TREATMENT OF BRINES USING COMMERCIAL ZEOLITES AND ZEOLITES SYNTHESIZED FROM FLY ASH DERIVATIVE

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Abstract

South Africa is one of the countries that have scarce natural resources that they have to preserve what is available at their disposal. South Africa is also fast becoming one of the countries with major industrial development. In South Africa, electricity is primarily generated by coal-fired power stations which are mostly concentrated in the Mpumalanga, Gauteng and Limpopo Provinces. These power stations use the concept of burning coal to produce electricity which generates a lot of fly ash and effluent water as a waste material. There are also active coal mines supplying coal to the power stations and abandoned coal mines that are a source of Acid Mine Drainage which is a threat to our environment if discharged untreated as it can pollute receiving streams, aquifers and can even kill aquatic and fish plant.

The objectives of this project was to ameroliate two waste materials, namely Acid Mine Drainage and Fly Ash and recover the solid residues for conversion into an adsorbent to treat brine. The solid residues were then converted into zeolite P through low temperature hydrothermal treatment. The adsorption capacity of the solid residues, zeolite P derived from the solid residues was compared to the commercial zeolite Y and fresh Arnot fly ash. The quality of the resulting water was assessed using different analytical methods before the reaction with adsorbents and after the reaction and a comparison was done based on the removal efficiency of elements

Zeolite P from solid residues was successfully synthesized as confirmed by XRD, BET and FTIR. Brine treatment with fly ash, solid residues, zeolite P and commercial zeolite Y adsorbents was done concentration on the following major elements Na, K, Mg, Ca and Si. Zeolite P had higher or similar removal efficiency that the commercial zeolite Y for the following elements K, Ca and Mg. Fly ash is the only adsorbent that managed to reduce the concentration of Na in brine and also had a good removal efficiency of Mg. Si leached out of all the adsorbents which could be ascribed to Si being the major component of these adsorbents which could indicate some dissolution of these adsorbents under the conditions tested.

Overall, zeolite P did not completely remove the major elements, especially for Na, but did result in a cleaner waste stream which would improve brine processing.

Declaration

I declare that, *Treatment of brines using commercial zeolites and zeolites synthesized from fly ash derivative* is my own work, that it has not been submitted before for any degree examination in any other university, and that all sources I have used or quoted have been indicated and acknowledged as complete references.

Thantaswa Millicent Sonqishe November 2008

Signed: ……………………….

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Dedication

I would like to dedicate this work to my late mother Ms. Linda Sonqishe and my late grandmother Mrs. F.T. Sonqishe and to future generations of South Africa who will find this work useful.

Glossary

TDS	Total Dissolved Solids
Eskom	Electricity Supply Commission
AMD	Acid mine drainage
FA	Fly Ash
RO	Reverse Osmosis
NF	NanoFiltration
CFA	Coal Fly Ash
ASTM	American Society for Testing and Materials
XRD	X-ray diffraction
AD	Acid Drainage
ARD	Acid Rock Drainage
CCBs	Coal Combustion By-products
FGDB’s	Flue Gas Desulphurisation By-products
ALD’s	Anoxic Limestone Drains
ED	Electro Dialysis
ESP	Exchangeable Sodium Percentage
CEC	Cation Exchange Capacity
PVC	Poly Vinyl Chloride
HDPE	High-Density Polyethylene
EC	Electrical Conductivity
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
JCPDS-ICD	Joint Committee on Powder Diffraction Standards-International Centre for Diffraction
N_2-BET	Nitrogen Brunauer-Emmett-Teller
SEM	Scanning Electron Microscopy
XRF	X-ray Fluorescence

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CHAPTER 1

Introduction

1.1 Overview

The major industrial development South Africa concentrated in the interior of its country (Heynike *et al* 1982). This region of the country has an average rainfall of only 700mm per annum. The Orange/Vaal river system serves as both the drainage system and the major source of water for this region. The extreme intensity of industrial development has resulted in a decline in the quality of water, the Total Dissolved Solids (TDS) being the most determinant parameter. Methods in which the increasing demand for water can be met include water recycling, sewage reclamation, interbasin transfer and tributary diversion (Buckley *et al*, 1987).

Water is an essential resource for power generation. It is used for steam generation, cooling, transportation, domestic services and in miscellaneous process water systems.
The quality of water required for each application varies from demineralised water with an electrical conductivity of less than 10µS/cm used as a boiler make-up to brackish salt water used for transportation of fly ash to the ash dams and as cooling water. The monitoring of water quality is vital for each application to ensure safety of personnel and prevent damage to equipment by scaling or corrosion and minimizing water treatment cost.

Lethabo Power Station uses raw water from the Vaal Dam and highly concentrated underground water from the New Vaal Coal Mine as “make-up” water for the cooling water systems. These two streams of water could introduce approximately 27 tons of salts per day into the cooling water systems (Eskom 2005). These salts must be removed on a continuous basis to prevent build up of salts above acceptable thresholds. If these salts are not removed, corrosion damage will cause premature failure of the condenser and associated plant. The removal of the salts is called desalination and this is achieved by a process known as osmosis.

Water treatment and recycling of water from industrial processes is an important business goal, especially when the industry is using large amounts of water. This goal can be achieved through industrial wastewater treatment by employing membrane processes. Employing these membrane processes will enable the affected industries to conform to effluent standard limits imposed by environmental regulations, but there is a downfall to these membrane processes which that being the by-product generated known as brine (Qdais and Moussa, 2004).

Acid mine drainage is regarded as another persistent environmental problem at many active and abandoned sulphide and coal mines (Gazea *et al.,* 1996). Pyrite and other sulphide minerals that are exposed to oxygen and water in the presence of oxidising bacteria, such as *Thiobacillus ferroxidants*, undergo oxidation to produce dissolved metals, sulphate, and very low pH which are main characteristics of acid mine drainage (AMD) (Gazea *et al.*, 1996).

Fly ash is a by-product formed as a result of coal burning in power plants. South African fly ash has a high alkalinity and therefore can be evaluated in wastewater treatment to precipitate heavy metallic ions. High capacity adsorbents such as zeolites are also used for brine or saline water treatment as the ion exchange material (Petrik *et al.,* 1242/1/05).

At UWC, investigation has been done lot of work has been done on the neutralization of AMD using fly ash (FA) and also synthesize zeolites from FA and AMD (Somerset, 2003 and Klink, 2003). My study focuses on the synthesis of zeolites from solids resulting from the neutralization of AMD with FA for brine treatment. This zeolite was compared with commercial zeolite Y, fly ash and solid residues.

1.2 Objectives

This study was undertaken to address issues facing the mining industry and coal fired power stations with respect to their waste minimization and waste disposal. The objective of this project was to investigate cheap adsorbents to treat wastewater / brine. The objectives are:

- Synthesize solid residues from neutralization of AMD with FA to stabilise brine.
- Synthesize zeolite P from solid residues resulting from neutralisation of AMD and FA for brine treatment.
- Compare zeolite P with FA, co-disposed solid residue, and a commercial zeolite Y on removal efficiency of major elements in brine treatment.
- Determine whether zeolite P, commercial zeolite Y, FA and solid residues are suitable candidates for brine treatment.

1.3 Layout

The thesis follows the outline listed below:

Chapter 2: Literature Review

In this chapter a detailed literature available on fly ash, acid mine drainage, brine and zeolites is discussed with current treatment options available for brine and AMD being revisited.

Chapter 3: Research Methodology

This chapter presents methods of analysis, sampling methods, instruments and equipment used to carry out the investigation.

Chapter 4: Results: Presentation and Discussion

This chapter covers results presented in the form of graphs, tables and also discusses the trends found in the research.

Chapter 5: Conclusions and Recommendations

This chapter addresses the objectives of the study and also concludes the research area of interest. It also recommend for some work that was not covered in this research due to time constraints.

References

Appendices

CHAPTER 2

Literature Review

2.1 Introduction

Brine is water saturated or nearly saturated with salt. Natural brines are waters with very high to extremely high concentrations of dissolved constituents-elements, ions, and molecules. Brines are commonly considered to be those waters more saline, or more concentrated in dissolved materials, than sea water (35 grams of dissolved constituents per kilogram of sea water). Brine can contain salt concentrations more than five times greater than the salt content of average sea water. Its disposal poses a serious threat as it could negatively affect surrounding environment. The disposal of brine is costly because of its composition and due to the large volumes to be handled (Al-Agha *et al.*, 2005; Vavra *et al.*, 2004).

Recycling and reuse of water from industrial processes is of vital importance for economic reasons, especially when the industry is using large amounts of water and they also have to comply with the effluent standard limits imposed by environmental regulations. Industrial wastewaters contain high heavy metal content and their sources are mining and metal industries. Heavy metal removal from wastewater is extremely important because of their toxic effects on living species. Several methods exist such as chemical precipitation flotation; ion exchange; adsorption and biological treatment are often used to remove heavy metals from wastewater.

Electrodialysis is a technique based in the transport of ions through selective membrane under the influence of an electrical field. This technique has proved its feasibility and high performance in the desalination of brackish water, the desalting of amino acids and other organic solutions, effluent treatment and or recycling industrial process streams and salt production.

Reverse osmosis (RO) and nanofiltration (NF) are relatively new processes, which were developed initially for the production of potable water from saline and brackish water. These processes have found applications recently in the treatment of industrial wastewater. According to research findings wastewater reclamation by RO offers great promise for conserving natural resources, as well as marked improvements of pollutant removal efficiency.

The conventional and most widely used method for treatment of industrial wastewater containing heavy metals is the chemical precipitation method. This process requires a large amount of treatment chemicals to decrease the heavy metals to levels that are acceptable according to government regulations. The sludge produced from the precipitation process has to be dewatered and disposed of into a landfill, which is an additional cost to the treatment process.

Modern society has become reliant on electricity as a source of power. South Africa, specifically in the Mpumalanga and Gauteng provinces possesses a large number of coal-fired power stations for power generation. The principle of a coal-fired power station involves burning of large quantities of coal to produce of electricity needed. Coal fired power stations in South Africa are situated close to the coal mining areas in order to minimize costs associated with coal transportation.

Coal combustion results in residues of fly ash, bottom ash and boiler slag. Coal Fly Ash (CFA) produced from the burning of coal has become a generic term for all types of coal combustion by-products, whereas fly ash is that portion of the ash stream composed of particles small enough (0.001 to 0.1mm) to be carried from the boiler in the flue gas (Korcak, 1998).

South African fly ash tend to be highly alkaline, with pH values of 10 or even higher as recorded in ash leachate when fly ash is disposed of in ash dams (Somerset, 2003).

AMD is characterised by high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2 (Feng *et al.,* 2000). When untreated AMD is discharged into public streams and rivers it pollutes the receiving streams and aquifers and can have detrimental effect on aquatic plant and fish life and the overall effect on streams and waterways can be very dramatic (Gazea *et al.,* 1996). In the worst-case scenario, all aquatic life virtually disappears; river bottoms become coated with a layer of rust like particles (Gazea *et al.,* 1996).

According to Gazea several methods are available for the treatment of acid mine waters which vary upon the volume of the effluent, the type and concentration of contaminants present. An effective treatment should be able to neutralise the effluent to a near or neutral pH, lower acidity and to reduce sulphate levels, iron and other metals down to environmentally acceptable limits. The treatment option must also be affordable or reasonably of low cost, easy to install and maintain, be able to produce limited quantities of by-products and recover at least 80% of the feed water.

The conventional mine drainage treatment systems involve neutralisation by addition of alkaline chemicals such as limestone, lime, sodium hydroxide, sodium carbonate or magnesia to water (Gazea *et al.*, 1996).

2.2 Fly Ash

Fly ash is the portion of the residue from the combustion of fuel that enters the flue gas stream. During this combustion process the ash is either collected by emission control devices (bag filters, electrostatic precipitators, etc.) or escapes to the atmosphere through stacks. According to Adriano all new large-scale coal-fired boilers are required to have equipment of "best available technology", regardless of the sulphur (S) content of the coal, used to prevent air pollution (Adriano *et al*., 1980). In most cases installation of fabric bag filters or electrostatic precipitators is required to remove particulates and "flue-gas desulfurizers" (scrubbers) to remove sulphur oxides (SO_x). Gordon therefore noticed that bag houses may remove more than 99% of the particulates in the flue gas stream but they still allow most of the fine particles (<1µm) to escape; scrubbers can extract more than 90% of the SO_x but their consistency is questionable (Gordon, 1978; Adriano *et al*., 1980).

Fly ash also known as the residue from the burning of pulverised coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas or collected by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones. However, there are three types of coal-fired boiler furnaces used in the power plant industry referred to as dry-bottom boilers, wet-bottom boilers, and cyclone furnaces. Dry-bottom furnace is also known as the most commonly used type of burning furnace.

According to Babcock and Wilcox Company, about 80 percent of all the ash leaves the furnace when pulverised coal is combusted in the form of dry ash in a dry-bottom boiler, whereas approximately 50 percent of the ash is retained in the furnace when the same type of coal is combusted in a wet-bottom (or slag-tap) furnace, the other 50 percent being entrained in the flue gas (Babcock and Wilcox Company, 1978). However in a cyclone furnace where crushed coal is used as a fuel the opposite applies, where only 20 to 30 percent leaves the furnace as dry ash and 70 to 80 percent is retained as boiler slag (tfhrc, 2007).

A general flow diagram of fly ash production in a dry-bottom coal-fired utility boiler is presented in Figure 1.

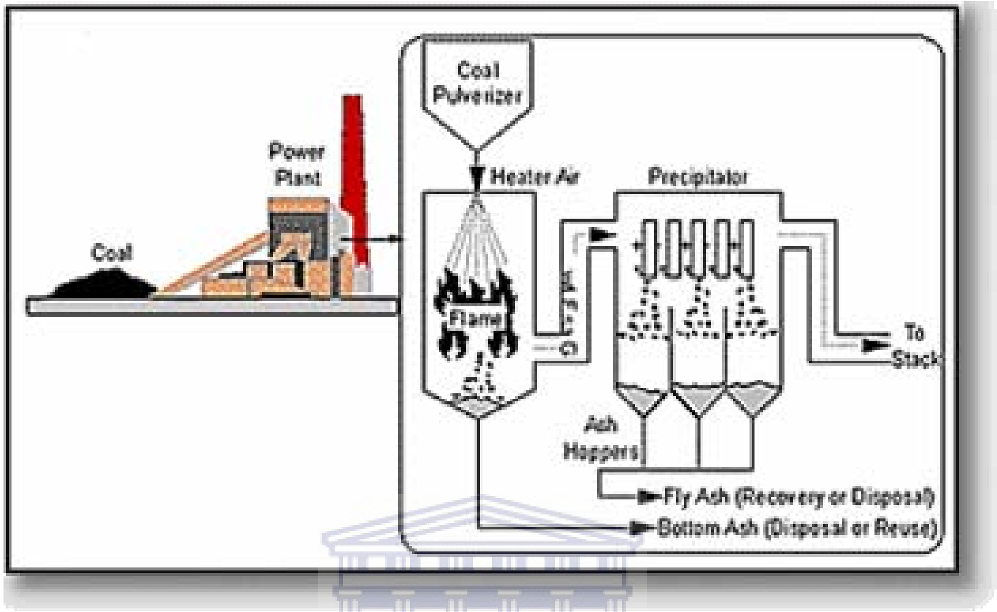

Figure 1: Production of fly ash in a dry-bottom utility with electrostatic precipitator (tfhrc, 2007).

2.2.1 Classification of ash

Coal variations from different sources, as well as differences in the design of coal-fired boilers can only mean that not all fly ash is the same. Although there may be differences in the fly ash from one plant to another, day-to-day variations in the fly ash from a given power plant are usually quite predictable, provided plant operation and coal source remain constant. There can be a substantial variation in fly ash obtained from burning coal with other fuels (such as natural gas or wood) or with other combustible materials (such as municipal solid waste, scrap tires, etc.), but as long as the basic operating parameters at the power plant do not change, fly ash from a known source should be a consistent quality-controlled product (tfhrc, 2007).

Specifications for fly ash use in Portland cement concrete are significant compared to stabilization, structured fill, and many other uses. During the late 1940s and 1950s a high demand for the use and acceptance of fly ash in the concrete industry created a need for national specifications for mineral admixtures. Proceedings for specifications began in 1948 by American Society for Testing and Materials (ASTM) and in 1953 ASTM Specification C350-54T was adopted for fly ash as admixture but only restricted to fine mixture. Fly ash was only covered in 1960 as a pozzolan. A pozzolan is a siliceous or a siliceous and aluminous material that possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at normal temperatures to produce compounds possessing cementitous properties.

Ash constituents are primarily oxides of Si (SiO_2), Al (Al_2O_3), Fe (Fe_2O_3), Ca (CaO), Mg (MgO), Na (Na_2O), K (K_2O) and Ti (TiO_2). Ash also consists of trace elements such as Ba, Cu, Sr, Ni, Cr, Zn, Cd, Mo, V, Hg, Se, Pb, and As etc. According to the chemical composition, ash has been classified as follows:

2.2.2 Class F

Fly ash of this class is produced from the combustion of anthracite or bituminous coal. The sum of content of three major oxides, silica (Si_2O_3), iron oxide (Fe_2O_3) and alumina (Al_2O_3) is greater than 70% and CaO content is less than 5%. This type of ash clearly possesses pozzolanic properties and also has high contents of unburnt carbon. Materials with pozzolanic properties contain glassy silica and alumina that will, in the presence of free lime, react with calcium in the lime to produce calcium silicate hydrates which are cementitious compounds (tfhrc, 2007). Low calcium ashes mainly class f contain quartz and mullite as major crystalline constituents (Singh *et al*., 2002).

2.2.3 Class C

Fly ashes produced from lignite or sub-bituminous coal belongs to this class. For these ashes, the CaO content is more than 20% hence they are referred to as high calcium ashes. In addition to pozzolanic properties they show cementitious properties. They also have low contents of unburnt carbon and are highly reactive. However, Manz reported that ashes from lignite and sub bituminous coal are not true pozzolans because of their high CaO content from parent coal, and form cementitous products without the addition of calcium hydroxide. Hence, the term 'mineral admixture' was adopted, which includes materials that are cementitious or pozzolanic or both (Manz, 1999).

2.2.4 Physical, Mineralogical and Chemical Properties of ash

Fly ash consists of fine, powdery particles that are predominantly spherical in shape, either solid or hollow and mostly glassy (amorphous) in nature. Davison noted that it also consists of many minute, glass-like particles, which range in size from 0.01 to 1.00µm (Davison *et al.,* 1974). Spherical-shaped particles constitute most of the fly ash especially in the finer fractions. The spherical, glassy and transparent appearance of fly ashes indicates the melting of silicate minerals during coal combustion (Adriano *et al*., 1980). According to Hodgson and Holliday, some spheres are hollow and referred to as cenospheres, while others are filled with small amorphous particles and crystals and referred to as plerospheres. Specific gravities for fly ash, bottom ash and boiler slag are 2.1 to 2.6, 2.5 and 2.6 respectively (Bern, 1976; Hodgson and Holliday, 1966).

The mineralogical composition of ash, which depends on geological factors, related to the formation and deposition of coal, its combustion conditions and emission control devices can be established by X-ray diffraction (XRD) analysis. Quartz, kaolinite, illite and siderite are dominant mineral phases. Untreated coal contains calcite, pyrite and hematite as less predominant minerals. Low ,calcium ashes, which are also referred to as class f, consist of quartz and mullite as major crystalline constituents, whereas high calcium fly ashes consist of quartzite and belite CS (Singh *et al*., 2002).

According to the scientific research undertaken it was proven that chemically all naturally existing elements can be found in fly ash (Kaakien *et al*., 1975; Klein *et al*., 1975). Major matrix elements in fly ash are Si, Al and Fe, together with significant percentages of Ca, K, Na and Ti (Rees and Sidrak, 1956; Natush *et al*., 1975). However, the chemical composition reveals that fly ash is usually an amorphous ferro-alumino silicate mineral, and may be represented by the following empirical formula (Fisher *et al*., 1976):

$$Si_{1.00}\ Al_{0.45}\ Ca_{0.051}\ Na_{0.047}\ Fe_{0.039}\ Mg_{0.020}\ K_{0.017}\ Ti_{0.011}$$

The following elements are present and expressed as oxides in the following mass percentages (Adriano *et al*., 1980):

- SiO_2, 65.3;
- Al_2O_3, 25.2;
- Fe_2O_3, 3.4;
- CaO, 3.1;
- Na_2O, 1.6;
- TiO_2, 0.98;
- MgO, 0.89;
- K_2O, 0.89

Generally, the composition of coal ash varies depending on the chemical make-up (source) of coal. However, researchers believe that knowledge alone on the chemical composition of ash is not all that is needed to predict its ability to release toxic constituents to soil and groundwater; its chemical components as well as its surface chemistry are necessary to predict the ability to contaminate (Evangelou, 1998).

Fly ash has a hydrophilic surface, is extremely porous with particle size being the most important physical characteristic determining the reactivity. Smaller ash particles have an advantage of being more reactive because they possess larger specific areas making a large percentage of particles available to attack by hydroxides. Another reason for smaller particles to be more reactive could be that they cool faster upon exiting the combustor, resulting in a more disordered and therefore reactive structure (Iyer *et al*., 2001).

2.2.5 Uses of ash

Fly ash can be, and is being, successfully used for different practical uses. Some of the applications are as follows (Singh *et al*., 2002; Evangelou, 1998; Korcak, 1998):

- Additive or sub-grade and sub-bases in pavement construction.
- Filler material, especially for the reclamation of low lying waste lands and refuse dumps, or the filling of mines to improve foundation soils
- Treatment of polluted water and soils unsuitable for agriculture.
- Canal lining.
- Drying of wet soils due to high permeability values.
- Removal of heavy metal from aqueous solution, by precipitation and adsorption.
- Building of different types of bricks and other building units.
- Manufacture of sintered aggregates for making lightweight concrete and for replacement of cement in mass concrete construction (such as dams and barrages).
- Improvement of soil moisture-holding capacity.
- Synthesis of zeolites (for heavy metal removal from water).
- Amendments for coal refuse piles and non-agricultural lands, especially reclaiming previously mined areas.

Fly ash as a waste material produced from combustion of coal is the largest by volume industrial waste generated in the world (Williams *et al*., 2002). Mehta noted that whereas fly ash is used to form blended cements only about 20% is currently used for the production of cement. This application has been investigated extensively for decades with early papers dating back to 1960 (Mehta *et al*., 1989). Glasser *et al* noted that the substitution of fly ash for cement in concrete had both economic and structural advantages (Glasser *et al*., 1987).

It has been reported that on the potential practical uses of these wastes lies environmental relevance in addition to industrial interest. Depending on the mineralogical and chemical characteristics, there are three types of fly ash are considered, that is Al-rich, Fe-rich and Al-Si-rich types are usually considered, new types of combustion by-products have to be considered given the development of new combustion and gasification technologies (Querol *et al*., 1997).

High coal consumption and mineral matter content result in large volumes of combustion wastes being generated every day. A small proportion of the waste generated is recycled, mainly for cement and concrete manufacture and as a solid additive, the remainder being discharged into fly ash ponds or landfills (Querol *et al*., 1997).

2.2.6 Disposal of fly ash

Some researchers consider disposal of fly ash as an environmental concern because of its ability to pollute groundwater with heavy metals and toxic ions (Evangelou, 1998.). The most widely common and accepted practice in the disposal of ash is holding it in settling ponds, stockpiling, and land filling. However, sluicing to holding ponds, where most solids inhabit and accumulate until they are removed for land filling or stockpiling, is by far the most common method (Adriano *et al*., 1980).

