per day, and as such, treatment with this technology, based on such a huge scale, would not be economically viable at this stage.
4. *Are you aware of similar technologies under development at this stage?*

Numerous studies with fly ash-based starting materials have been done; however, technologies based on FA/AMD-starting materials is a fairly new process.

5. *Do you think the demand for this type of technology will increase?*

Based on the finding that this technology may be implemented in the removal of cation, as well as anion pollutants, it will certainly have a growing curiosity in terms of potential synthesis of anion exchange material.

6. *What are the barriers that needs to be overcome before FA/AMD-related zeolites can be competitive with other ion exchange materials?*

The problem of leaching needs to be eliminated which may be done by possibly treating the solid residue starting material with dilute acid to extract potential leachable elements.

The method of synthesis needs to be optimised, in order to use low temperature activation methods, as to avoid unnecessary operating costs.

The mass per volume effluent during decontamination processes, needs to be adjusted, as the current 5g per 100ml will not be feasible on a large industrial type scale (80Ml of effluent per day).
CHAPTER 8

References


79. Reid, D. (2005). \texttt{(d.reid@uct.ac.za)} \textit{X-ray fluorescence Spectroscopy sample preparation procedure}. Private email message to N.R. Hendricks, \texttt{(nrhendicks@uwc.ac.za)}.

80. Spath, A. (2004). \texttt{[aspath@uct.ac.za]} \textit{Sample dilutions for ICP-MS analysis}. Private e-mail message to N.R. Hendricks \texttt{[nrhendricks@uwc.ac.za]}.


Appendices

Appendix A

XRF Results

**Appendix A1-** XRF results for co-disposal precipitate (AFA-NAVppt) and synthesized zeolite (ArnavZ₃)

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<th>University of Cape Town</th>
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<td>XRF and XRD facility</td>
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<td>Department of Geological Sciences</td>
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<table>
<thead>
<tr>
<th>% AFA-NAV</th>
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<tr>
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<tr>
<td>TiO₂</td>
<td>0.620</td>
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Appendix B

Appendix B1 – The ICP-MS results for the Decontamination Experiments conducted with the Model solutions artificially polluted with selected metals

Appendix B1.1 – ICP-MS results for the Solid/Solution variation investigations

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Appendix B1.2 – ICP-MS results for Time variation experiments

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Appendix B1.2 (b) – ICP-MS Results

**UCT DEPARTMENT OF GEOLOGICAL SCIENCES**

**ICP-MS FACILITY**

**Quantitative analysis**

all data in ppb

Analyst: A. Spath

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Appendix B1.3 – ICP-MS results for Temperature Investigations

**UCT DEPARTMENT OF GEOLOGICAL SCIENCES**

**ICP-MS FACILITY**

Quantitative analysis

all data in ppb

Analyst: A. Spath

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Appendix B1.4 – ICP-MS Results for Concentration Variation Investigations

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Appendix B1.4 (b) – ICP-MS Results

## UCT DEPARTMENT OF GEOLOGICAL SCIENCES

### ICP-MS FACILITY

Quantitative analysis

all data in ppb

Analyst: A. Spath

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## Appendix B1.4 (c) – ICP-MS Results

### UCT DEPARTMENT OF GEOLOGICAL SCIENCES

### ICP-MS FACILITY

#### Quantitative analysis

all data in ppb

Analyst: A. Spath

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Appendix B1.4 (d) – ICP-MS Results

**UCT DEPARTMENT OF GEOLOGICAL SCIENCES**

**ICP-MS FACILITY**

Quantitative analysis

**all data in ppb**

Analyst: A. Spath

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Appendix B1.5 - ICP-MS results for the effect of competing ions on metal removal

Appendix B1.5 (a) – Table for relating sample names to concentrations

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N.A. = not added
Appendix B1.5 (b) – ICP-MS results for competing ions added

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Appendix B1.6 – ICP-MS results for Trace- and anionic metals Investigation

**UCT DEPARTMENT OF GEOLOGICAL SCIENCES**

**ICP-MS FACILITY**

Quantitative analysis
all data in ppb

Analyst: A. Spath

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Appendix B1.7 – ICP-MS Results for Experiments conducted on comparison of
Removal Capacity of ArnavZ₃ with comm. Faujasite(CBV 400) and with commercial chelating Resin (Lewatit TP207)