Fail and Wochok reported that approximately one million hectares of land remain practical wastelands due to damage incurred from strip mining of coal. They further noticed that the spoils are unproductive and support only small amounts of vegetation, subjecting the rest to severe erosion. However fly ash has been confirmed efficient in reclaiming spoil areas (Capp and Spencer, 1970; Capp and Gilmore, 1973; Fail and Wochok, 1977). When reclaiming spoil areas, the quantities of fly ash, which may be used usually, exceed that for cropland disposal. The amount of fly ash required to reclaim spoil areas depend upon the pH of the fly ash, the extent to which it is weathered and the pH of the spoil to be reclaimed.

In cases where unweathered fly ashes are applied at high rates, a period of about one year is required as stabilisation period to create uniform plant growth (Martens and Beahm, 1978). However, where application of weathered fly ash was effected, uniform growth of crops frequently occurred the season preceding the initial fly ash application. At the same application rate it was observed that unweathered fly ash yields a much higher pH and / or salt content in the soil-fly ash mixture than does weathered fly ash. High salinity and pH, which tends to be buffered out with time, therefore are responsible for growth depressions, which occur immediately after applications of unweathered fly ash to soils (Evangelou, 1998).

Researchers therefore recommended that abandoned ash-holding ponds and stockpiles could be re-vegetated to give a temporary cover until the ash was used or a proper final disposal may be arranged. It was suggested then that a thin layer of soil (5 to 8 cm) could make possible the establishment of plants and provide both physical and chemical favourable conditions for plant growth (Cope, 1962; Hodgson and Holliday, 1966; Scanlon and Duggan, 1979).

Fly ash is normally stored in silos from which it can be used or disposed of in a dry or wet form. Water can be added to the fly ash to allow for stockpiling or land filling in a conditioned form (approximately 15 to 30 percent moisture), or for disposal by sluicing into settling ponds or lagoons in a wet form. Approximately 75 percent of the fly ash produced is handled in a dry form or moisture-conditioned form, making it easier to recover and recycle and the rest is mixed water and pumped into ash dams. Therefore the main advantage to the conditioning of fly ash is the reduction of blowing and dusting loose particles during truck transport and outdoor storage (tfhrc, 2007).

2.2.7 Dry disposal method

Coal ash in its dry form is carried away to the place of disposal, or the place of use by means of the following:

- Closed truck or rail wagons
- Pneumatic conveying system (using pressure conveying system or vacuum conveying system)

Pneumatic conveying system is one of the most commonly and widely accepted disposal methods. Dry disposal methods posses some of the most important advantages like the fact that the cementitious properties of the ash do not alter; the bottom and the fly ash can be collected and stored separately. This type of ash disposal has a severe impact on the environment such as air quality, effect on topsoil, crops and toxicological effect on humans (Lister *et al*., 1996).

2.2.8 Wet disposal method

During wet disposal of ash, the ash mixed with water and is pumped through the pipelines into the ash dams. The ash dams are partitioned into smaller areas to create lagoons. The lagoon formation aids in the compartmentalization of the whole area and ash is disposed off alternatively in each lagoon up to monitored levels before switching over to another lagoon. Furthermore once lagoons have reached their capacity either reconstruction of new lagoons or raising of the existing dyke is required. This method of ash disposal is quite simple to operate and has minimal effects on the environment and local air quality. However, Lister *et al*. think that this method makes it difficult to distinguish between bottom ash and fly ash since they are mixed together and as such not available in separate forms for utilisation. This method has some advantages since it is stores in a contained area and disadvantages being that it requires large amounts of water to make slurry and recirculation of this water is quite costly and also requires large piece of land, which is difficult to reclaim. Heavy metals (which are toxic in nature) tend to leach from the ash matrix thus contaminating ground water. Lister *et al*. also noticed that the biggest disadvantage of this disposal method is that it demands large areas of land, which are practically irretrievable in the future (Lister *et al*., 1996).

2.3 Acid Mine Drainage (AMD)

Acid mine drainage (AMD) is acidic water loaded with high concentrations of iron, sulphate and other metals that forms under natural conditions when geologic materials containing pyrite are exposed to the atmosphere or oxidising environments (acid drainage, 2007).

AMD is considered as on of the most serious and persistent environmental problem facing many active, abandoned sulphide minerals and coal mining sites. Acid rock drainage (ARD) or acid drainage (AD) collectively known as AMD is commonly thought to be associated with coal mining, but it can occur under natural conditions or where sulphides in geologic materials are encountered in metal mining, highway construction, and other deep excavations (Christensen *et al*.,1996).

AMD is characterised by high concentrations of dissolved heavy metals and sulphates and can have pH as low as 2. These characteristics may prohibit discharge of this type of untreated effluent to public streams, as they might have a negative impact on aquatic plant and fish life. The receiving streams of this untreated effluent become polluted, affecting aquifers and the overall effect can be very dramatic. In the worse case scenario all aquatic life may die and river bottoms become coated with a rust-like layer.

2.3.1 Chemistry and formation of Acid Mine Drainage

When pyrite and other sulphide minerals are exposed to oxygen and water in the presence of oxidising bacteria sulphide minerals oxidise to produce dissolved metals sulphate and sulphuric acid. Iron sulphides common in coal regions are predominantly pyrite and marcasite (FeS_2) and are identified as responsible for AMD formation.

Oxidation of pyrite, which is most abundant sulphide mineral can be summarised by the following reactions (Stumm and Morgan, 1981; Klink, 2003):

$$2FeS_2 + 7/2O_2 + 7H_2O \rightarrow 2Fe(OH)_3 + 4H_2SO_4 \quad (1)$$

This reaction demonstrates the oxidation of pyrite by oxygen.

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (2)$$

$$Fe^{2+}(aq) + 5/2H_2O + \frac{1}{4}O_2(aq) \rightarrow Fe(OH)_3\,(s) + 2H^+(aq) \quad (3)$$

$$Fe^{2+}(aq) + \frac{1}{4}O_2(aq) + H^+ \rightarrow Fe^{3+}(aq) + \frac{1}{2}H_2O(l) \quad (4)$$

$$FeS_2(s) + 14Fe^{3+}\,(aq) + 8H_2O\,(l) \rightarrow 15Fe^{2+}\,(aq) + 2SO_4^{2-}(aq) + 16H^+ \quad (5)$$

Reaction (2) demonstrates the weathering of pyrite in the presence of oxygen where pyrite undergoes oxidation to release ferrous iron, sulphur is also oxidised to sulphate. Two moles of acidity are generated in this reaction for every mole of pyrite oxidised.

Ferrous iron undergoes hydrolysis in reaction (3) with the formation of ferric hydroxide.

In reaction (4) ferrous iron is oxidised to ferric iron. This reaction is pH dependent where the reaction proceeds slowly under acidic conditions in the absence of bacteria and is also referred to as the ‘rate determining step’ in this overall acid generation sequence.

Reaction (5) is the oxidation of additional pyrite by ferric iron. The ferric generated in reaction (4) can directly attack pyrite and acts as a catalyst generating much greater amounts of iron, sulphate and acidity. This is the cyclic and self-propagating part of the overall reaction and takes place very rapidly and continues until either ferric iron or pyrite is depleted.

Generation of AMD would slow or cease if any of the processes presented by the reactions were slowed down or stopped altogether.

2.3.2 Existing methods for the treatment of Acid Mine Drainage (AMD)

Several methods exist for the treatment of acidic mine waters commonly known as acid mine drainage (AMD), depending upon the volume of the effluent, the type and concentration of contaminants available. An effective treatment is intended at producing water of neutral pH, low acidity; reduce levels of the sulphates iron and other metals present down to accepted environmental limits. Furthermore the process to be considered for this AMD treatment must be affordable, easy to install and maintain, recover a fair amount of clean water while producing limited quantities of solid by-products.

Various techniques being developed to treat AMD. In the subsurface, various natural and man-made alkaline materials have been tested for their neutralisation potential; these include coal combustion by-products (CCBs, flue gas desulphurisation by-products (FGDBs), oxic and anoxic limestone drains (ALDs) (Aljoe, 1996; Schueck *et al*., 1996; Haefner *et al*., 1997; Hedin *et al*., 1994; Skousen *et al*., 1992).

2.3.3 Membrane technologies for water treatment

2.3.3.1 Desalination

Desalination is defined as the removal of salts from water. Desalination is primarily the production of water suitable for domestic and industrial use from saline waters such as seawater and brackish water. It can be easily distinguished from demineralisation, which is the production, for special industrial process requirements, of very high-purity water from water that may be quite fit for human consumption. Desalination can further be clarified with reference to the dissolved solids contained in the water. It has been noted, based on the scientific research undertaken, that seawater averages about 35 000 ppm of total dissolved solids (TDS), whereas brackish waters are in the range of 2000 ppm upwards. The maximum allowed figure for continual consumption is about 500 ppm of TDS (Porteous, 1983).

2.3.3.2 The need for desalination

Several researchers have identified the need for desalination based on the following factors (Porteous, 1983).

- Production of 1016 kg of steel requires over 182 000 litres of water; production of 1016 kg of aluminium requires 1 364 000 litres of water. Producing 1016 kg of petrol in a refinery from crude oil needs 91 000 litres) of water; producing 1016 kg of artificial fibres from a chemical needs about 909 000 litres of water.
- One litre of beer produced needs about 350 times its volume of water during its production.

Considering these and other similar statistics for other industries, it is evident that one ton of an industrial product represents an average use of the order of 200 tons of water. Therefore in terms of tonnage produced of the water supply industry of an industrial country about 99.5 % is industrial activity, while all the rest is only about 0.5 %. This implies that there are some important fundamentals, which were ignored, like the fact that industrial expansion is impossible without water in large quantities, and unless water can be obtained at very reasonable prices than all the other materials involved in industrial product, then industrial production will be practically expensive (Porteous, 1983).

2.3.3.3 Reverse Osmosis (RO)

The term osmosis defines a process whereby a salt-water solution is placed on one side of a semi-permeable membrane and water on the other side. There is natural tendency for water to diffuse through the membrane to the solute side until it reaches an osmotic equilibrium pressure. Reverse osmosis is a process whereby the pressure applied on the solute side is significantly greater than osmotic pressure then the water diffuses from the solution through the membrane thus leaving the salts behind. In this process approximately 80% of the water is forced through the membranes, resulting in 20% of the water containing most of the salts left as a by-product called brine. The main advantage of this process is that it can reduce the volume of saline water by as much as 80% leaving the residue called brine to be disposed in an environmentally friendly manner. Reverse Osmosis (RO) is a continuous process; the membrane requires no regeneration and is capable of separating the feed fluid into two streams; a concentrate stream, which contains a lot of impurities, and a pure water stream called permeate. The membrane in the RO prevents dissolved ions from passing through and also acts as a molecular filter retaining bacteria, viruses and most organic material contaminating natural waters (Porteous, 1983; Eskom, 2005).

2.3.3.4 Electrodialysis (ED)

Electrodialysis is a process in which ions are transported through a membrane from one solution to another under the influence of a direct current electrical potential. Research shows that electro dialysis is used in systems and other processes to produce high-purity water for high-pressure boilers, electronics and manufacture of pharmaceutical products. Production of potable and process water from brackish water has been noticed as one of the principal uses of electrodialysis.

2.4 Brine

2.4.1 What is brine?

Brines are inorganic saline process waters or sludges from desalination units in mining or industry. Brine is also labelled as desalination by-product. Desalination is a water treatment process that removes salts from water and approximately 60% of the residual water from desalination plants is brine. According to Al-Algha *et al*. brine contains high concentrations of Total Dissolved Solids (TDS) and sometimes even high concentrations of chemical products and toxic metals (Al-Algha *et al*., 2005). Brine reported is a by-product of freshwater production from desalination with salinity of about twice that of seawater.

2.4.2 Characteristics of brine

Brine is characterised by high TDS from Na, Ca, K, Mg, SO_4 and Cl. Due to the treatment processes involved in the thermal desalination plant temperatures of brine as a by-product range from 90-110°C, and high temperatures of disposed brine impact negatively on marine life and surrounding environment (Al-Algha *et al*., 2005). Chemistry of brine plays a secondary role and has a great effect on the environment. Chemical constituents classified based on treatment purposes are the following:

- Original chemicals - found originally in brackish, seawater, mine water and cooling water circuit depending on the feed water that desalination plant is using, therefore feed water contains salts of Cl; Na; K; Ca; Mg; NO_3; SO_4; HCO_3; etc. These chemicals are rejected with brine after treatment. However it was noticed that desalination plants produce residues that may contain high salt concentrations, above those of feed water (seawater sodium chloride concentration is about 35,000 mg/l and desalination plant residues have a concentration of 46,000 to 80,000 mg/l).

- Treatment chemicals – used mainly during different treatment processes for defouling of plant equipment, pre-treatment and desalination treatment. Chemicals from pre-treatment of the feed water include chlorine, sulphur dioxide, coagulants (e.g., ferric chloride), carbon dioxide, polyelectrolytes, antiscalants (e.g. polyacrylic acid), sodium bi-sulphite, antifoam agents and polymers.
- Flushing chemicals – chemicals used for flushing pipelines and cleaning the membranes in Reverse Osmosis (RO) plants (these chemicals may include sodium compounds, hydrochloric acid, citric acid, polyphosphate, biocides, and copper sulphate. In most cases, these chemicals are discarded along with brine (Al-Algha *et al*., 2005).

2.4.3 Environmental impact due to brine disposal

Brine disposal is a primary environmental issue associated with desalination. Disposing of this desalination by-product is a concern and is also costly because of its constituents and large volumes that must be handled. According to Vavra *et al.* several researchers for brine disposal represents an urgent environmental problem as it could badly affect the surrounding environment. However, disposal of brine effluents that are residues of Reverse Osmosis (RO) in the desalination of brackish and industrial water remains a persistent environmental problem. On several occasions it has been solved by pumping it into the sea or into solar evaporation ponds however, all of these seemed quite costly (Vavra *et al*., 2004).

Brine water contaminants need to be removed before it can be used for any beneficial surface application (Vavra *et al*., 2004). Researchers have resorted to solve this persisting environmental problem by concentrating brine effluent to a certain volume by means of membrane technologies like electro dialysis. Employing these technologies, reducing the volume of the brine effluent and therefore disposal works out cheaper (Korngold *et al*., 2005).

Sodium absorbs more water molecules per unit (mole) of charge than most ions like K^+, Mg^{2+}, Ca^{2+} commonly found in soil-water environment. Hence when brine (NaCl) is discharged into the soil-water environment, fully hydrated Na ions tend to be absorbed by clay and organic particles. This absorption causes the particles to be waterborne, a process also known as dispersion. During this process called dispersion soils become impermeable to water; lakes; streams; and rivers experience large increases in suspended solids (clays and organics). It was noticed that most clay soils undergo dispersion at an Exchangeable Sodium Percentage (ESP) of about 15 and at this ESP level soils tend to be toxic because they lose the potential to function as porous media where water infiltration and gas exchange are restricted (Evangelou, 1998).

There are three factors that need to be considered when disposing brine in a field that is used or to be used for agricultural purposes, assuming that brine does not contain boron as a toxic ion (Evangelou, 1998).

- The first factor is the type of crop grown. It was noticed that different crops tolerate different levels of salt concentrations. Some clovers for example are extremely sensitive to certain concentrations of salt, while some grasses, like tall fescues are quite tolerant.
- The second factor to be considered is the cation exchange capacity (CEC) of the soil. A soil with a CEC of 10 meq/100g can be able to tolerate approximately 209 kg of sodium per acre (10% of CEC) before it reaches its critical toxicity threshold. At the same time a soil with a CEC of 20 meq/100g can only tolerate up to 417 kg of sodium per acre before it reaches its maximum critical threshold.
- The third factor to be considered is the texture of soil: a sandy soil can tolerate very little sodium chloride salt before it becomes toxic, whereas a clay-type soil can accept a lot more, owing to its higher CEC and water holding capacity (Evangelou, 1998).

Constituents of brine water discharged from desalination plants depend on several factors like desalination technology used, quality of feed water, quality of water produced, pre-treatment cleaning and RO membrane storage methods used. Following are the most important environmental issues of desalination plant:

- Impact on sewage system – brine discharged into the sewer system causes high pressure on the wastewater treatment process, thus making it more difficult and requiring special treatment.
- Impact on groundwater – contamination of the underlying groundwater aquifer with highly saline brine residue is considered a very important issue by researchers.
- Impact on soil – brine has both physical chemical effects on soil:
  Damage soils physical properties by increasing the concentration of sodium accumulated on the surface, thus forming a hard crust on the soil surface, high temperature of brine kills micro organisms in soil, affecting soil fertility.

A chemical impact on soil is very hazardous because brine has toxic materials that can damage the structure and composition of soil. Reducing the soils water-holding capacity and its ability to transmit plant nutrients can be caused by brine disposal on land. Several authors noticed that it might cause a decrease in crop yield due to an overall poor soil quality (Assaf, 2001; Al-Algha *et al*., 2005).

- Impact on marine life – brine discharge has harmful effects on marine life in large-scale desalination plants. High concentration of dissolved ions poses a negative effect on marine life and can be expressed by the following: (Al-Algha *et al*., 2005; California Coastal Commission, 1993).

1. High temperatures of brine discharged on the ocean affect migration patterns of sea inhabitants along the coast. Some marine species can feel the change in salinity or temperature and will avoid the area affected and move further

offshore. However, due to that, the marine species are forced to swim over longer distance, further away, leaving the area of highest food concentration.

2. The high salt concentration of the discharged brine effluent and inconsistency in salinity levels may kill organisms near the outer surface that cannot tolerate either high salinity levels or sudden changes in the levels of concentrations. Brine is also denser than seawater and sinks to the bottom, potentially causing adverse impact on bottom dweller organisms. In addition to that the salt of brine influences rates of sedimentation and is highly important for determining the well being of marine organisms that may be buried or loaded by an increase in deposition of unstable and / or finely suspended materials.

3. Research undertaken proves that brine contains heavy metals that have a harmful impact on the marine environment and can cause death to fishes and aquatic life. Heavy metals may become concentrated in the upper part of seawater, which is highly toxic to fish eggs, plankton, and larvae that are located in the area affected.

4. It has been found that all desalination plants use acids like chlorine or other biocides, which are harmful to marine resources, to clean pipes and other equipment and sometimes for pre-treatment of feed water.

General impact – brine is known to contain chemicals such as antiscalants that are used in pre-treatment of feed water, washing solutions and rejected backwash from the feed water; all of these have a negative impact on the surrounding environment.

2.4.4 Existing methods for brine treatment

Several methods exist for the removal of toxic and heavy metal ions from aqueous solution; these include ion exchange, reverse osmosis, precipitation and adsorption. Adsorption is by far the most versatile and widely used process. Activated carbon has been the standard adsorbent for the reclamation of municipal and industrial wastewaters. Due to the high-cost of activated carbon, production of its low-cost alternatives has been the focus of research in this area for many years.

These sorbents for the heavy metals and toxic ion sorption ranged from natural materials to industrial and agricultural by-products, such as fly ash carbonaceous material, metal oxides, zeolites, moss, hydroxides, lignin, clays, biomass, peanut hulls, pyrite fines, goethite and coral sand

Brine disposal is an environmental concern since it contains high concentrations of Total dissolved solids (TDS) and sometimes even high concentrations of chemical products and toxic metals (Al-Algha *et al*, 2005). Coastal areas dispose their brine off into the ocean but that practice has raised concerns as well since it can lead to degradation of fauna and flora, unless the concentrated brine can be disposed far from the coast, which would unnecessarily increase overall costs (Le Dirach *et al*., 2005).

The brine is disposed of on the dry ash dump by mixing it with ash. The brine is used at the ash conditioners to dampen the ash prior to transporting it to the ash dumps. The cementing properties (pozzolanic properties) of the ash are used to encapsulate the salts contained in the brine. This combats dust problems and the salts are also prevented from polluting the environment (Eskom Generation Communication, 2005).

At the same time inland areas are still struggling to discharge their brine in an environmentally friendly manner. The challenge facing brine treatment and disposal is that brine needs to be concentrated first to avoid working with large volumes of effluent then disposed of in a way not to contaminate groundwater and streams heaps for the ash particles to encapsulate and lock the heavy metals and toxic ions not to contaminate groundwater.

The challenge that inland areas are facing now with the practice they engaging in is that the ratio of ash to brine should equate so as to ensure that most of the heavy metals and toxic ions available in brine are removed as it is disposed in the ash heaps and will be locked as ash particles has that property of encapsulating heavy metals and toxic ions.

2.5 Zeolites

2.5.1 Origin

Zeolites form a family of aluminosilicates and have been studied by mineralogists for over 200 years (Barrer *et al*., 1978). Alex Frederick Cronstedt, a Swedish mineralogist, discovered zeolites in 1756. The term zeolites originated from his observation that upon heating a natural mineral, stilbite, and the stone began to dance about as the water evaporated. The material was named ‘zeolite’, which came from the Greek words meaning “stone that boils” (The Abbey Newsletter, 1996).

According to Barrer, fine crystals are often found lining the cavities and cracks in basaltic rocks of volcanic origin. Those cavities are considered to be formed by bubbles of fluids in the parent magma, and apparently zeolites develop as a result of chemical action on the magma of these fluids, or of fluids, which have consequently replaced them. Generally, researchers noticed that the bulk compositions of the zeolites have a tendency to correlate with those of the parent rock as more aluminous zeolites are linked with rocks lacking silica and more siliceous zeolites with rocks high in silica (Barrer *et al*., 1978).

Natural zeolites may originate from volcanic ash. The chemical reaction of glassy volcanic ash (source of aluminosilicate) with pervading pore water changes the glass fraction into various zeolite crystalline mineral phases over geological time scales under certain conditions. Many pure zeolite types can also be prepared via hydrothermal synthetic routes. The hydrothermal synthesis of aluminosilicate zeolites corresponds to the conversion of a mixture of silicon and aluminium compounds, alkali metal cations, organic molecules in some cases and water via an alkaline supersaturated solution into a microporous crystalline aluminosilicate. Synthetic zeolites play a major role on industrial scale, in terms of catalysis, molecular sieving and environmental protection.

2.5.2 Description of zeolites

Zeolites are often described as crystalline aluminosilicate with a cage structure. They are often referred to as crystalline hydrated aluminosilicate whose framework structure surrounds cavities or pores occupied by cations and water molecules, both of which have considerable freedom of movement allowing ion exchange and reversible hydration (The Abbey Newsletter, 1996).

They are also referred to as tectosilicates, as they are produced by joining together these tetrahedrons, resulting in a three-dimensional anionic network. Each oxygen atom is shared between one tetrahedron and one of four adjacent tetrahedrons. However, this means that there are no unshared oxygens in the framework. Thus in all tectosilicates (zeolites, felspars and felspathoids) for every Si^{4+} replaced in the framework by Al^{3+}, a negative charge is created and neutralized by an electrochemical equivalent of cations resulting in a (Al+Si):O ratio of 1:2. The framework in zeolites is sufficiently open to accommodate water molecules as well as cations. Therefore the openness in zeolites frameworks imparts characteristic properties, which means that water molecules and cations can move easily within the crystals (Barrer *et al.,* 1978).

Zeolites are also defined as crystalline aluminosilicate materials with regular uniformed, Angstrom sized channel/pore system. They have the following unique properties (Moscou, 1991; Maxwell and Stork, 2001):

- Microporous character with uniform pore dimensions;
- Ion-exchange properties;
- Ability to possess acidity;
- High thermal stability;
- High hydrothermal stability.

Amongst the unique properties that zeolites posses are the extremely large specific surface areas. However, surface areas of fully crystalline zeolites are typically in the order of 400 600 m^2/g, of which approximately 66-85 % is internal in the microporous channel. Zeolites are very stable over 1000°C, which attribute allows thermal regeneration of these catalysts and zeolites are resistant to attrition posing few handling problems. Their surface properties can either be hydrophilic of hydrophobic. An Al rich zeolite attracts water, whereas a Si rich zeolite will repel water. There are more than 200 unique zeolitic structures that occur naturally and those that are synthesized.

Unit cell formulae differ for each unique zeolite structure, depending on the configuration of the framework and its composition. The empirical unit cell formula of a zeolite is of the type: $M_{2/n}O \bullet Al_2O_3 \bullet xSiO_2 \bullet yH_2O$, where M is any alkali or alkaline earth atom, n is the charge on that atom, x is a number from 2 to 10, and y is a number from 2 to 7. For example, for zeolite Y (faujasite) the formula is $(Na_{58})(Al_{58}Si_{134}O_{384})\bullet 240H_2O$. Atoms within the second set of parentheses are structural atoms, because with oxygen they make up the rigid lattice framework of the structure. Those within the first set of parentheses are known as exchangeable ions, because they can be replaced (exchanged) more or less easily with other cations in aqueous solution, without affecting the aluminosilicate framework.

Zeolites that occur naturally may originate from volcanic ash. The chemical reaction of glassy volcanic ash (source of aluminosilicate) with pervading pore water changes the glass fraction into various forms of zeolite crystals. Many pure zeolite types can also be prepared via hydrothermal synthetic routes. The hydrothermal synthesis of aluminosilicate zeolites corresponds to the conversion of a mixture of silicon and aluminium compounds, alkali metal cations, organic molecules in some cases and water via an alkaline supersaturated solution into a microporous crystalline aluminosilicate. Synthetic zeolites play a major role on industrial scale, in terms of catalysis, molecular sieving and environmental protection.

The negative charge of the framework is caused by the replacement of Si^{4+} with Al^{3+}. The residing excess negative charge requires the introduction of charge compensating cations to stabilize the structure. These charge compensating cations are not incorporated into the lattice framework or covalently bound to the zeolite structure, but have considerable freedom of movement and can readily be substituted with a host of other cations. The charge balancing cation associated with the framework acid site is usually a Group I element such as Na or K. Group II elements such as Mg and Ca are also used to change pore diameters, exchange- or catalytic properties. Various other metals such as Pt and Pd can also be exchanged into the zeolite, to form bi-functional catalysts. For catalytic reactions the charge balancing cation is exchanged with NH_4^+ and then calcined at 500°C to activate and generate the acidic, H-form of the zeolite catalyst.

The Si/Al ratio usually determines the amount of exchangeable cations that may be present within the pores of a zeolite and this, as well as the relative accessibility of the cation, will define to what extent the cations may be exchanged. The lowest Si/Al ratio is 1:1, due to the next nearest neighbour (NNN) exclusion principle, thus T-O-T linkages may not accommodate two adjacent Al atoms. The highest Si/Al ratio is unlimited, but depends on whether a completely siliceous composition is stable for a particular structure.

Among the active sites on the zeolite surface, some have a fixed charge and thus represent the effective negative charge of the zeolite; as such they may be referred to as permanently active charged sites or Brönsted acid sites. Thus, the bridged ≡Al-O-Si≡ functional groups represent Brönsted acid sites which can be used for potential ion exchange, acid catalysis or complex formation (Ikhsan *et al*., 1999; Tamura, 2004). Catalytic activity is determined by the relative amount of bridging hydroxyl groups and this in turn is typically determined by the amount of Al incorporated in the framework.

The strength of the acid site is a function of its isolation. Typically weak acid sites occur in material with a Si/Al ratio of <12, in other words Al rich materials, and strong acid sites above this ratio. A basic catalyst is prepared by substituting a metal such as Titanium for the Al.

2.5.3. Exchange properties of zeolites

Natural and synthetic zeolites have a rather rigid framework structure. Their structures are associated with certain unique features, among which are strictly uniform pore diameters and widths, giving rise to a pronounced “sieving action”, on the molecular scale. Larger cations are partially or completely excluded by the zeolite pore size, whereas smaller species can be exchanged or sorbed, and as such, zeolites have found wide scale applications as molecular sieves. Zeolites offer extremely large specific surface areas and are typically microporous. According to the IUPAC classification, micropores have a diameter (d_p) smaller than 2 nm (Wietkamp, 2000).

Located inside the zeolite framework are channels, channel intersections and/or intersections with dimensions ranging from 0.2 to 1 nm, which connect the strictly uniform pore apertures with larger void volumes, known as super cages. Inside the pore apertures can be found water molecules or mono- and divalent cations, such as Na^+, K^+, Ca^{2+} and Mg^{2+}. The negative charge of the framework, caused by the replacement of Si^{4+} with Al^{3+}, is compensated by these small cations. The ready exchangeability, and relatively innocuous nature of the charge-balancing cations, renders them particularly suitable for the removal of undesirable species (particularly metal ions) from wastewaters (Shevade and Ford, 2004). However, before a metal ion can move from the aqueous solution through the pores, it normally needs to shed some of its hydration shell – a process which differs from one metal cation to the next since the extent of hydration depends on the size of the bare metal ion.

The water contained within the framework channels desorbs upon exposing the zeolite to elevated temperatures: it is lost at about 250°C. The process, termed dehydration or zeolite activation, is reversible, which means that the zeolite can re-adsorb 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 25 % of their dry mass. Similarly, they can also accommodate solvent molecules on the basis of their size, without any change in the external volume of the crystal. Following the 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 (Helfferich, 1962).

An equally important parameter of zeolites is the Si/Al ratio. It is responsible for their thermal and hydrothermal stability, as well as their acidity and relative hydrophobicity. The specification of this ratio also gives the zeolite species its significance in environmental protection. A small Si/Al ratio is indicative of an increased number of terminal Al-OH surface functional groups at the solid-water interface. It consequently leads to a great capacity for ligand exchange (Misak, 2000), the overall effect being better performance in terms of metal removal from contaminated waters and hydrophilicity. For zeolites such as those under discussion in the current research applications, it was found that the total exchange capacity may depend on the experimental conditions and considerably differ from the theoretically determined value (Misak, 2000).

The cationic exchange capacity CEC can be defined as a measure of the charge compensating cations per unit of weight or volume of the zeolite. It represents the number of cations available for exchange (Inglezakis and Grigoropoulou, 2003). 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 cation exchange capacity. The CEC of an ion exchanger portrays its efficiency in environmental protection at an industrial level, for its application in the removal of undesired species from polluted effluents.

The first step in the process of determination of the CEC of zeolite is to determine the amount of cations contained in its structure, which are available for exchange. Not all exchangeable cations are always available for ion exchange processes. This can be attributed to several reasons:

- Depending on the pore size of the zeolite, some of the incoming ions may be too large to fit into the pores and channels of the aluminosilicate framework, and are thus excluded.
- Some of the exchangeable cations may be components of impurities, such as feldspar, quartz and salts, which were not completely crystallised during the "zeolitisation" process.
- Since the structure of zeolites is made up of cages combined in a specific manner, some of the inorganic groups may be located in inaccessible sites of the mineral structure.

The character of selectivity of zeolites towards ions contained in the surrounding solution changes as a function of both ion exchange capacity and pore size. Zeolites with high exchange capacities (high charge densities) can easily strip the hydration shell of a water-cation complex. In zeolites 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 prefer ions with a hydrate layer having the lowest possible stability, since shedding part of the hydration layer will then be easier.

In view of all these unique properties inherent in zeolites, a host of functions pertaining to zeolites can be summarised, with respect to industrial applications and environmental protection:

- Chemical sieving
- Gas adsorption: removal of specific toxic gases
- Water adsorption: reversible adsorption of water without chemical or physical change in the zeolite matrix
- Utilisation as industrial catalyst and in fluid catalytic cracking of heavy distillate
- Ammonia removal from urban, agricultural and industrial wastewaters.

The amount of exchangeable cations that may be present within the pores of a zeolite, as well as the relative accessibility of the cation is usually determined by the Si/Al and this ratio also defines to what extent the cations may be exchanged.

2.5.4. Synthesis of zeolites from fly ash

Zeolites of very high purity are not always necessary for different applications. Waste materials or waste products including fly ash, can also be used as raw materials for the synthesis of zeolite-containing materials, for many purposes. Fly ash generated from coal-fired power stations is a fine silt-sized powder that contains many unburnt residuals. Some of the main components of fly ash are SiO_2 and Al_2O_3. These are present in similar chemical ratios to that required for zeolite formation, and therefore fly ash can be used as a raw material for synthesizing zeolites (Lin and Hsi, 1995). Fly ash from brown coal (as burnt in South Africa) proves advantageous for the synthesis of zeolite-containing products in that it is already thermally treated during the combustion process. After the combustion process some silica and alumina contained in the ash already exists in an activated form. Kaolin particles in the coal are converted into metakaolin that can then be easily transformed into zeolites (Stamboliev *et al*., 1985).

Fly ash is treated with sodium hydroxide at different concentrations for varying times and temperatures. This produces different zeolite-containing materials, with varying percentages of different zeolites. The use of more extreme hydrothermal conditions and various pH’s can also affect the type of zeolite synthesised (Iyer and Scott, 2001).

Fly ash has a high content of reactive phases such as aluminosilicate glass and a large surface area. Fly ash with a low Si/Al ratio can be used to produce low-Si zeolites. Low-Si zeolites have high ion exchange capacities, a high selectivity for polar molecules and high porosities. Zeolites synthesized from fly ash have important industrial applications for example as sorbents for the removal of ions and molecules from solutions such as waste waters and radioactive wastes, from gases, and as replacements for phosphates in detergents (Querol *et al*., 1997).

Querol and co-workers in Spain have developed many processes for zeolite synthesis from fly ash based on hydrothermal conversion (Querol *et al*., 2001). Different processes have resulted in the synthesis of low-Si sodium (Al rich) and potassium zeolitic (NaP1, A, X, KM, chabazite, faujasite) material. These zeolite types have a high Al^{3+}/ Si^{4+} ratio, showing a high ion-exchange potential, especially for heavy metals and ammonium. It is predicted that such synthesized zeolitic material will have significant application in wastewater decontamination technology (Querol *et al*., 2001).

Synthesis of fly ash zeolites at pilot scale was investigated by Querol *et al.* using different Spanish fly ash. They concluded that the optimization of the synthesis yields have to be specified for each fly ash type due to differences in the mineralogical and chemical compositions. However, Querol and co-workers also determined that there was high reproducibility at the pilot scale using the one fly ash source to produce zeolite NaP1 and this zeolite produced was similar in properties to the lab-scale synthesised (Querol *et al*., 2001).

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Considerable work on zeolite synthesis from fly ash and other uses of fly ash was presented recently at a conference in Spain (Nugteren, 2001). It seems likely that research interest into uses of fly ash will increase over the coming years.

Conversion of fly ash into zeolite has the advantage of the following:

- The cation exchange capacity is increased from < 0.05 meq g^{-1} for fly ash to between 0.3 and 4.7 meq g^{-1} (Querol et al., 2002).
- The surface area increase from < 50 m^2/g for fly ash to greater than 200 m^2/g for zeolites.

2.5.5. Previous work on zeolite synthesised from fly ash and solid residue

Zeolites FAU and P have been successfully synthesised from fly ash and solid residues resulting from the neutralisation of acid mine drainage and fly ash at the Environmental and Nano Sciences group at the University of the Western Cape. The solid waste residues resulting from the neutralisation of Navigation AMD with Arnot fly ash were successfully transformed into zeolite adsorbents with two methods. With the first method using hydrothermal synthesis at high temperature (600ºC) Zeolite Y (FAU or faujasite) containing a sodalite mineral phase was synthesised and with the mild temperature method (100ºC), relatively pure zeolite P was synthesised. Both of these prepared zeolite materials were characterised with XRD and presented a high crystallinity. The fly ash was successfully transformed into zeolite P using the mild temperature method (100ºC) (Petrik *et al*., 1546/1/07).

The stability of the two zeolite adsorbents prepared from waste was tested with the TCLP test before being used for sorption tests. No significant levels of toxic elements were leached out from these adsorbents synthesised from waste solid residues. This underlines the value of these materials for long-term trapping of toxic elements present in the waste solid residues used as feedstock (Petrik *et al*., 1546/1/07).

The first method to prepare zeolite comprises a fusion at 600ºC (high temperature synthesis method). It followed the procedure outlined by Somerset which was a modification of the alkaline hydrothermal treatment of FA to produce faujasite outlined by Rayalu *et al*.,(2000) (Somerset, 2003) . During the study conducted by Somerset the conventional zeolite synthesis was optimised for the synthesis of faujasite using South African fly ash and also solid waste residues collected at near neutral pH using different FA to AMD ratios (Burgers, 2002).

Several mild temperature methods were previously tested by Mavundla and Petrik (Mavundla, 2004). In the first hydrothermal treatment method at 100°C for 24 hours, using solid waste residues as a starting material, the zeolite phase obtained was sodalite.

Another method, termed the two-step method, was adapted from Hollman *et al*., 1999). It allowed solid residues reacted with NaOH for 96 hours to be successfully converted into zeolite P, with quartz remaining. The reflux method at 100°C developed by Unine was also tested (Mavundla, 2004; Undine, 1998).

2.5.5.1. High temperature synthesis method

The dry solid waste residues were fused with a solution of sodium hydroxide (NaOH) in a solid: solution ratio of 1:1.2. The fusion mixture was obtained by grinding the reactants with a mortar and pestle and once a fine, homogeneous mixture was obtained, it was heated to 600°C for approximately 1-2 hours. The resultant fused product was then allowed to cool down to room temperature before being ground and milled again with a mortar and pestle. The fused product was subsequently mixed with deionised water, in a solid: water ratio of 1:6. The slurry (or gel) thus obtained was thoroughly mixed, and then aged for 8 hours. The mixing and ageing process was done in a high density glass McCartney (Schott) bottle. After ageing, crystallisation of the slurry was achieved by placing the mixture in a thermostat oven at 100°C for 24 hours. The crystallised product was allowed to cool down to room temperature for approximately 30-60 minutes. The solid product was recovered by filtration and thoroughly washed with deionised water until a filtrate pH of 10-11 was obtained. The product was subsequently dried at 70°C and transferred into an airtight glass or plastic vial-type container (Petrik *et al*., 1546/1/07).

This product had a fairly well developed crystalline structure, indicating that zeolite Y (faujasite) formation had been successful (Figure 2). However some of the formed zeolite Y phases were transformed into hydroxysodalite. Such transformations can be attributed to an excessive enrichment of the fly ash-based zeolite with the alkaline activator (NaOH) (Hollman *et al*., 1999).

A comparison of the synthesised product with a commercial faujasite, namely CBV 400 is also presented in Figure 2. It reveals that the XRD pattern of the fly ash-based zeolite match with the commercial grade faujasite pattern but contains a sodality impurity.

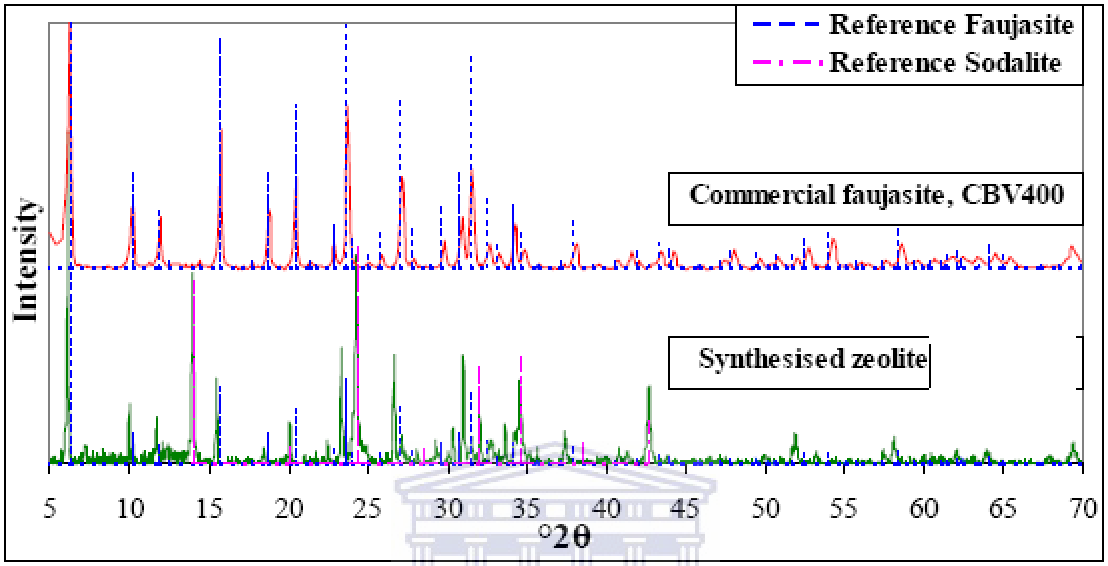


Figure 2: XRD patterns of the zeolite Y synthesised at 600°C from fly ash and the commercial faujasite CBV400 (Petrik *et al*., 1546/1/07).

The CEC values obtained were between 0.84 and 2.00 meq/g. Characteristic CEC values calculated for natural zeolites based on theoretical formulae are in the order of 2 to 5 meq/g as described by F.A. Mumpton, Chairman of the International Committee on Natural Zeolites.

The pore volume and surface areas of all three materials were considerably higher than for the parent fly ash (between 0.24 – 0.31 cm^3/g), indicating the potential of these materials to act as adsorbents. The relatively large average pore sizes determined relates to the presence of numerous larger mesopores in these materials in addition to the usual micropores of the typical pure zeolite A phase which are in the 3-7 Å size range.

2.5.5.2. Low temperature synthesis method

This method consists of two steps: a pre-treatment, called the ageing step, and a mild temperature thermal treatment under reflux at ~100°C. The ageing period of the gel solution is important to obtain the desired crystalline phase and to accelerate crystallisation (Ertl *et al*., 1997). The ageing process must be carried out at room temperature or at a slightly increased temperature, remaining below the temperature of the thermal treatment (Barrer, 1982). During the ageing phase, there is a partial monomerisation of the silica particles catalysed by the hydroxyl ions. This induces an increase of monomeric silica in the liquid phase, which is then available as feedstock for the hydrothermal treatment.

The ageing step consisted of mixing specific amounts of the solid residues with a highly concentrated (5M) NaOH solution. The slurry thus obtained was left to age at 40-45°C for 1-2 days under stirring. After this ageing period, the slurry underwent a thermal treatment. It was heated to 85-100°C under a reflux system for 1-4 days. At the end of the thermal treatment, the synthesised solid product was washed with deionised water until the rinsing water reached a pH of about 9. The solid product was then separated from the solution by centrifugation and dried overnight at 100°C.

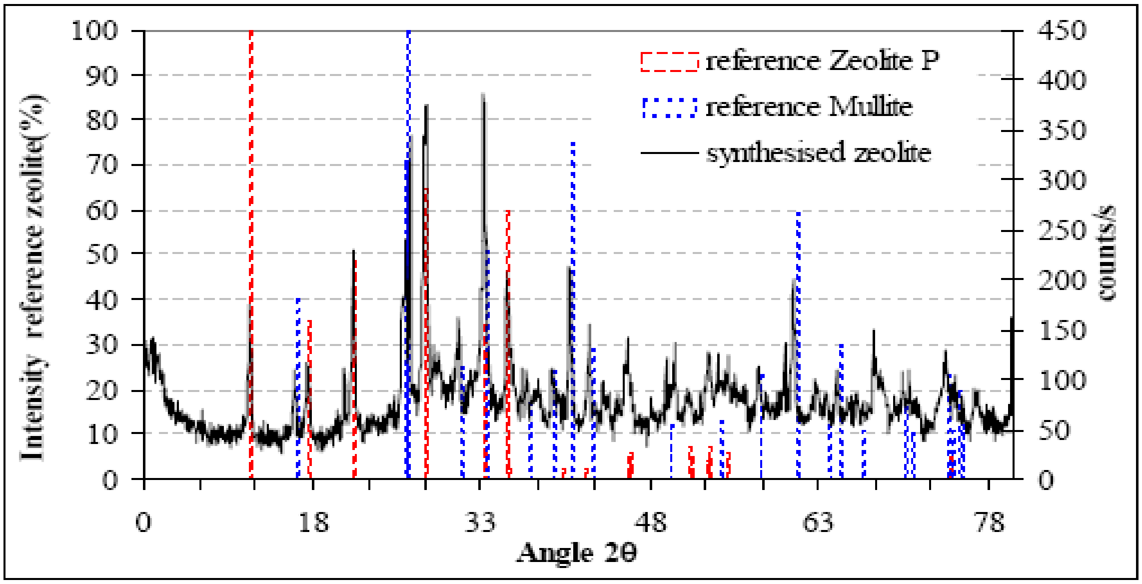


Figure 3: XRD spectrum of the product synthesised from solid residues after 24h of ageing and 96h of thermal treatment at 100ºC (Petrik *et al*., 1546/1/07).

The mild temperature synthesis at 100ºC resulted in a product containing zeolite P and mullite (Figure 3). The pore size of zeolite P is smaller than that of faujasite, and is defined by an 8 membered ring. As a result of this difference in pore size, zeolite Y is a more favoured configuration for adsorption as it can accommodate a greater amount and variety of elements. However, zeolite P is well known and frequently used as adsorbent and ion-exchange material. Mullite has a dense orthorhombic structure. Its framework consists of alternating octahedrons of Al and tetrahedrons of Si. Mullite could form during a thermal treatment at 100ºC (Kong *et al*., 2003), but in this experiment its presence represented the unconverted mullite phase from the original fly ash.

The mild temperature hydrothermal treatment using solid waste residues as feedstock should be conducted for more than 48h, as 96 hours of thermal treatment produced crystalline zeolite product.

- The mild temperature hydrothermal treatment was assumed to require a minimum temperature of 85°C.
- There was no difference in the mineralogy of the product produced at 85°C or 100°C.

- Zeolite P was synthesised in every low temperature experiment, but the presence of residual fly ash-derived mullite phase in the product indicated that not all the Si feedstock was available to be converted into zeolite under the applied conditions.

The synthesis of zeolite P directly from fly ash has been investigated as well. In the synthesis of the zeolite with solid residue it was shown that even after 72 h there were still Quartz and Mullite phases present as impurity phases with zeolite P. Therefore, the synthesis of zeolite P with FA was optimised in terms of the NaOH concentration. Figure 2.4 shows the XRD spectra of solid zeolite phases obtained from hydrothermal synthesis. Increasing the NaOH concentration reduces the height of the Quartz peak (in particular between 1 M and 3 M NaOH) indicating the more optimum dissolution of the Quartz as feedstock for the synthesis of zeolite P. The increase of the zeolite phase is also apparent from the increasing intensity of the low angle peaks compared to that of Quartz, showing that optimization of the hydroxide concentration increased the purity of the zeolite phase (Petrik *et al*., 1546/1/07).