Appendix B1.7 (a) - Table Relating Samples Names and Time intervals

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Appendix B1.7 (b) – ICP-MS Results for ArnavZ₃

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Appendix B1.7 (d) - ICP-MS Results for Commercial Faujasite (CBV 400)

## UCT DEPARTMENT OF GEOLOGICAL SCIENCES

### ICP-MS FACILITY

Quantitative analysis

All data in ppb

Analyst: A. Spath

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Appendix B1.8 – ICP-MS Results for Experiments conducted with Actual Co-disposed Process Waters, collected at varying pH’s

Appendix B1.8 (a) – Table of information of sample names and corresponding pH of sample collection

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Appendix B1.8 (b) – ICP-MS Data

### UCT DEPARTMENT OF GEOLOGICAL SCIENCES

### ICP-MS FACILITY

#### Quantitative analysis

all data in ppb

Analyst: A. Spath

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Appendix B1.9 - ICP-MS results for CEC Experimental Investigations

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n.d. = not detected

Analyst: A. Spath
Appendix C

Appendix C – The BET surface area, pore volume and pore size of the zeolitic material

Appendix C1 – Synthesized zeolite:ArnavZ₁

BET Surface Area: 173.2960 m²/g

Micropore Area: 90.4553 m²/g

External Surface Area: 82.8407 m²/g

BJH Adsorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 Å Diameter: 100.5318 m²/g

BJH Desorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 Å Diameter: 100.9419 m²/g

Volume
Single Point Adsorption Total Pore Volume of pores less than 1951.2388 Å Diameter at P/Po 0.98999377: 0.269012 cm³/g

Micropore Volume: 0.041626 cm³/g

BJH Adsorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 Å Diameter: 0.238064 cm³/g

BJH Desorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 Å Diameter: 0.236164 cm³/g

Adsorption Average Pore Diameter (4V/A by BET): 62.0931 Å
Appendix C2 – Synthesized zeolite: ArnavZ2

BET Surface Area: 230.7319 m²/g

Micropore Area: 150.0002 m²/g

External Surface Area: 80.7318 m²/g

BJH Adsorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 Å Diameter: 90.8840 m²/g

BJH Desorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 Å Diameter: 84.7863 m²/g

Single Point Adsorption Total Pore Volume of pores less than 1899.2525 Å Diameter at P/P₀ 0.98971585: 0.247663 cm³/g

Micropore Volume: 0.069469 cm³/g
BJH Adsorption Cumulative Pore Volume of pores
between 17.000000 and 3000.000000 Å Diameter: 0.185018 cm³/g

BJH Desorption Cumulative Pore Volume of pores
between 17.000000 and 3000.000000 Å Diameter: 0.179774 cm³/g

Pore Size

Adsorption Average Pore Diameter (4V/A by BET): 42.9352 Å

Appendix C3 – Synthesized Zeolite: ArnavZ3

BET Surface Area: 327.3412 m²/g

Micropore Area: 125.5389 m²/g

External Surface Area: 101.8023 m²/g

BJH Adsorption Cumulative Surface Area of pores
between 17.000000 and 3000.000000 Å Diameter: 113.7415 m²/g
BJH Desorption Cumulative Surface Area of pores
between 17.000000 and 3000.000000 Å Diameter: 105.0550 m²/g

Volume

Single Point Adsorption Total Pore Volume of pores less than
2111.5173 Å Diameter at P/Po 0.99076358: 0.309738 cm³/g

Micropore Volume: 0.057921 cm³/g

BJH Adsorption Cumulative Pore Volume of pores
between 17.000000 and 3000.000000 Å Diameter: 0.260154 cm³/g

BJH Desorption Cumulative Pore Volume of pores
between 17.000000 and 3000.000000 Å Diameter: 0.247512 cm³/g

Pore Size

Adsorption Average Pore Diameter (4V/A by BET): 54.4974 Å
### Appendix D: XRD Data

Appendix D1: Table relating appendix library patterns to sample names and corresponding XRD patterns as in text.

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