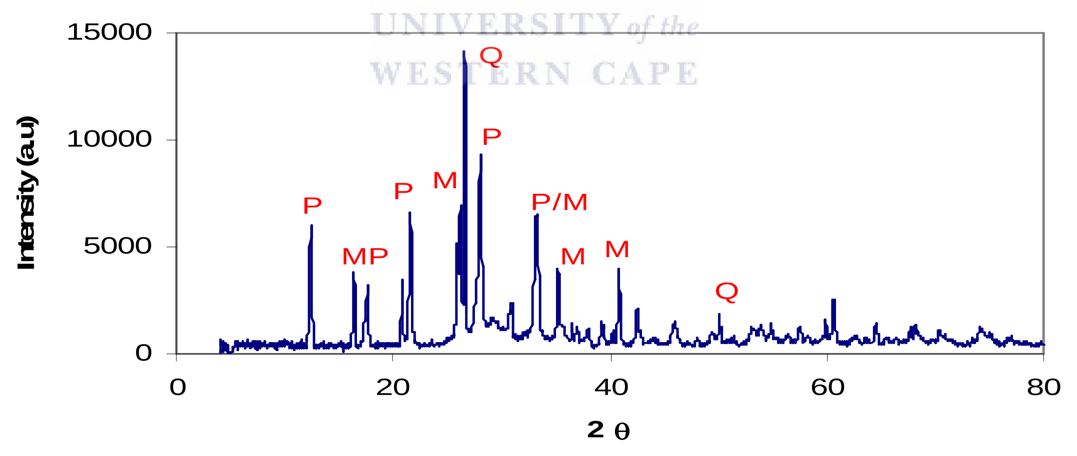
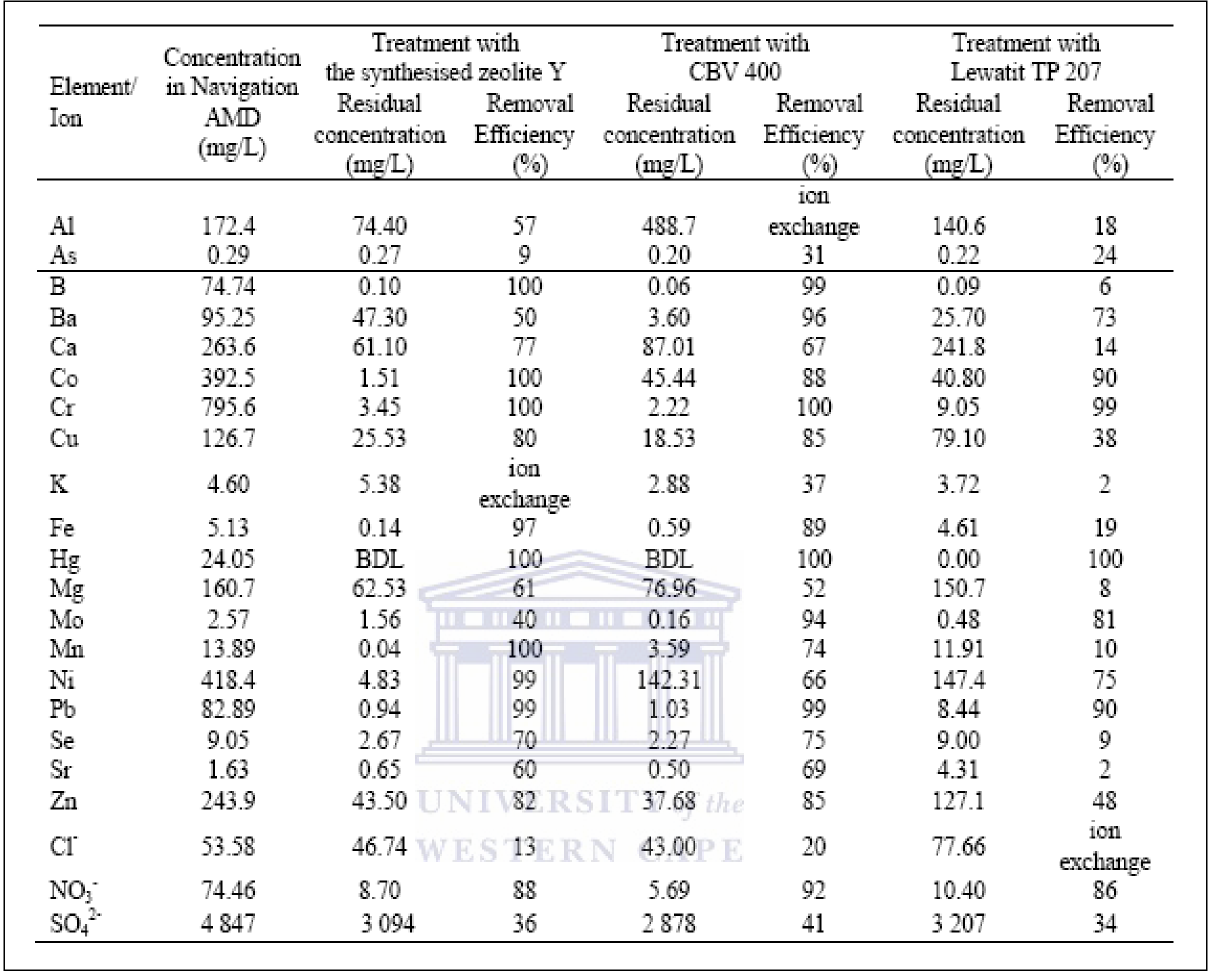


Figure 4: The XRD spectra of 5 M NaOH solution used in the synthesis of zeolite P with fly ash (P = zeolite P, M = Mullite, Q = Quartz and S = hydroxysodalite) (Petrik *et al*., 1546/1/07).

2.5.6. Use of zeolites synthesised from fly ash in waste water treatment

Extensive research by the Environmental and Nano Science Group at UWC has been done on the application of the zeolite produced from fly ash on the beneficiation of acid mine drainage. Table 1 below shows the removal of elements from Navigation acid mine drainage (AMD) for zeolite Y synthesised from fly ash in comparison with commercial zeolite (faujasite CBV 400) and commercial resin (Lewatit TP 207). The zeolite Y synthesized at high temperature adsorbed a greater quantity of metals from raw Navigation AMD than the commercial faujasite CBV 400. The commercial faujasite removed a higher percentage of Sr and K and adsorbed a greater quantity of all the anions analyzed, NO_3^-, SO_4^{2-} and Cl^-. The synthesized zeolite Y exchanged K for the toxic species in the raw AMD effluent. This explains the increase of K concentration in the solution. The adsorption performance of the commercial ion exchange resin, Lewatit TP 207, was not good, with the highest metal removal being Fe at 20%. Lewatit TP 207 performed better with removal of the anions and removed 85% of NO_3^- and 35% of SO_4^{2-} but exchanged Cl^- with the solution. The synthesized faujasite removed Cr, Co, Ni, Pb and Hg almost completely while the commercial faujasite, CBV 400, removed only Cr, Pb and Hg completely. The commercial faujasite removed slightly more Zn and Cu than the synthesized zeolite Y. The synthesized zeolite removed close to 55% of Al while the commercial zeolite exchanged Al with the solution. The commercial faujasite removed more Ba, Se, Mo and As than the synthesized zeolite. The commercial ion exchange resin, Lewatit TP 207, completely removed Cr and Hg, and showed good removal ratios 90% of removal for Co, Mo, Pb, Ni, Zn and Ba (50-90%). For Cu, Al, As and Se the removal was much smaller, between 5 and 35% (Petrik *et al*., 1546/1/07).

Table 1: Removal of major elements from Navigation AMD with the zeolite Y synthesized at 600°C, the commercial faujasite CBV 400 and the commercial resin Lewatit TP 207 (Petrik *et al*., 1546/1/07).



Element/ Ion	Concentration in Navigation AMD (mg/L)	Treatment with the synthesised zeolite Y		Treatment with CBV 400		Treatment with Lewatit TP 207	
		Residual concentration (mg/L)	Removal Efficiency (%)	Residual concentration (mg/L)	Removal Efficiency (%)	Residual concentration (mg/L)	Removal Efficiency (%)
Al	172.4	74.40	57	488.7	ion exchange	140.6	18
As	0.29	0.27	9	0.20	31	0.22	24
B	74.74	0.10	100	0.06	99	0.09	6
Ba	95.25	47.30	50	3.60	96	25.70	73
Ca	263.6	61.10	77	87.01	67	241.8	14
Co	392.5	1.51	100	45.44	88	40.80	90
Cr	795.6	3.45	100	2.22	100	9.05	99
Cu	126.7	25.53	80	18.53	85	79.10	38
K	4.60	5.38	ion exchange	2.88	37	3.72	2
Fe	5.13	0.14	97	0.59	89	4.61	19
Hg	24.05	BDL	100	BDL	100	0.00	100
Mg	160.7	62.53	61	76.96	52	150.7	8
Mo	2.57	1.56	40	0.16	94	0.48	81
Mn	13.89	0.04	100	3.59	74	11.91	10
Ni	418.4	4.83	99	142.31	66	147.4	75
Pb	82.89	0.94	99	1.03	99	8.44	90
Se	9.05	2.67	70	2.27	75	9.00	9
Sr	1.63	0.65	60	0.50	69	4.31	2
Zn	243.9	43.50	82	37.68	85	127.1	48
Cl^-	53.58	46.74	13	43.00	20	77.66	ion exchange
NO_3^-	74.46	8.70	88	5.69	92	10.40	86
SO_4^{2-}	4 847	3 094	36	2 878	41	3 207	34

The removal ability of the synthesized zeolite P was also compared to a commercial resin. It was found that the overall efficiency of the cationic Amberjet resin is poorer than the synthesized zeolite P and the resin leached out some toxic elements such as Co, B, and Cr. For both synthesized and commercial zeolite adsorbents applied, the optimum dosage of zeolite appears to be 10 g/L with a contact time of 1 hour. At this concentration, the removal efficiency of the zeolite P synthesized from the waste residues is good and overall better than that of the commercial zeolite CBV 400 adsorbent. It was possible to efficiently remove Fe, Al, K, Ca, Sr, Li, B, Mg, Be, Ba, Mn, V, Co, Cd, as well as some Zn, Se and Mo from the effluent. The zeolites applied were thus able to considerably remove a variety of residual toxic elements from the neutralized effluent even when applied in low concentrations of 1mg of zeolite adsorbent per litre of AMD (Petrik *et al*., 1546/1/07).

However, some elements such as Si, and also Cr that were present in trace quantities are leached from the zeolite P, and Na is ion exchanged out of both zeolites by the preferential uptake of the toxic elements. As and Se removal was time dependent. With both zeolites, the optimum contact time for maximum adsorption is 1 hour. It is noteworthy that apart from Na, the monovalent and divalent cations Li, K, Ca and Mg and Sr were well removed from the neutralized secondary process effluent by the zeolite P prepared from waste solid residues (Petrik *et al*., 1546/1/07).

These results also demonstrate the opportunity of using the zeolite P prepared from waste solid residues at low temperature for treatment of neutral mine waters or brines containing high levels of mono and divalent cations (Petrik *et al*., 1546/1/07).

CHAPTER 3

Research Methodology

3.1 Sampling

3.1.2 Water Sampling

3.1.2.1. Acid Mine Drainage

The sample of AMD was collected at Navigation Coal Mine as shown in the map below and preserved in such a way so as not to lose its integrity. Sampling was done only when necessary to avoid ageing. Samples were collected as close to the target type as possible and sampling of a moving stream was done at mid-depth for homogeneity and extra precaution was taken, as some of the points were extremely dangerous. Disposable powder free Poly Vinyl Chloride (PVC) gloves were used during the sampling process.

Prior to sampling each high-density polyethylene (HDPE) sample bottle was rinsed several times with the water to be sampled in order to equilibrate, filled to the brim and tightly closed to exclude any CO_2. The samples were kept in the fridge unfiltered and not acidified for pH and EC analysis, after these determinations were carried out the sample was filtered using 0.45µm membrane, acidified with 1mL concentrated HNO_3 for trace element analysis. A label giving the information about the site, the date of sample collection, pH and EC measurement on site was put on the sample bottle. The samples were transported on ice via a courier to the University of Western Cape, Chemistry Department and refrigerated at 4°C as soon as they reached the destination (Azzie, 2002; Klink, 2003).

3.1.2.2. Brine

The samples were collected at Lethabo Power Station as shown in the map below and preserved in such a way so as not to lose their integrity. Sampling was done only when necessary to avoid ageing. Samples were collected as close to the target type as possible and sampling of a moving stream was done at mid-depth for homogeneity and extra precaution was taken, as some of the points were extremely dangerous. Disposable powder free Poly Vinyl Chloride (PVC) gloves were used during the sampling process.

Prior to sampling each high-density polyethylene (HDPE) sample bottle was rinsed several times with the water to be sampled in order to equilibrate, filled to the brim and tightly closed to exclude any CO_2. The samples were kept in the fridge unfiltered and not acidified for pH and EC analysis after these determinations were carried out the sample was filtered using 0.45µm membrane, acidified with 1mL concentrated HNO_3 for trace element analysis. A label giving the information about the site, the date of sample collection, pH and EC measurement on site was put on the sample bottle. The samples were transported on ice via a courier to the University of Western Cape, Chemistry Department and refrigerated at 4°C as soon as they reached the destination (Azzie, 2002; Klink, 2003).

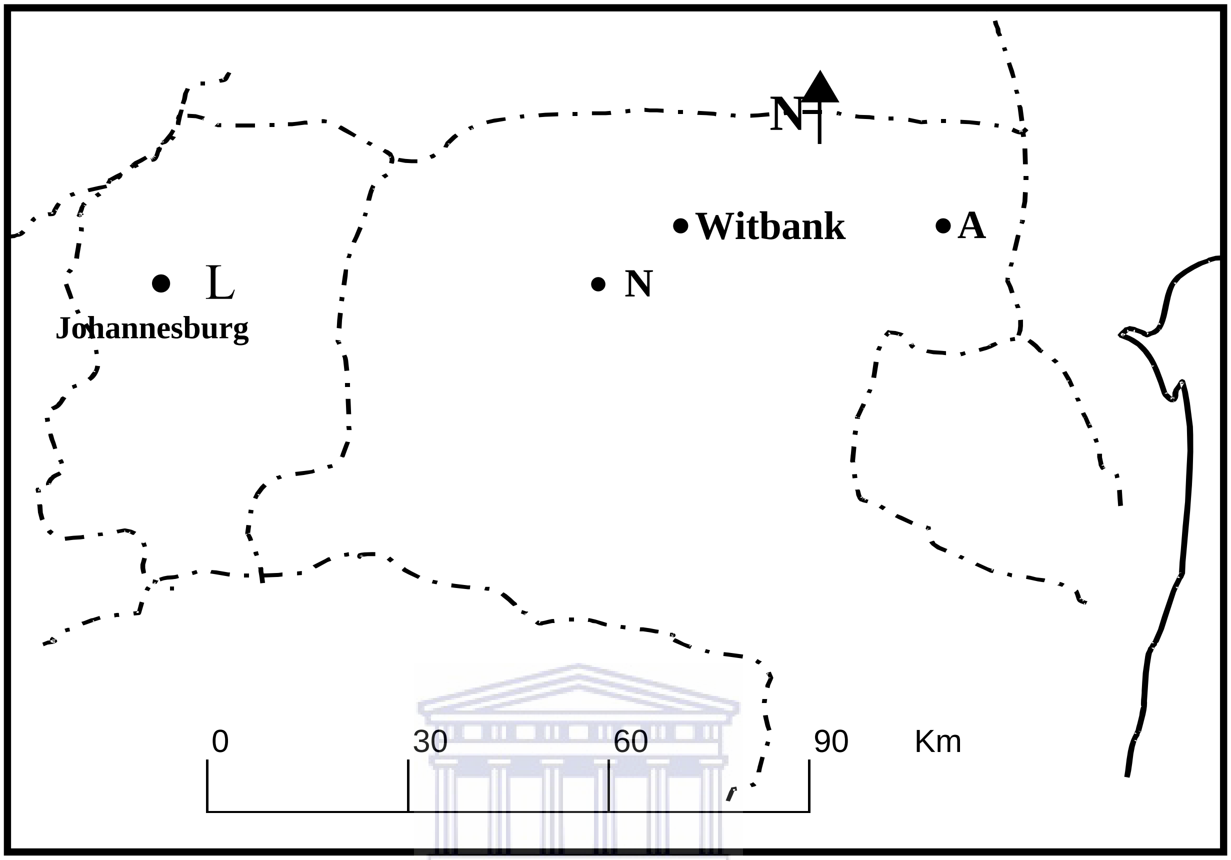


Figure 5: The location of the AMD, FA and Brine sites used in this study**.**

Legend: N that of Navigation mine, A that of Arnot colliery, L that of Lethabo Power station and K that of Bank colliery (Adapted from: Somerset, 2003)

This figure shows the Navigation coal mine, where AMD was collected in ponds at the mining site. The second site is Lethabo Power Station where brine was collected and also fly ash was collected from Arnot Power Station opencast operations and surface streams.

3.1.3 Fly ash sampling

Fresh samples were taken directly from hoppers on the ash collectors at Arnot Powers Station as indicated on the map above, usually collected from the flue gas by means of electrostatic precipitators, bag houses or mechanical devices such as cyclones (downstream of the economisers). The fly ash was sampled while still hot and stored in sealed plastic bags in buckets and some sampled in stainless steel containers tightly closed. Sample containers were precontaminated with fly ash prior to sampling, filled to the brim to exclude as much CO_2 as possible then tightly sealed with a lid. As with the water samples information was recorded about the location and date on the sample container.

3.2 Storage of samples

3.2.1 Storage of water samples

High-density polyethylene (HDPE) bottles were used for water sampling and the samples were also stored in the same type of bottles. The samples were stored according to the respected analysis to be undertaken. For trace metals the samples upon receipt at University of Western Cape, Chemistry Department the samples were filtered using 0.45 μm membrane, EC measurements were taken, sample diluted with deionised water until the EC was less than 1.5 mS/cm and the preserved with 1mL concentrated nitric acid refrigerated at 4°C ready for analysis.

However the samples for EC, pH and TDS analysis were also sampled and stored in the same type of bottle just like for trace analysis but they did not require any preparation and preservation. The samples were analysed for these parameters as soon as possible while they were also refrigerated at 4°C for storage purposes.

3.2.2 Storage of fly ash samples

The fly ash were sampled and stored in sealed plastic bags, which were placed in plastic or metal containers, tightly sealed to avoid CO_2 ingress. Sample containers were stored in a dark cool place away from direct sunlight and heat to avoid temperature fluctuations (Klink, 2003).

3.3 Sample Transport

AMD and brine samples were refrigerated during transportation. The samples were stored in ice until they reached the laboratory. On receipt in the laboratory sample bottles were again refrigerated at 4°C. Fly ash samples were transported via a courier service kept in sealed plastic bags in metal or plastic containers. During their transportation they were stored away from direct sunlight and heat.

3.4 Experimental Methods

3.4.1 Acid Mine Drainage and Fly Ash

During these experiments 350ml of natural AMD was shaken continuously with 100g of unweathered dry fly ash stirring by means of an overhead stirrer varying the contact time and ratios (Table 2). This experimental procedure was carried out to neutralize AMD using fly ash and to later utilise the co-disposed solid residues to react with process waters. When the pH of the reaction was below 8 the reaction was stopped and the mixture was filtered through Whatman No. 1, co-disposed solids were dried at 70°C in an oven and kept to be used for synthesising co-disposed zeolites. These co-disposed zeolites were reacted with brine and process waters. The filtrate resulting from this reaction was kept refrigerated and later used as process water in the reactions below.

Table 2: Navigation AMD neutralised with Arnot FA

Reactions	Ratio	Volume of AMD added in ml	Mass of FA added in g
Navigation AMD + Arnot FA	1:3.5	350	100

3.4.2 Synthesis of zeolite P

To optimize synthesis time, 20 g (0.50 mols) NaOH and 20 g co-disposed solids were weighed and 100 ml of ultra pure water was used to dissolve NaOH. Ageing was done under stirring for 48 h on a hotplate with sealable plastic bottle containing the slurry and the temperature of the slurry was monitored between 47 and 48°C and the rotational speed was kept between 750 and 1000 rpm. After ageing, 150 ml ultra pure water was added to the aged slurry and the slurry was transferred to Parr-bombs and placed in the oven at 100°C for hydrothermal synthesis. Two sub-samples were taken out every 24 h. Every second sample was washed and filtered until the pH was below 9 as it was recorded for every wash. Once the pH below 9 was reached, the samples were dried and ground for FTIR and XRD analysis.

3.4.3 Brine and solid residues

Ratios 1:3 and 1:10 were used for this reaction (Table 3), 30ml of brine was added to 1g of co-disposed solids and 10ml of brine was added to 1g co-disposed solids respectively in a reaction flask varying contact times from 30 minutes, 60 minutes and 120 minutes. pH and EC change were monitored after five-minute intervals up until thirty minutes and thereafter half an hour for two hours. After two hours the reaction was stopped and reaction mixture filtered through Whatman No.1 where the filtrate was dissolved with deionised water to desired EC, acidified and refrigerated for trace metal analysis. The samples obtained from brine treatment with fly ash were labelled CDSBr and this annotation was used thought the thesis.

Table 3: Brine reacted with solid residues

Reactions	**Ratio**	**Volume of brine added in ml**	**Mass of solid residues added in g**
Brine + co-disposed solids	1:3	30	1
Brine + co-disposed solids	1:10	10	1

3.4.4 Brine and fly ash

Ratios 1:3 and 1:10 were used for this reaction (Table 4), 30ml of brine was added to 1g of fly ash and 10ml of brine was added to 1g fly ash respectively in a reaction flask varying contact times from 30 minutes, 60 minutes and 120 minutes. pH and EC change were monitored at five minute intervals up until 30 minutes for half an hour contact and thereafter continued for an hour up to two hours taking EC and pH measurements from time to time. After two hours the reaction was stopped and the reaction mixture was filtered through Whatman No.1 where the filtrate was dissolved with deionised water to desired EC, acidified and refrigerated for trace metal analysis. The samples obtained from brine treatment with fly ash were labelled FABr and this annotation was used thought the thesis.

Table 4: Brine reacted with Arnot FA

Reactions	Ratio	Volume of brine added in ml	Mass of FA added in g
Brine + Arnot FA	1:3	30	1
Brine + Arnot FA	1:10	10	1

3.4.5 Brine and commercial zeolite Y

Ratios 1:3 and 1:10 were used for this reaction (Table 5), 30ml of brine was added to 1g of commercial zeolite Y and 10ml of brine was added to 1g commercial zeolite Y respectively in a reaction flask varying contact times from 30 minutes, 60 minutes and 120 minutes. pH and EC change were monitored at five minute intervals up until 30 minutes for half an hour contact and thereafter continued for an hour up to two hours taking EC and pH measurements from time to time. After two hours the reaction was stopped and the reaction mixture was filtered through Whatman No.1 where the filtrate was dissolved with deionised water to desired EC, acidified and refrigerated for trace metal analysis. The samples obtained from brine treatment with fly ash were labelled ZeoBr and this annotation was used thought the thesis.

Table 5: Brine reacted with commercial zeoliteY

Reactions	**Ratio**	**Volume of brine added in ml**	**Mass of commercial zeolite Y added in g**
Brine + commercial zeolite Y	1:3	30	1
Brine + commercial zeolite Y	1:10	10	1
Brine + commercial zeolite Y	1:4	40	1

3.4.6 Brine and zeolite P

Ratios 1:3 and 1:10 were used for this reaction (Table 6), 30ml of brine was added to 1g of co-disposed zeolites and 10ml of brine was added to 1g co-disposed zeolites respectively in a reaction flask varying contact times from 30 minutes, 60 minutes and 120 minutes. pH and EC change were monitored at five minute intervals up until 30 minutes for half an hour contact and thereafter continued for an hour up to two hours taking EC and pH measurements from time to time. After two hours the reaction was stopped and the reaction mixture was filtered through Whatman No.1 where the filtrate was dissolved with deionised water to desired EC, acidified and refrigerated for trace metal analysis. The samples obtained from brine treatment with fly ash were labelled ZeoCDSBr and this annotation was used thought the thesis.

Table 6: Brine reacted with zeolite P

Reactions	**Ratio**	**Volume of brine added in ml**	**Mass of zeolite P added in g**
Brine + zeolite P	1:3	30	1
Brine + zeolite P	1:10	10	1

3.5 Analytical Methods

3.5.1 pH

3.5.1.1 Principle

pH measure of a solution is a measure of an indication of acidity or basicity of a solution. pH measurement is regarded as one of the most important and frequently used tests in the water chemistry. It is also used in the alkalinity and carbon dioxide measurements and many other acid-base equilibria.

The pH of a solution is also a measure of the hydrogen ion activity (a_{H^+}) in solution:

$$\mathbf{pH = -\log a_{H^+}}$$

A pH-measuring device is essentially a battery where the positive terminal is the measuring electrode and the negative terminal is the reference electrode. The measuring electrode, which is sensitive to the hydrogen ion, develops a potential (voltage) directly related to the hydrogen ion concentration of the solution. The reference electrode provides a stable potential against which the measuring electrode can be compared.

When immersed in a solution, the reference electrode potential does not change with the changing hydrogen ion concentration. A solution in the reference electrode also makes contact with the sample solution and the measuring electrode through a junction, completing the circuit (Sensorland, 2007).

3.5.1.2 Procedure

The pH measurement was done using a HANNA HI 991301 portable pH/EC/TDS/Temperature meter. The pH meter was calibrated before use with buffer solutions (2 point automatic buffer recognition at pH 4.01 and 7.01 or 10.01 as appropriate to the pH range being determined). Duplicate sample measurements were performed at room temperature.

3.5.2 Electrical Conductivity (EC)

3.5.2.1 Principle

Electrical conductivity of a solution is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, on their total concentration, mobility, valence, and relative concentrations and also on the temperature of measurement. There is a relationship between electrical conductivity and total dissolved solids because the more impurities or total dissolved solids are there in a solution the higher the electrical conductivity of that solution. The electrical conductivity is reported in micromhos per centimetre (µmhos/cm) or (µS/cm) therefore 1µmhos/cm = 1µS/cm.

3.5.2.2 Procedure

The EC was determined using a portable HANNA HI 991301 pH/EC/TDS/Temperature meter. The EC/TDS meter was calibrated before use and during determinations for accuracy using standard solutions (1 point automatic at 12.88 mS/cm, 6.44 ppt, 9.02 ppt. Duplicate sample measurements were performed at room temperature.

3.5.4 Trace metal concentrations by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

3.5.4.1 Principle

ICP-MS is a very powerful tool for trace (ppb-ppm) analysis. It is rapidly becoming the technique of choice in many analytical laboratories for the accurate and precise measurements needed for modern demanding applications. In ICP-MS, a plasma or gas consisting of ions, electrons and neutral particles is formed from Argon gas. The plasma is used to atomise and ionise the elements in a sample. The resulting ions are then passed through a series of cones into the high vacuum mass analyser. The isotopes of the elements are identified by their mass-to-charge ratio (*m/e*) and the intensity of a specific peak in the mass spectrum is proportional to the amount of that isotope (element) in the original sample (Missouri, 2007).

3.5.4.2 Procedure

Trace metal water analysis was carried out using the ICP-MS. For accuracy during sample measurement reference material NIST was also analysed of which the results for the samples were to correspond with the material. Prior to analysis water samples were filtered using a 0.45μm cellulose acetate, diluted with deionised water until the EC was below 1.5 mS/cm and then preserved with 1ml concentrated nitric acid stored in the refrigerator below 4°C ready to be analysed. The samples for ICP-MS were prepared by the author and only sent to UCT for analysis because this ICP-MS facility is not available in the premises where the student is undertaking research.

3.5.5 X-ray diffraction (XRD)

XRD of solid products was performed using a Philips Analytical graphite monochromator with CuKα radiation, and an angle 2θ range from 5 to 70 with a 0.1° interval and a speed of 0.05°/s. The mineral phases present in the sample were identified by comparison with the Joint Committee on Powder Diffraction Standards-International Centre for Diffraction (JCPDS-ICD) reference library.

3.5.6 Surface area and pore volume determination

The physical analysis of the synthesised zeolitic products was conducted by the application of gravimetric nitrogen Brunauer-Emmett-Teller (N_2-BET) surface analysis technique. BET analysis has the ability to provide information on the specific surface area, total pore volume, pore size and pore size distribution of a particular specimen. If needed Hg porosimetry is an additional measure to differ between macro and micro pores.

3.5.7 Scanning Electron Microscopy (SEM)

SEM is used to inspect the topography of particles. Here it was used to observe the size and shape of crystals in the zeolitic material synthesised at mild and high temperatures. The energy dispersive X-ray spectroscopy (EDS) analyser was coupled to the SEM. EDS gives the elemental composition of a specific area of the sample chosen with SEM. Prior to analysis, the samples were dried, ground and coated with graphite, to make them conductive.

3.5.8 X-ray Fluorescence (XRF) Spectroscopy

The major oxides and minor heavy metals in solid feedstocks and products were measured by XRF, using a Philips 1404 XRF wavelength dispersive spectrometer, with 6 crystals and an Rh X-ray tube target. To prevent interaction of the X-rays with air particles, samples were analyzed under a vacuum.

The next chapter will be dealing with results obtained using the methods that are explained and even tabulated in this chapter and it will help us identify the best method and the type of adsorbent that best suits the type of brine water to be treated.

CHAPTER 4

Results and Discussion

4.1 Introduction

In this chapter analysis of the AMD and brine waste steams was done followed by the characterization of the different adsorbents, namely the fly ash, co-disposed solid residues and the zeolite produced from the co-disposed solid residues. Neutralisation of Navigation AMD using Arnot fly ash was done in order to obtain solid residues that were later used as adsorbents to treat brine. The focus on the results was on the major ions as referred to on the text being Na; Ca; K; Mg and Si as they are regarded as the major constituents of brine.

4.2 Analysis of the AMD and brine waste streams

4.2.1. AMD composition

The initial pH and EC of AMD was 2.63 and 8.06 mS/cm, respectively. The major component is SO_4^{2-} with a concentration of 4847 mg/l. The other major elements are Cr, Ni, Co, Zn, and Ca in the range of 250mg/l to 800 mg/l. The other elements and anions present in AMD are Pb, Cl^-, NO_3^-, Mg, Cu, Ba, B, Al (concentrations ranging between 60mg/l and 200 mg/l). The following elements (As, K, Fe, Hg, Mo, Mn, Se and Sr) were found to be between 0.5 mg/l and 25 mg/l.

Table 7: Initial concentration in Navigation AMD.

Element	**Concentration in Navigation AMD (mg/l)**
Cr	795.6
Ni	418.4
Co	392.5
Ca	263.6
Zn	243.9
Al	172.4
Mg	160.7
Cu	126.7
Ba	95.25
Pb	82.89
B	74.74
Hg	24.05
Mn	13.89
Se	9.05
Fe	5.13
K	4.60
Mo	2.57
Sr	1.63
As	0.29
Cl^-	53.58
NO_3^-	74.46
SO_4^{2-}	4847.00

4.2.2. Brine composition

The initial composition of the brine, prior to the contact with adsorbent is provided in Table 8. The initial pH and EC of brine was 7.8 and 15.83 mS/cm, respectively. The major component is Na with a concentration of 4719 mg/l. The other major elements are Mg, Ca, K and Si in the range of 40 mg/l to 200 mg/l. The minor and trace elements present in brine are B, Al, P, Fe, Sr, Li, Ti, Cr, Mn, Ni, Cu, Zn, Mo, Ba and Pb (concentrations ranging between 5 mg/l and 0.1 mg/l). The following elements were below detection limits in the brine: Be, V, Co, As, Se and Cd.

Table 8: Initial concentration of the brine.

Element	Concentration (mg/l)
Na	4719.1
Mg	198.4
K	114.7
Ca	112.0
Si	42.6
Sr	4.8
Fe	3.3
Al	2.8
B	1.6
P	1.6
Li	0.5
Cu	0.5
Ni	0.4
Cr	0.4
Mn	0.4
Ti	0.3
Zn	0.2
Mo	0.1
Ba	0.1
Pb	0.1

4.3 Characterization of fly ash, co-disposed solid residue and zeolite formed from the co-disposed solids residue

Fly ash generated from coal-fired power stations is a fine silt-sized powder that contains many unburnt residuals. Some of the main components of fly ash are SiO_2 and Al_2O_3 as seen in Table 1. These are present in similar chemical ratios to that required for zeolite formation, and therefore fly ash can be used as a raw material for synthesizing zeolites (Lin and Hsi, 1995). Zeolite P is formed in a chemical system containing the following species: $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$. As can be seen from Table 1 the solid residue provides the chemical environment required for the formation of zeolite P.

Table 9: The XRF analysis of the fly ash, co-disposed solid residues and the zeolite P synthesized from the co-disposed solid residues.

Major element	**Concentration (wt %)**		
	Fly ash	**Solid residues**	**Zeolite P**
Si (as SiO_2)	53.4	45.88	37.56
Al (as Al_2O_3)	23.4	24.57	25.77
Ti (as TiO_2)	1.34	1.195	
Fe (as Fe_2O_3)	4.72	6.308	5.60
Mn (as MnO)	0.06	0.1	0.12
Mg (as MgO)	2.70	2.39	2.38
Ca (as CaO)	8.43	7.145	8.61
Na (as Na_2O)	0.35	0.407	7.61
K (as K_2O)	0.49	0.513	0.07
P (as P_2O_5)	0.35	0.679	0.22
S (as SO_3)	4.5	3.477	0.40
Cr (as Cr_2O_3)	0.03	0.037	
Ni (as NiO)	0.01	0.011	
H (as H_2O)		1.154	
Loss on ignition	2.36	5.141	11.31

Zeolite P was synthesis using a method which consisted of two steps: a pre-treatment, called the ageing step, and a mild hydrothermal treatment at 100°C (see Section 3.4.2). The ageing period of the gel solution is important to obtain the desired crystalline phase and to accelerate crystallization (Ertl *et al*, 1997). The ageing process must be carried out at room temperature or at a slightly increased temperature, remaining below the temperature of the thermal treatment (Barrer, 1982). During the ageing phase, there is a partial monomerisation of the silica particles catalysed by the hydroxyl ions. This induces an increase of monomeric silica in the liquid phase, which is then available as feedstock for the hydrothermal treatment.

The mild temperature synthesis at 100ºC resulted in a solid product containing zeolite P, quartz and mullite (Figure 6b). The pore size of zeolite P is smaller than that of faujasite, and is defined by an 8 membered ring. As a result of this difference in pore size, zeolite Y is a more favoured configuration for adsorption as it can accommodate a greater amount and variety of elements. However, zeolite P is well known and frequently used as adsorbent and ion-exchange material. Mullite has a dense orthorhombic structure. Its framework consists of alternating octahedrons of Al and tetrahedrons of Si. Mullite could form during a thermal treatment at 100ºC (Kong, 2003), but in this experiment its presence represented the unconverted mullite phase from the original fly ash.

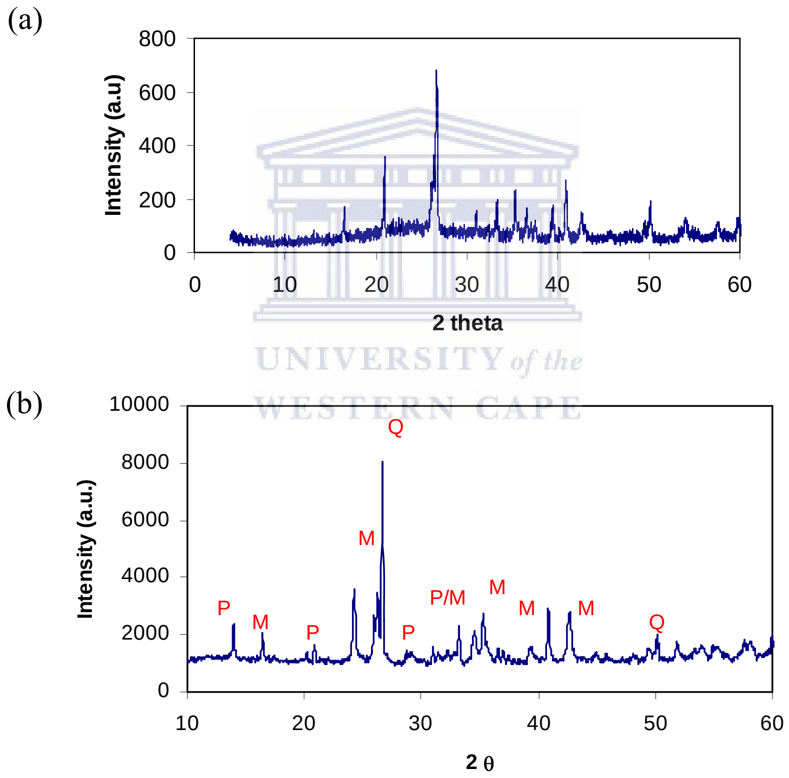


Figure 6: X-ray diffraction spectra of (a) fly ash and (b) zeolite P synthesis after 48 hours at 100°C **(**P = zeolite P, M = Mullite, Q = Quartz).

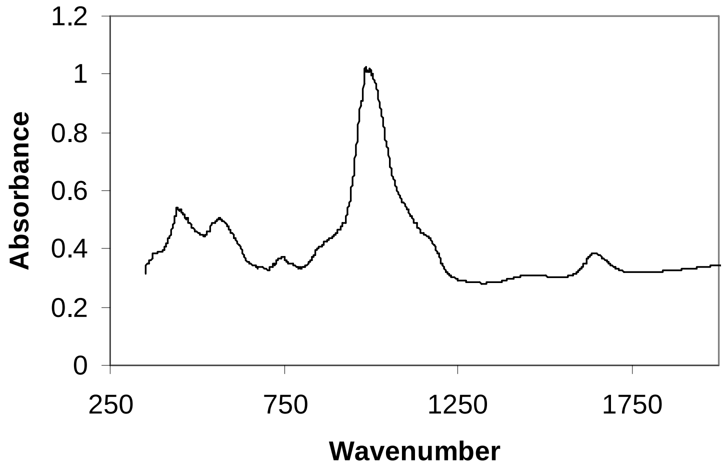


Figure 7: Infrared spectra of product synthesised from solid residues after 48 h of thermal treatment at 100°C.

The FTIR spectra (Figure 7) of the washed product showed a sharp peak at 1000 cm^{-1}. This peak is characteristic of the formation of linear molecules and polymers of silicate, according to the FTIR spectroscopy assignments of silicate species given by Bass and Turner (Bass and Turner, 1997). Moreover the zeolite structural framework bands appear to be fully formed in the region below 700 cm^{-1}. From the spectra, 48 h of hydrothermal treatment was found to be sufficient for the crystallization of the zeolite crystalline framework. Upon inspection of the difference between unwashed and the washed solids spectra, the peak at about 1500 cm^{-1} in unwashed solids indicates that there are soluble species, which could be leached that remain incorporated in the solid.

The third indication that a microporous zeolite P is formed is the increase in the nitrogen BET surface area from 1-2 m^2/g for fly ash to 61 m^2/g for the zeolite P synthesized from the co-disposed solid residues. The increase in surface area is not as high as would be expected if this were a pure zeolite P phase, and the XRD shows that other phases present included quartz and mullite.

The treatment of the brine with the zeolite P was compared to a commercial zeolite Y sample obtained from Zeolyst (namely, CBV400). Si/Al ratio of this commercial zeolite Y was 2.5.

Table 10 shows the surface area, pore volume and exchangeable cations of the commercial zeolite Y and Figure 11 gives the XRD spectra of this zeolite.

Table 10: Surface area, pore volume and exchangeable cations of the commercial zeolite Y

	Surface area(m^2/g)	Pore Volume(cm^3/g)	Exchangeable cations (meq/100g)			
			Na^+	Ca^{2+}	Mg^{2+}	K^+
Commercial Zeolite Y	327.3	0.31	107.3	1.95	0.25	0

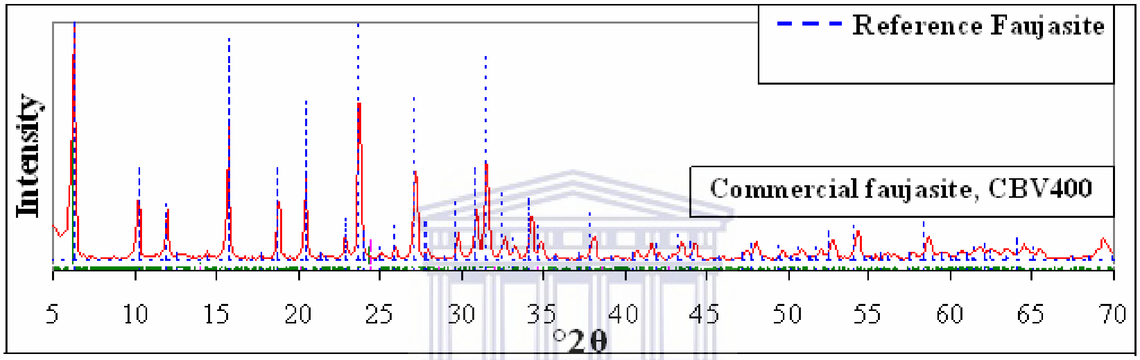


Figure 8: XRD patterns of the commercial zeolite Y synthesised at 600°C from fly ash and the commercial faujasite CBV400 (Petrik *et al.*, 1546/1/07).

4.4 Reproducibility of the analytical results

4.4.1 Reproducibility of the ICP analysis

Reproducibility of the analytical results was done by using a certified quality control standard that was compared to the analysed standard and the results were close to the certified reference material. Mg showed a higher percentage relative standard deviation of 7.80%, Na (4.40%) and Ca showed a good reproducibility of (0.69%). The samples were analysed in replicates and they show closeness as it can be seen on table 10 below.

Table 11: Replicate concentrations of elements in mg/l

	QC std					
	Certified (mg/l)	**Analysed (mg/l)**	**% RSD**	**Replicate 1 (mg/l)**	**Replicate 2 (mg/l)**	**Average (mg/l)**
Ca	9.8	9.87	0.69	2.36	2.32	2.34
Mg	0.097	0.10	7.80	4.94	5.01	4.97
Na	0.095	0.09	4.40	242.78	244.70	243.74

4.4.2 Reproducibility of the neutralisation of Navigation AMD with Arnot fly ash

Replicate analysis was done for the neutralisation of Navigation AMD with Arnot fly ash for the reproducibility of the results. The results showed a good reproducibility as the replicates were close to each other as shown in table 11.

Table 12: Replicate values of pH and EC in neutralisation of Navigation AMD with Arnot fly ash

Time	pH replicate 1	pH replicate 2	Average	EC replicate 1	EC replicate 2	Average
10	4.06	4.05	4.06	5.96	5.9	5.93
20	4.01	4.08	4.05	5.8	5.66	5.73
30	4.9	4.89	4.90	7.61	7.66	7.64
40	5.02	5.02	5.02	7.57	7.41	7.49
50	5.37	5.35	5.36	7.53	7.36	7.45
70	5.56	5.58	5.57	7.36	7.36	7.36
80	5.66	5.63	5.65	7.24	7.16	7.2
90	6.05	6.08	6.07	7.05	7.08	7.07

4.5 Neutralisation of AMD with FA to obtain co-disposed solid residues

In this section neutralisation reactions were performed in order to obtain co-disposed solid residues that were later used as adsorbents for brine stabilisation. The experimental details are in Section 3.4.1. The concept of adding fly ash to AMD was to increase the pH of the AMD resulting from the high CaO present in the fly ash. Increasing the pH of the AMD will aid in the removal of the toxic elements from the AMD by precipitation or/and adsorption.

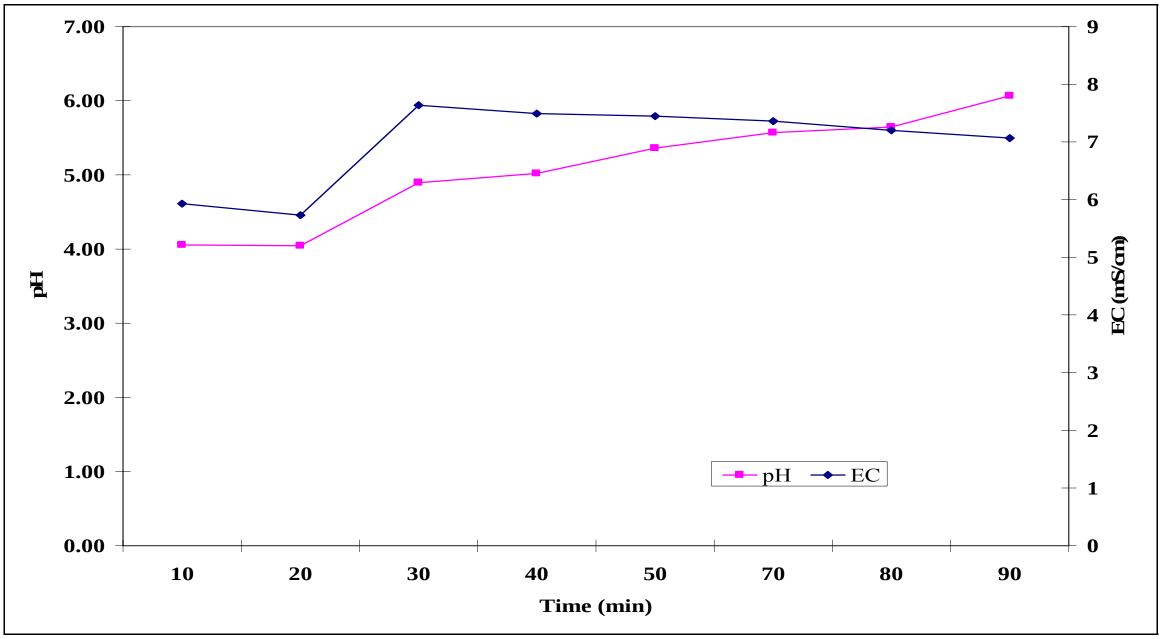


Figure 9: pH and EC for the neutralisation of Navigation AMD using Arnot fly ash.

Figure 9 shows the EC and pH variation with time when fly ash is added to AMD. The slurry started with an initial pH of about 4.5, the reaction was run for 120 minutes taking EC and pH measurements in 20 minute intervals to monitor the reaction. The pH levelled off at 6.5 after 30 minutes. However EC measurements fluctuated throughout the reaction as the initial EC was between 1 and 2 and EC value decreased in the first 20 minutes to zero, but then increased rapidly as the reaction proceeds and then decreased again in the last hour to stabilize.

4.6 Brine treatment with adsorbents

This section describes the treatment of brine with fly ash, co-disposed solid residue and zeolite P formed from the co-disposed solid residues. These adsorbent were compared with a commercially obtained zeolite Y.

4.6.1 pH and EC analysis

The initial pH and EC values of brine were reported to be 7.8 and 15.83mS/cm respectively. It can be seen in figures 10 (a), (b) and 11 (a) , (b) pH for brine reacted with commercial zeolites has decreased from the initial brine pH and remained constant at about 4, however fly ash based adsorbents pH and EC increased pH was specifically elevated and remained constant. It has been reported that the significant alkalinity of these adsorbent materials may contribute to removal of certain elements by precipitation (Balfour *et al.*, 2008). EC was seen to decrease gradually in all investigated adsorbents; the slight decrease in EC can be attributed to the adsorption of the elements onto the adsorbents therefore decreasing the level of dissolved ions in water (Balfour *et al.*, 2008).

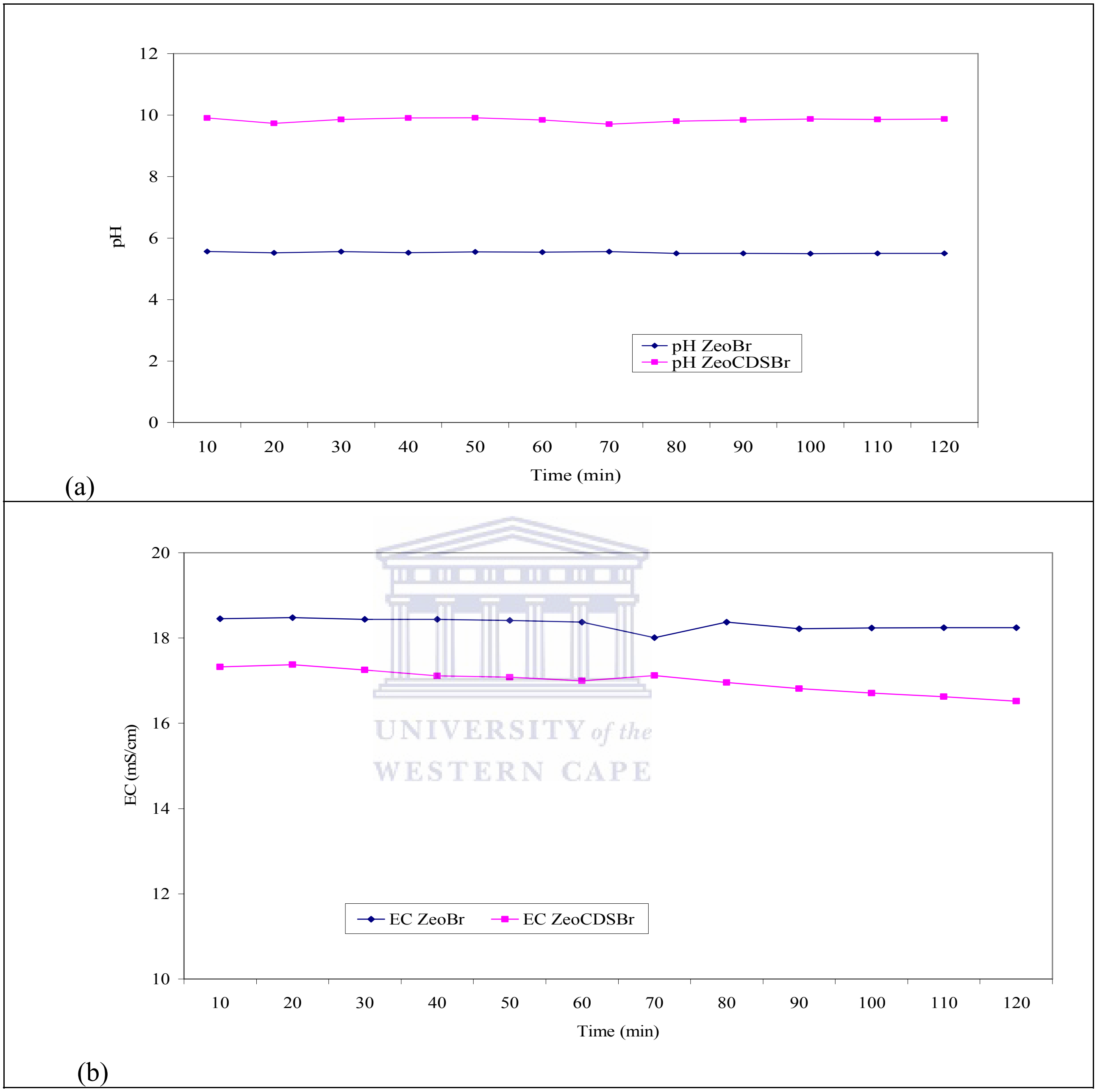


Figure 10: (a) pH and (b) EC of brine reacted with different adsorbents at ratio 1:3 and 120 minutes contact time (ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P).

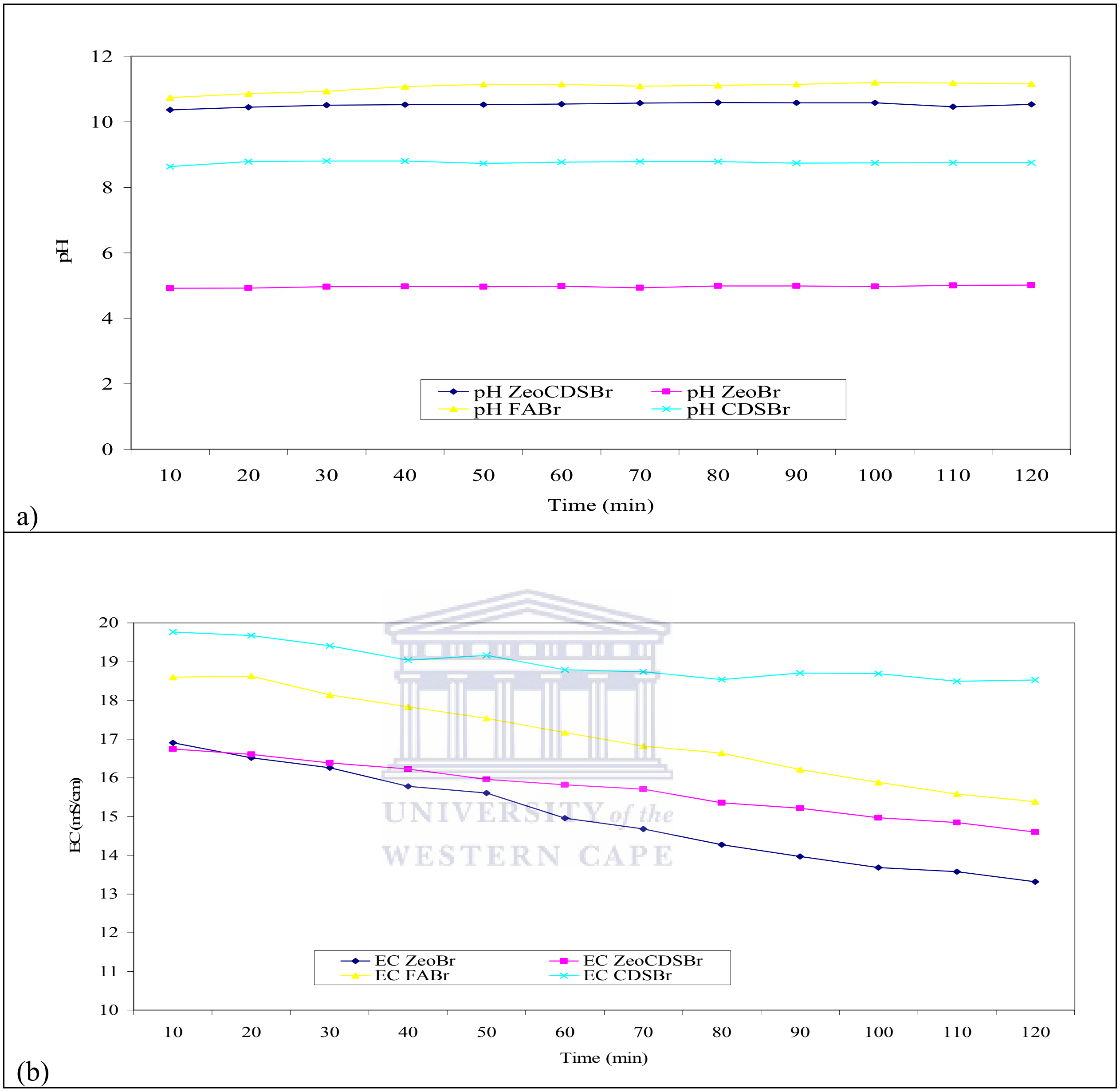


Figure 11 (a) & (b): pH and EC of brine reacted with different adsorbents at ratio 1:10 and 120 minutes contact time (ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P, CDSBr = solid residues, FABr = fly ash).

These figures show that contact time and the type of commercial zeolite did not affect the pH and EC of the brine considerably.

4.6.2 Elements removed from the brine with the absorbents

This table illustrates the sample codes used in the experiments for the brine treatment.

Table 13: Sample codes for the reactions of brine with the adsorbents

Sample code	**Reaction**
ZeoBr	Brine with commercial zeolite Y adsorbent
ZeoCDSBr	Brine with zeolite P adsorbent
FABr	Brine with Arnot fly ash adsorbent
CDSBr	Brine with solid residue adsorbent

4.6.2.1 Commercial zeolite Y

This section shows the results of the major elements from the treatment of brine with the commercial zeolite Y adsorbent at ratios 1:3 and 1:10 varying contact time from 30 minutes, 60 minutes and 120 minutes (see Section 3.4.5 for experimental details)**.**

In Figures 12 and 13 it can be seen that K, Ca and Mg, levels are high in brine with high concentrations initially from 130 mg/l to 210 mg/l but after 30 minutes of reaction in contact with the commercial zeolite Y adsorbent these levels are reduced to about half the initial concentrations. Si started off with lower concentration of 50 mg/l but after 30 minutes of the reaction it leached out of the zeolite.

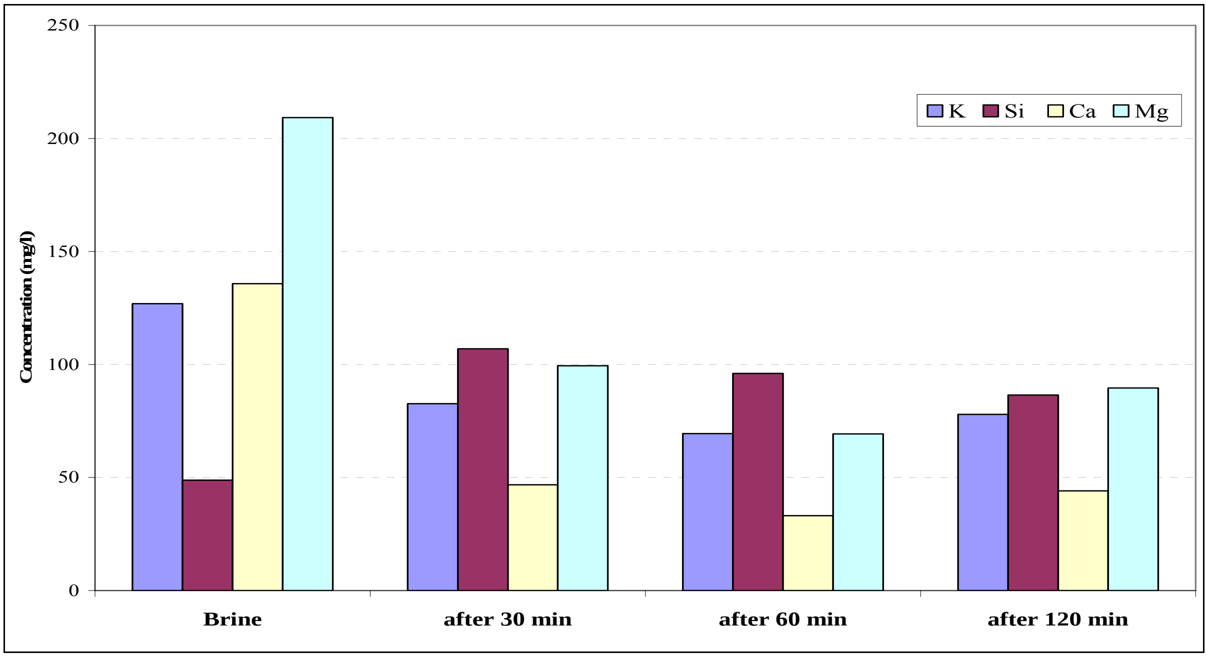


Figure 12: Concentration of major ions with ratio 1:3 and different contact times in a reaction of brine with commercial zeolite Y.

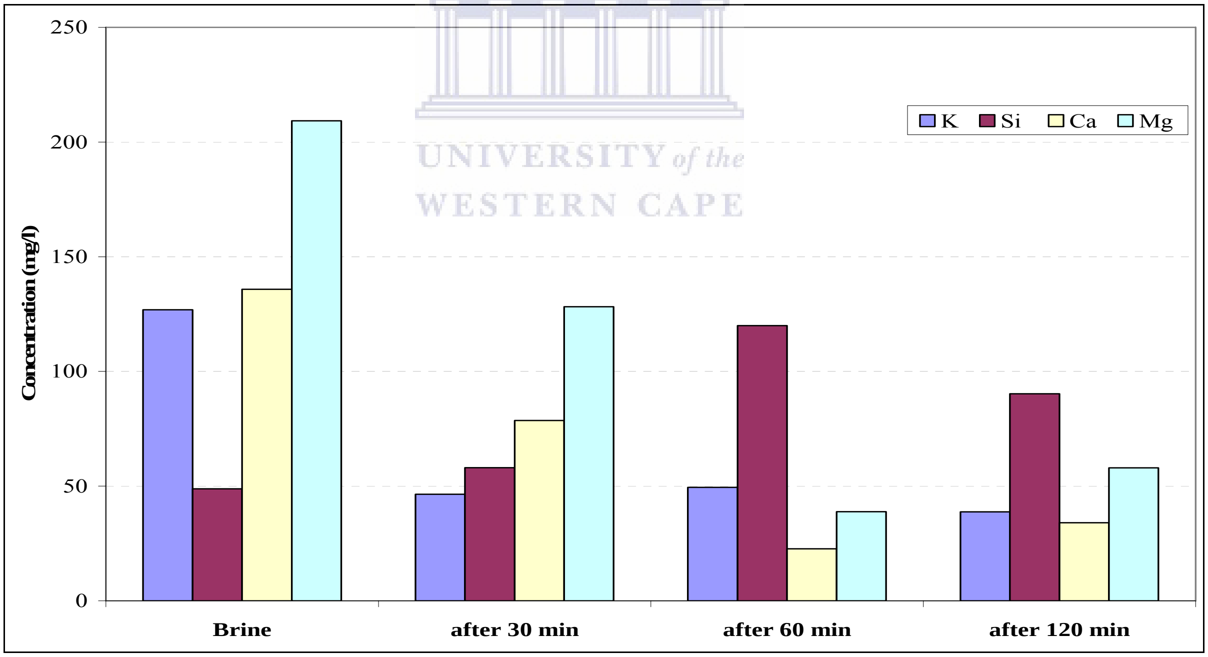


Figure 13: Concentration of major ions with ratio 1:10 and different contact times in a reaction of brine with commercial zeolite Y.

In Figure 14, it can be seen that Si was at 50mg/l initially but leached out of the adsorbent at ratio 1:3 to about 100mg/l and at ratio 1:10 it later reduced to its initial concentration, on the other hand Mg was reduced from its initial concentration of about 210mg/l to below 100mg/l at ratio 1:3. In Figure 15, Si brine started off with 50mg/l concentration increased to about 100mg/l at ratio 1:3 and at ratio 1:10 increased further to about 120mg/l which could be seen as leaching. Mg was successfully removed from the initial concentration of about 210mg/l to below 50mg/l at ratio 1:10.

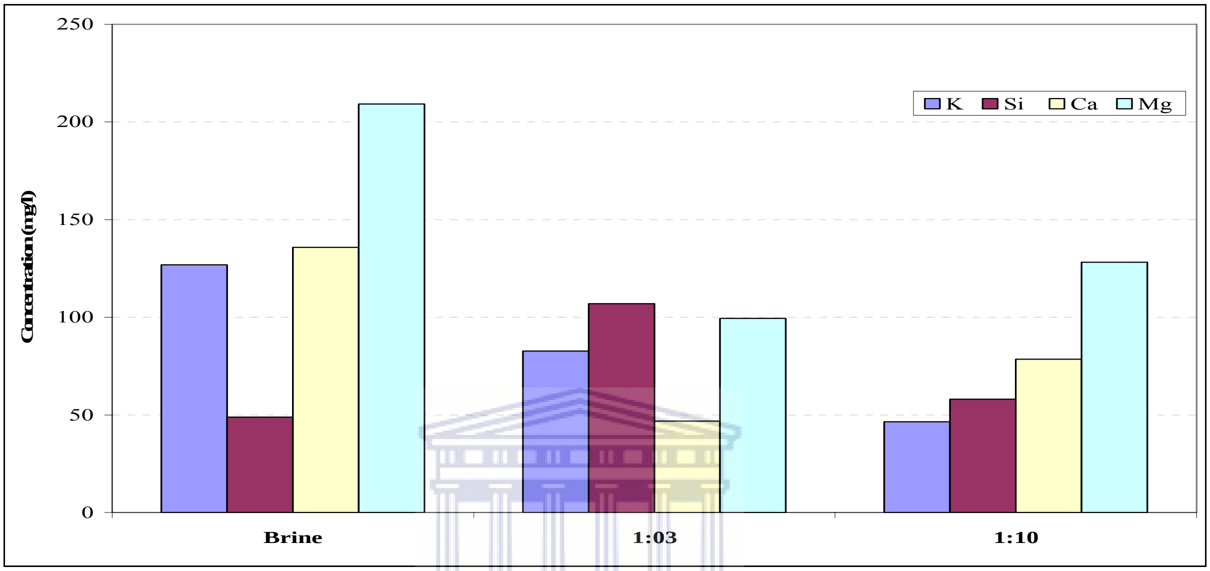


Figure 14: Concentration of major ions at 30 minutes contact time and different ratios in a reaction of brine with commercial zeolite Y.

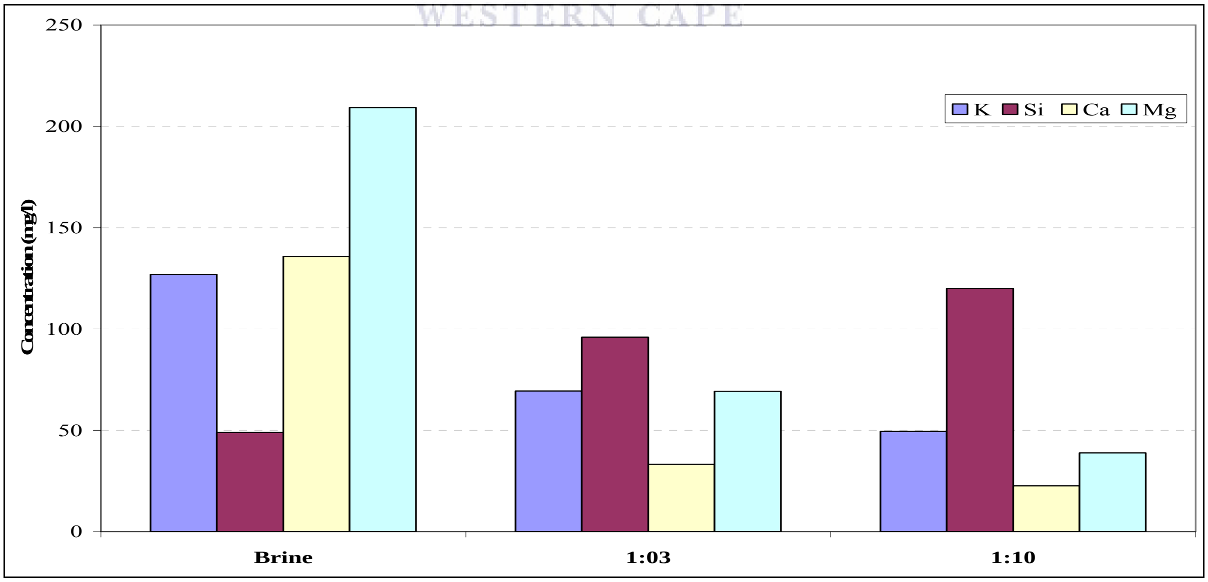


Figure 15: Concentration of major ions at 60 minutes contact time and different ratios in a reaction of brine with commercial zeoliteY.

In Figure 16 the brine solution concentration of Si was 50mg/l and increased to 80mg/l and 90mg/l at ratios 1:3 and 1:10 respectively.Ca was removed successfully as it was about 210mg/l initially in brine but contact with commercial zeolite Y decreased levels to about 60mg/l at ratio 1:10. K levels were decreased as well from the initial brine concentration of about 130mg/l before the reaction started to about 40mg/l at ratio 1:10.

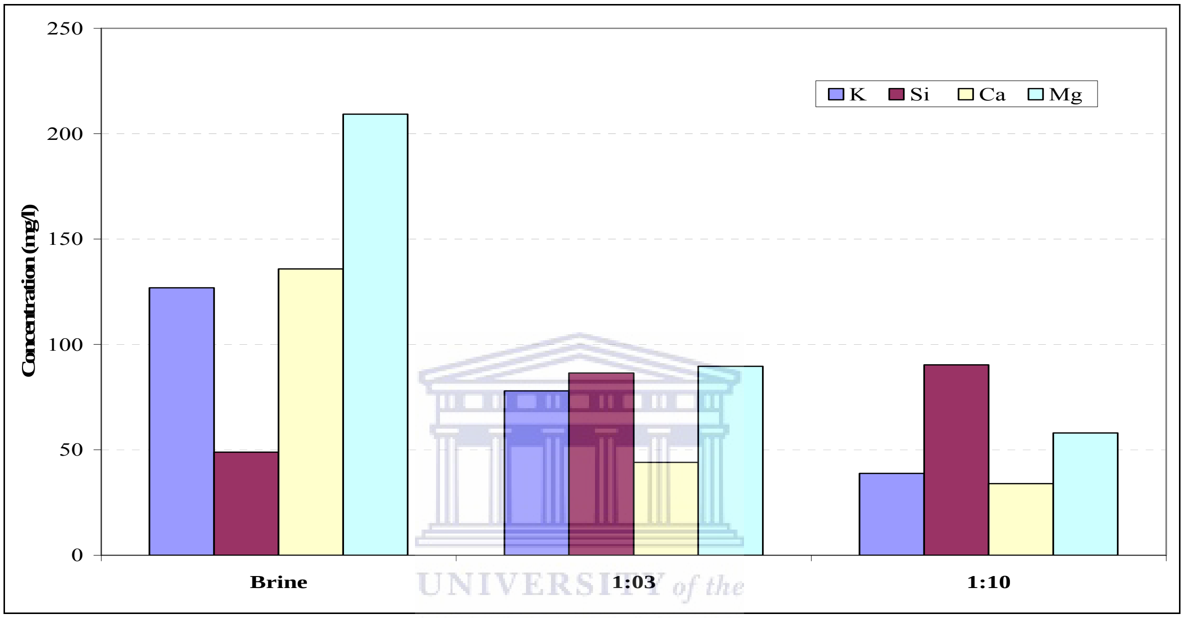


Figure 16: Concentration of major ions at120 minutes contact time and different ratios in a reaction of brine with commercial zeolite Y.

4.6.2.2. Zeolite formed from the solid residue (zeolite P)

This section shows the results of the major elements from the brine treatment with the zeolite P adsorbent made from solid residue at ratios 1:3 and 1:10 varying contact time from 30 minutes, 60 minutes and 120 minutes (see Section 3.4.6 for experimental details)**.**

In Figure 17 brine started off with Mg at higher concentration of 210mg/l but the zeolite P managed to decrease the concentration to about 70mg/l, Ca started off with an initial concentration of 140mg/l but managed to decrease throughout the reaction to a concentration just below 50mg/l. K is also decreased gradually during the reaction just like Ca, however Si seems to be leaching as the concentration increased during the reaction.

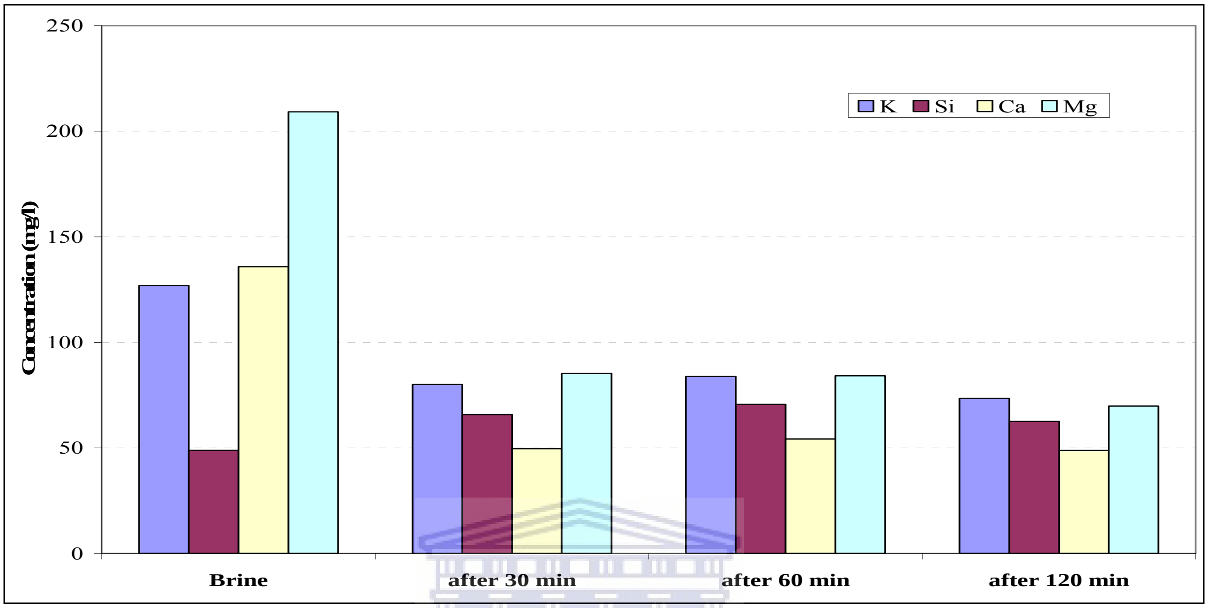


Figure 17: Concentration of major ions with ratio 1:3 and different contact times in a reaction of brine with zeolite P.

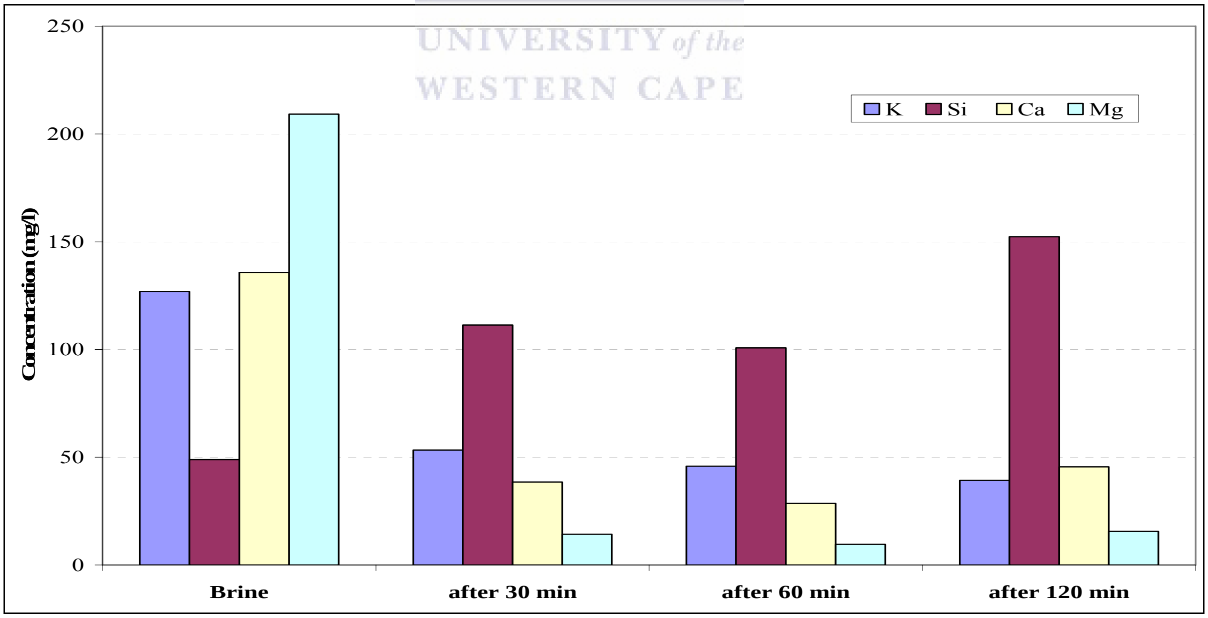


Figure 18: Concentration of major ions with the ratio 1:10 and different contact times in a reaction of brine with zeolite P.

In Figures 18, 19; 20 and 21 Na; Ca and K were removed successfully by the adsorbent used irrespective of the contact time, the adsorbent was effective at decreasing the concentrations that the reaction started off with to low concentrations below 100mg/l and below 50mg/l. Si seems to be leaching as it started with low concentrations just below 50mg/l and increased during the contact time with the zeolite to a concentration just above 100mg/l, in figure 19 and 20 there seemed to be a slight difference with contact time and varied Si concentration, Si levels did not increase as much as in the case of the reaction time of 120 minutes, however this can mean that with zeolite P the longer the reaction time the more it leaches out of the adsorbent.

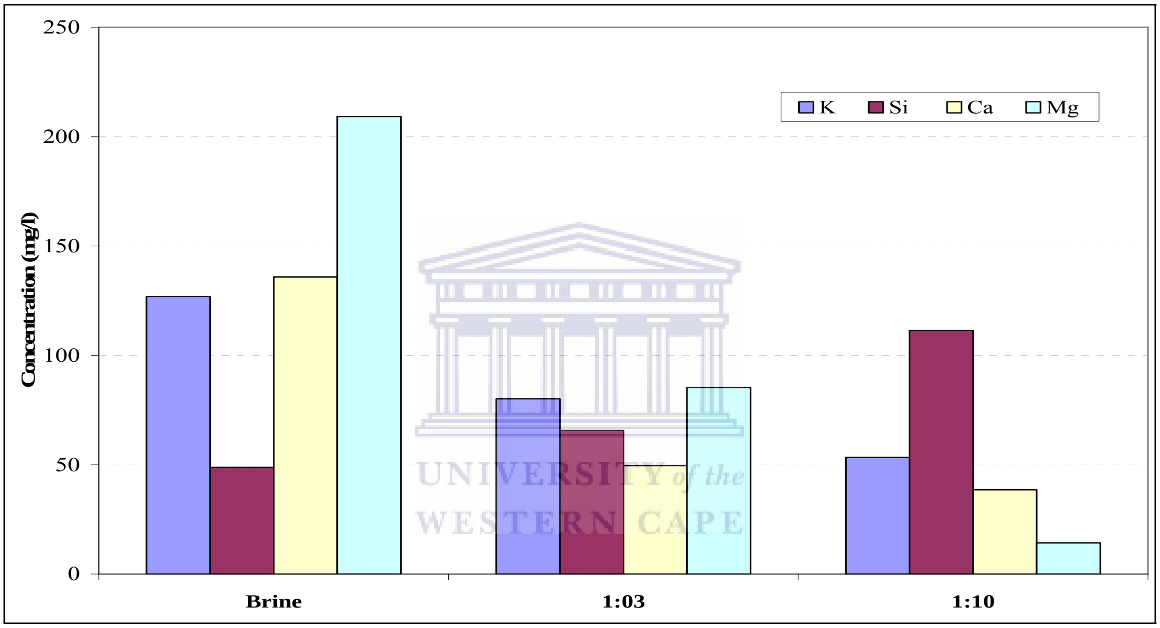


Figure 19: Concentration of major ions at 30 minutes contact time with different ratios in a reaction of brine with zeolite P.

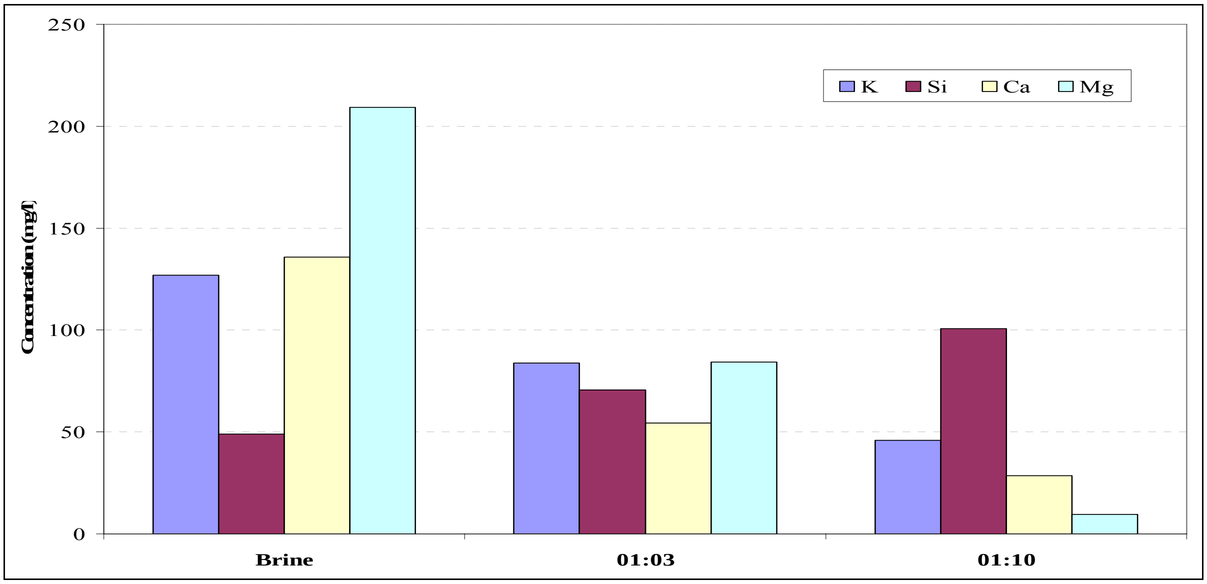


Figure 20: Concentration of major ions at 60 minutes contact time with different ratios in a reaction of brine with zeolite P.

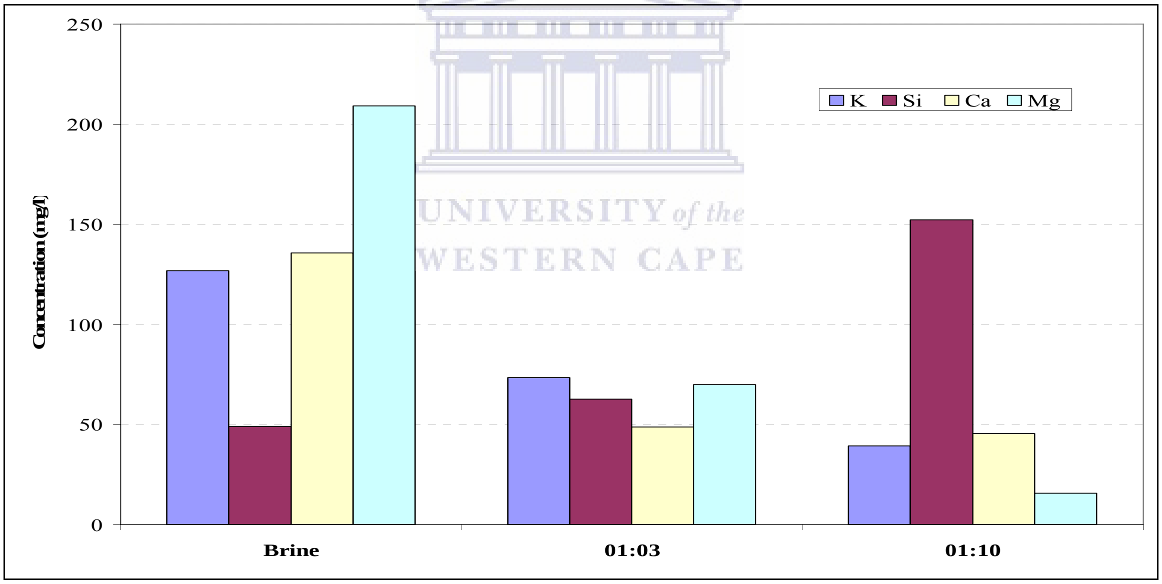


Figure 21: Concentration of major ions at 120 minutes contact time with different ratios in a reaction of brine with zeolite P.

4.6.2.3 Fly ash

This section shows the results of the major element from the brine treatment with the Arnot fly ash adsorbent at ratios 1:3 and 1:10 varying contact time from 30 minutes, 60 minutes and 120 minutes (see Section 3.4.4 for experimental details).

In Figures 22 and 23, K and Mg seem to have decreased their concentrations in brine a lot during the reaction. Si in figure 22 have increased from the initial concentration, whereas Ca seems to be leaching with this adsorbent as the concentration increased from the initial brine of about 80mg/l to about 250mg/l and 390mg/lfor fig. 22 and 23 respectively. However in figure 23 Si is seen as decreasing gradually during the reaction.

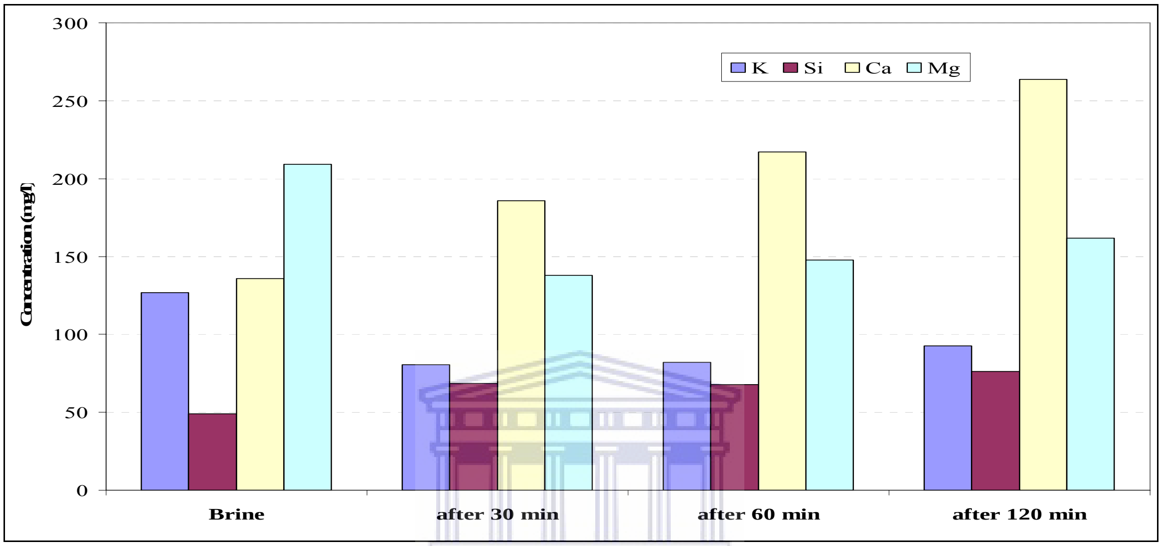


Figure 22: Concentration of major ions with ratio 1:3 and different contact times in a reaction of brine with Arnot fly ash.

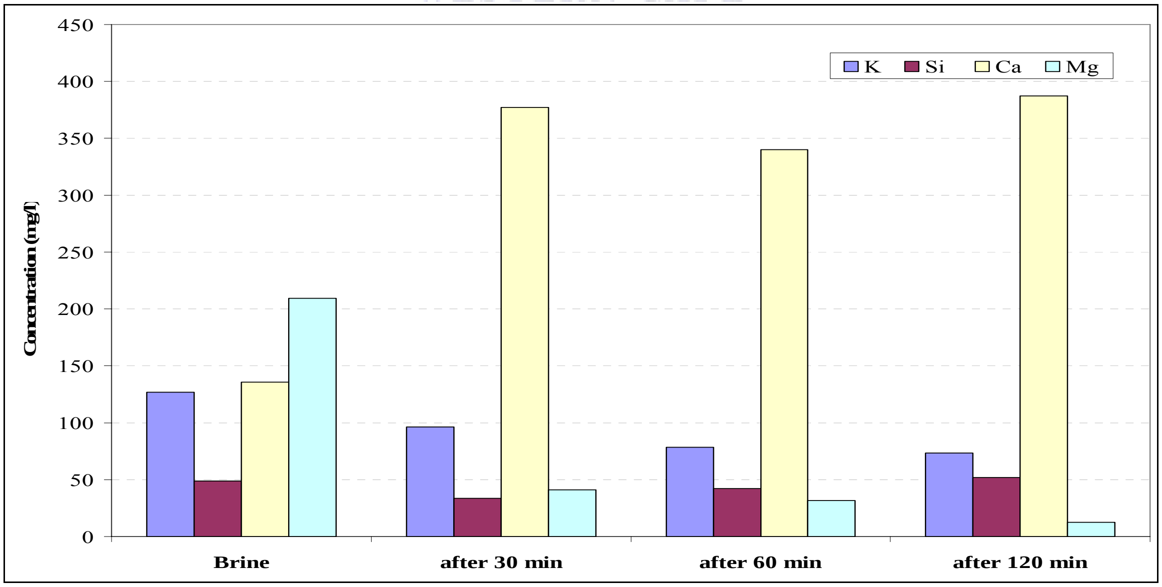


Figure 23: Concentration of major ions with ratio 1:10 and different contact times in a reaction of brine with Arnot fly ash.

Trends in Figures 24 and 25 seem to be the same, in both figures Ca is leaching out of the adsorbent as it increases during the reaction. Mg in both cases is reduced successfully from an initial concentration just above 200mg/l to a concentration of about 30mg/l. K and Si are both reduced gradually in the reaction. However trends are different for 120 minutes reaction time in Figure 26, Ca seems to have increased a lot in a longer reaction time and also in ratio 1:10 with increase in the amount of the Arnot fly ash adsorbent added to the reaction. Mg on the other hand is completely removed as it started off with a concentration of about 210mg/l and was reduced to 10mg/l.

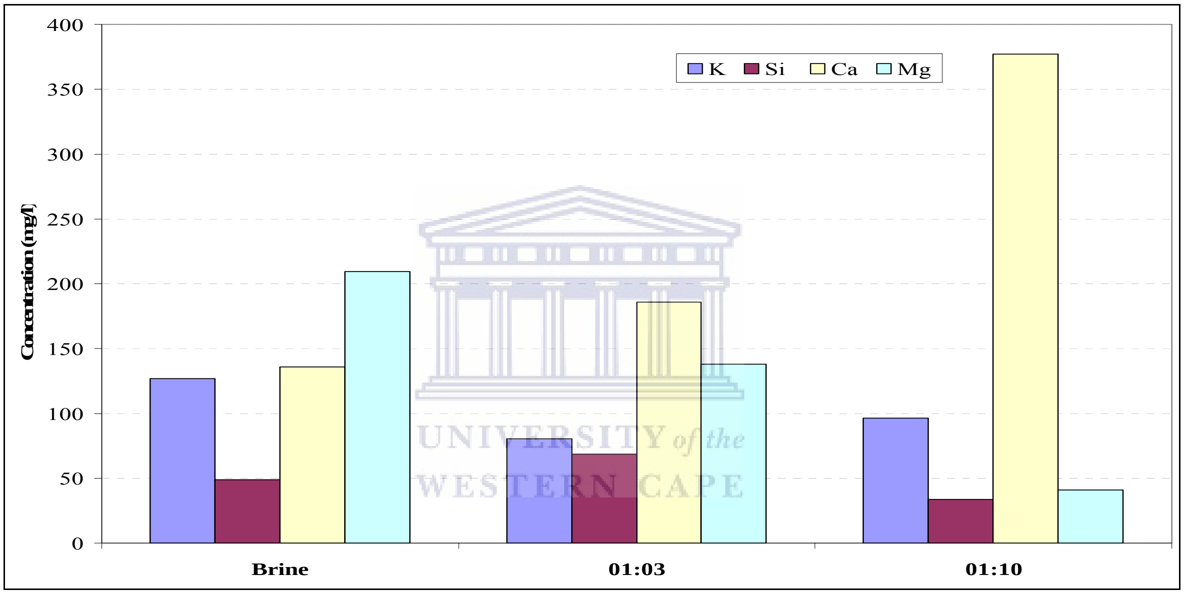


Figure 24: Concentration of major ions at 30 minutes contact time with different ratios in a reaction of brine with Arnot fly ash.

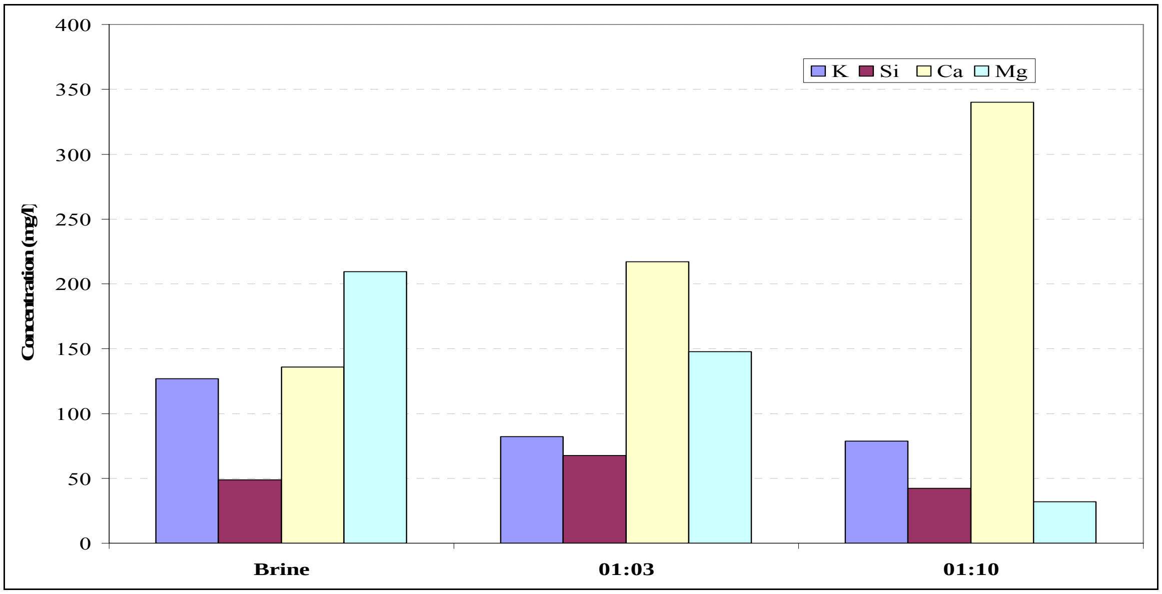


Figure 25: Concentration of major ions at 60 minutes contact time with different ratios in a reaction of brine with Arnot fly ash.

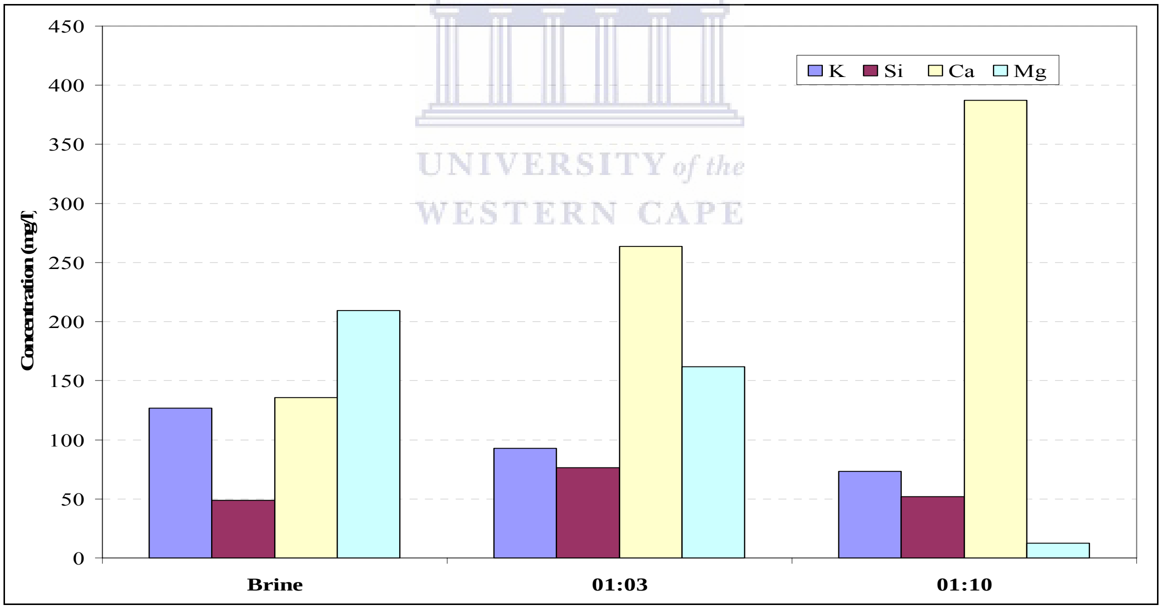


Figure 26: Concentration of major ions at 120 minutes contact time with different ratios in a reaction of brine with Arnot fly ash.

4.6.2.4. Solid residue

This section shows the results of the major elements from the brine treatment with the solid residue adsorbent resulting from neutralisation of Navigation AMD with Arnot fly ash at ratios 1:3 and 1:10 varying contact time from 30 minutes, 60 minutes and 120 minutes (see Section 3.4.3 for experimental details)**.**

It can be seen in Figures 27 & 28 that Ca concentration in brine has increased drastically during the reaction which could mean that it is leaching from the solid residue adsorbent. In figure 27 Ca started off with a concentration of about120mg/l and increased to about 520mg/l during the reaction, whereas in Figure 28 in a reaction where the amount of adsorbent added to the reaction has due to variation of ratio's the concentration of Ca increased from about 120mg/l to about 1050mg/l in the first 30 minutes of the reaction.

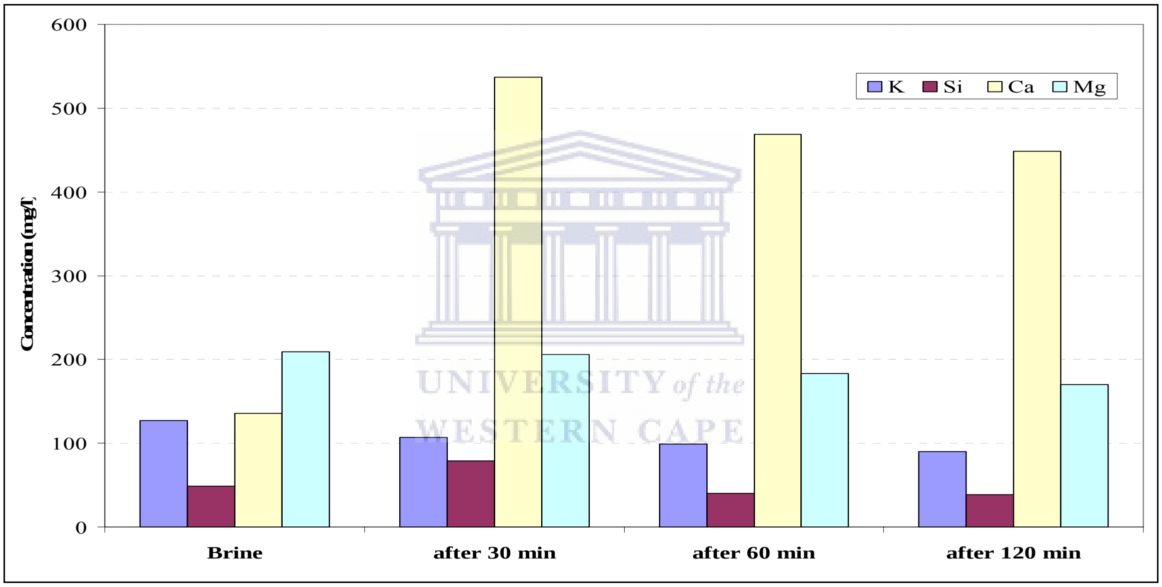


Figure 27: Concentration of major ions with ratio 1:3 and different contact times in a reaction of brine with solid residue.

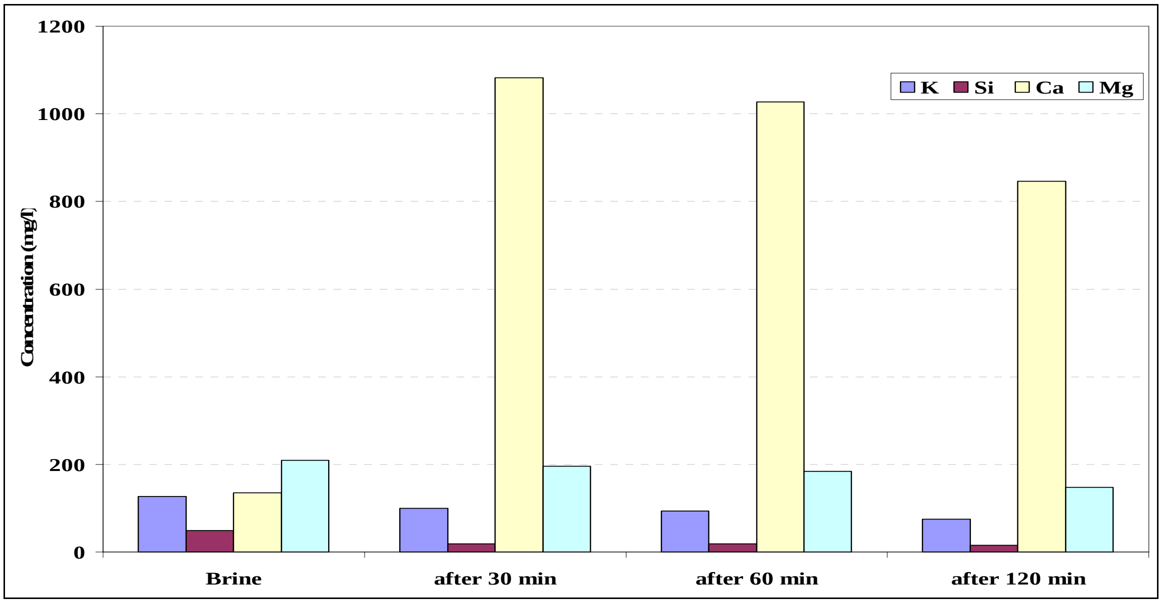


Figure 28: Concentration of major ions with ratio 1:10 and different contact times in a reaction of brine with solid residue.

It can be seen in Figures 29, 30 & 31 that Ca is leaching, it started with low concentrations and the concentration increased during the reaction. Solid residues have successfully removed Si compared to other adsorbents like commercial zeolites and co-disposed solids where it leached instead. Mg on the other hand is reduced by contact with the solid residue as well unlike with other adsorbents where it leaches.

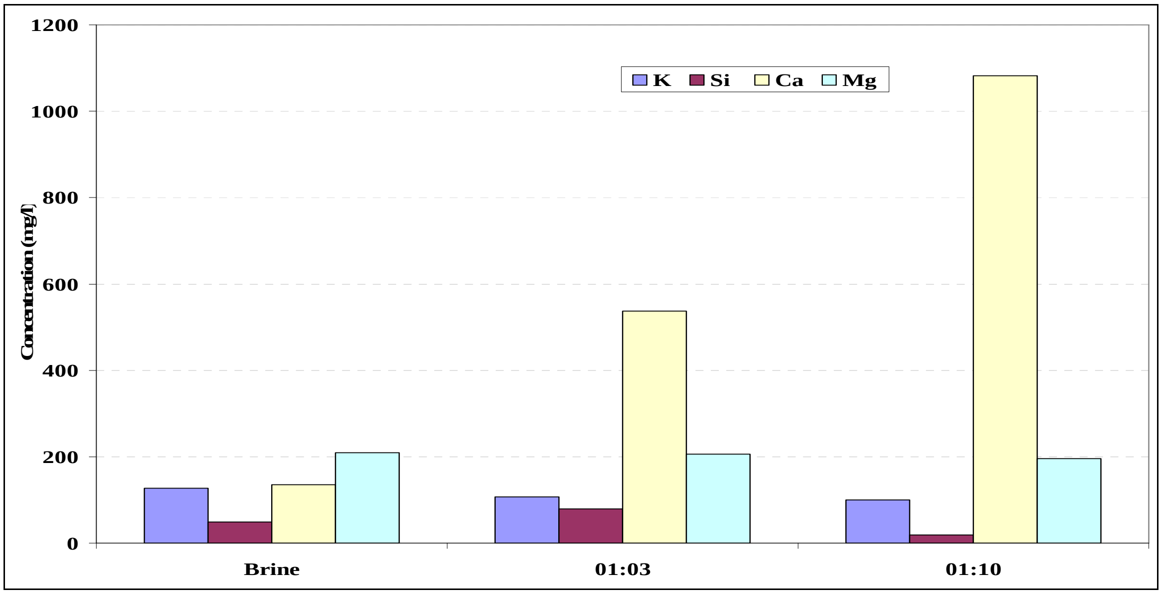


Figure 29: Concentration of major ions at 30 minutes contact time with different ratios in a reaction of brine with solid residue.

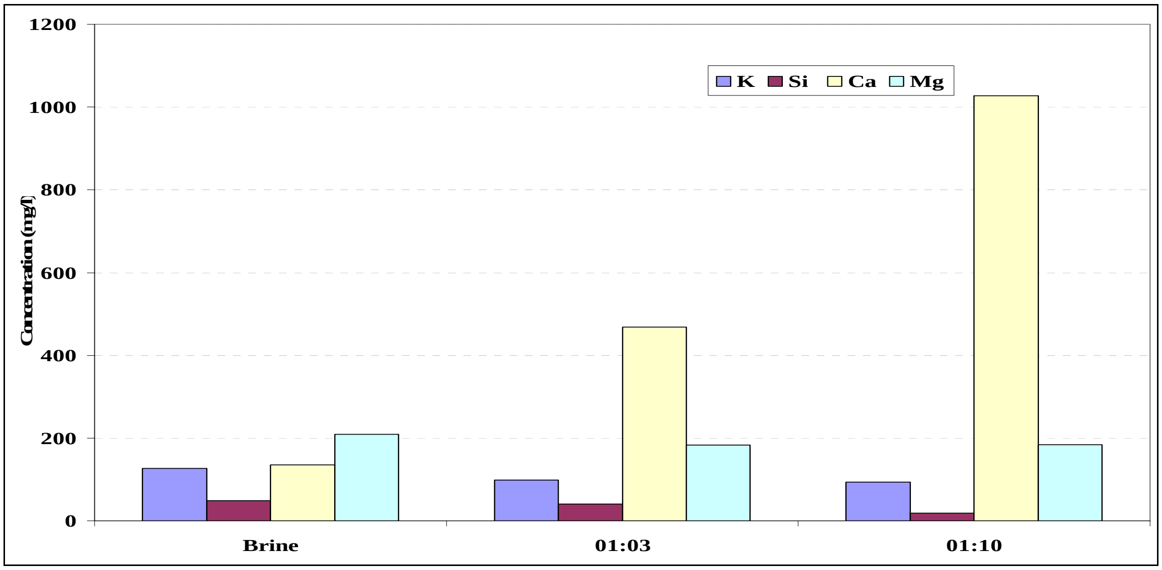


Figure 30: Concentration of major ions at 60 minutes contact time with different ratios in a reaction of brine with solid residue.

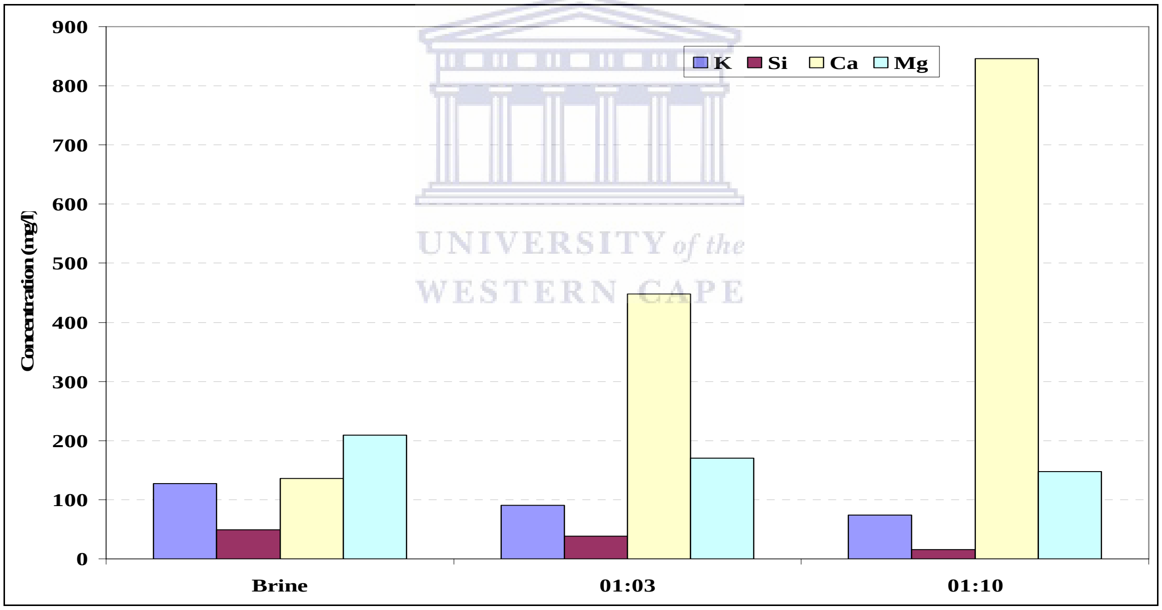


Figure 31: Concentration of major ions at 120 minutes contact time with different ratios in a reaction of brine with solid residue.

4.6.2.5 Comparison of the different adsorbents

This section compares the different adsorbents in terms of their removal efficiency of the major elements from the brine.

Fly ash seemed to have a better Na removal efficiency (Table 14) for ratio 1:3 at 30 minutes (26%); 60 minutes (23%); 120 minutes (14%) and at ratio 1:10 at 30 minutes (10%); 60 minutes (27%); 120 minutes (33%) whereas for other adsorbents Na (Table14) is seen to leach. However, the amounts leached were very small (between 1 and 8%). The low removal of Na could be ascribed to the high Na concentration in the brine and to the fact that Na is exchanged out of the zeolites during the uptake of more problematic species.

Table 14: Removal of Na in brine using different adsorbents (where ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P, CDSBr = solid residues, FABr = fly ash).

Sample Identity	**Time Minutes**	**`Ratio 1:3 Na (mg/l)**	**Residual Conc. (mg/l)**	**Removal Efficiency%**	**Ratio 1:10 Na (mg/l)**	**Residual Conc. (mg/l)**	**Removal Efficiency%**
Brine		**4603.55**			**4603.55**		
ZeoBr	30	4874.81	Leaching	**Leaching**	4720.03	Leaching	**Leaching**
ZeoBr	60	3652.11	951.44	**21**	4620.65	Leaching	**Leaching**
ZeoBr	120	4538.47	65.08	**1**	3584.76	1018.79	**22**
ZeoCDSBr	30	4667.08	Leaching	**Leaching**	5044.42	Leaching	**Leaching**
ZeoCDSBr	60	4982.70	Leaching	**Leaching**	4448.08	155.47	**3**
ZeoCDSBr	120	4284.57	318.98	**7**	3494.18	1109.37	**24**
FABr	30	3424.15	1179.40	**26**	4153.05	450.50	**10**
FABr	60	3538.02	1065.53	**23**	3344.66	1258.89	**27**
FABr	120	3936.76	666.79	**14**	3093.94	1509.61	**33**
CDSBr	30	4687.42	Leaching	**Leaching**	4373.70	229.85	**5**
CDSBr	60	4295.59	307.96	**7**	4037.11	566.44	**12**
CDSBr	120	3981.91	621.64	**14**	3267.39	1336.16	**29**

Commercial zeolite for the removal of K (Table 15) it can be seen that there is a better removal efficiency. Ratio 1:10 at 30 minutes (63%); 60 minutes (61%); 120 minutes (69%) whereas ratio 1:3 has a lower removal efficiency 30 minutes (35%); 60 minutes (45%); 120 minutes (39%). Solids residues also have a good removal efficiency as well, ratio 1:3 30 minutes (37%); 60 minutes (34%); 120 minutes (42%) and for ratio 1:10 30 minutes (58%); 60 minutes (64%); 120 minutes (69%). Zeolite P also had good removal of K from the brine (42 % (120 minutes 1:3) and 69% (120 minutes 1:10).

Table 15: Removal of K in brine using different adsorbents (where ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P, CDSBr = solid residues, FABr = fly ash).

Sample Identity	**Time Minutes**	**Ratio 1:3 K (mg/l)**	**Residual Conc.(mg/l)**	**Removal Efficiency%**	**Ratio 1:10 K (mg/l)**	**Residual Conc. (mg/l)**	**Removal Efficiency%**
Brine		**126.86**			**126.86**		
ZeoBr	30	82.67	44.19	**35**	46.50	80.36	**63**
ZeoBr	60	69.43	57.43	**45**	49.40	77.46	**61**
ZeoBr	120	77.92	48.94	**39**	38.79	88.07	**69**
ZeoCDSBr	30	80.12	46.74	**37**	53.36	73.50	**58**
ZeoCDSBr	60	83.85	43.01	**34**	45.85	81.01	**64**
ZeoCDSBr	120	73.51	53.35	**42**	39.21	87.65	**69**
FABr	30	80.42	46.44	**37**	96.27	30.59	**24**
FABr	60	82.10	44.76	**35**	78.54	48.32	**38**
FABr	120	92.78	34.08	**27**	73.42	53.44	**42**
CDSBr	30	107.00	19.86	**16**	99.44	27.42	**22**
CDSBr	60	99.19	27.67	**22**	93.17	33.69	**27**
CDSBr	120	90.19	36.67	**29**	74.54	52.32	**41**

For Si removal (Table 16), the removal efficiency is not very good for all the adsorbents used, instead it leaches out in zeolites P and commercial zeolite Y which could be because according to the XRF analysis Si is one of the major components of all the adsorbents used in the reactions. Solid residues have higher removal efficiency at ratio compared to other adsorbents. The leaching was significant for the commercial zeolite Y, zeolite P and the fly ash.

Table 16: Removal of Si in brine using different adsorbents (where ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P, CDSBr = solid residues, FABr = fly ash).

Sample Identity	**Time Minutes**	**Ratio 1:3 Si (mg/l)**	**Residual Conc.(mg/l)**	**Removal Efficiency%**	**Ratio 1:10 Si (mg/l)**	**Residual Conc. (mg/l)**	**Removal Efficiency%**
Brine		**48.89**			**48.89**		
ZeoBr	30	106.96	Leaching	**Leaching**	58.03	Leaching	**Leaching**
ZeoBr	60	96.01	Leaching	**Leaching**	119.90	Leaching	**Leaching**
ZeoBr	120	86.44	Leaching	**Leaching**	90.29	Leaching	**Leaching**
ZeoCDSBr	30	65.79	Leaching	**Leaching**	111.42	Leaching	**Leaching**
ZeoCDSBr	60	70.72	Leaching	**Leaching**	100.78	Leaching	**Leaching**
ZeoCDSBr	120	62.60	Leaching	**Leaching**	152.27	Leaching	**Leaching**
FABr	30	68.55	Leaching	**Leaching**	33.70	15.19	**31**
FABr	60	67.71	Leaching	**Leaching**	42.17	6.72	**14**
FABr	120	76.36	Leaching	**Leaching**	51.94	Leaching	**Leaching**
CDSBr	30	78.79	Leaching	**Leaching**	19.10	29.79	**61**
CDSBr	60	40.11	8.78	**18**	18.32	30.57	**63**
CDSBr	120	38.47	10.42	**21**	15.27	33.63	**69**

Ca (Table 17) was successfully removed by the commercial zeolites and the zeolite P but leaching was observed for the fly ash and solid residues. Zeolite P had a good removal efficiency ratio 1:3 30 minutes (63%); 60 minutes (60%); 120 minutes (64%) and for ratio 1:10 30 minutes (72%); 60 minutes (79%); 120 minutes (66%) whereas commercial zeolite Y had a removal efficiency ratio 1:3 30 minutes (66%); 60 minutes (76%); 120 minutes (68%); and for ratio 1:10 30 minutes (42%); 60 minutes (83%); 120 minutes (75%). South African fly ash has a high percentage of CaO in its composition (Table 8). This CaO is in the amorphous phase and may be dissolved and leached in to the brines. The commercial zeolite Y does not contain Ca in its framework and therefore no leaching was observed. Zeolite P does have Ca in it but this Ca may be incorporated in the framework or tightly associated with acid site and therefore did not leach out into the brine and it fact adsorption of the Ca onto zeolite P was observed.

Table 17: Removal of Ca in brine using different adsorbents (where ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P, CDSBr = solid residues, FABr = fly ash).

Sample Identity	Time Minutes	Ratio 1:3 Ca (mg/l)	Residual Conc. (mg/l)	Removal Efficiency%	Ratio 1:10 Ca (mg/l)	Residual Conc. (mg/l)	Removal Efficiency%
Brine		**135.79**			**135.79**		
ZeoBr	30	46.80	89.00	**66**	78.58	57.22	**42**
ZeoBr	60	33.13	102.67	**76**	22.68	113.12	**83**
ZeoBr	120	44.06	91.73	**68**	34.00	101.79	**75**
ZeoCDSBr	30	49.63	86.17	**63**	38.48	97.32	**72**
ZeoCDSBr	60	54.30	81.49	**60**	28.56	107.23	**79**
ZeoCDSBr	120	48.81	86.98	**64**	45.50	90.30	**66**
FABr	30	185.81	Leaching	**Leaching**	377.26	Leaching	**Leaching**
FABr	60	216.99	Leaching	**Leaching**	339.90	Leaching	**Leaching**
FABr	120	263.68	Leaching	**Leaching**	387.15	Leaching	**Leaching**
CDSBr	30	537.24	Leaching	**Leaching**	1082.17	Leaching	**Leaching**
CDSBr	60	468.45	Leaching	**Leaching**	1027.19	Leaching	**Leaching**
CDSBr	120	448.33	Leaching	**Leaching**	845.86	Leaching	**Leaching**

The adsorbents shown in Table 18 have a good removal efficiency for Mg except for the solid residues at ratio 1:3 30 minutes (1%); 60 minutes (12%); 120 minutes (19%) and for ratio 1:10 30 minutes (7%); 60 minutes (12%); 120 minutes (29%). The highest removal efficiency was obtained by the zeolite P (95% at 1:10 ratio at 60 minutes).

Table 18: Removal of Mg in brine using different adsorbents (where ZeoBr = commercial zeolite Y, ZeoCDSBr = zeolite P, CDSBr = solid residues, FABr = fly ash).

Sample Identity	Time Minutes	Ratio 1:3 Mg (mg/l)	Residual Conc. (mg/l)	Removal Efficiency%	Ratio 1:10 Mg (mg/l)	Residual Conc. (mg/l)	Removal Efficiency%
Brine		**209.22**			**209.22**		
ZeoBr	30	99.44	109.77	**52**	128.19	81.03	**39**
ZeoBr	60	69.26	139.96	**67**	38.85	170.36	**81**
ZeoBr	120	89.63	119.58	**57**	57.99	151.23	**72**
ZeoCDSBr	30	85.30	123.92	**59**	14.28	194.94	**93**
ZeoCDSBr	60	84.18	125.03	**60**	9.58	199.64	**95**
ZeoCDSBr	120	69.84	139.37	**67**	15.59	193.63	**93**
FABr	30	137.82	71.39	**34**	40.84	168.38	**80**
FABr	60	147.63	61.59	**29**	31.73	177.49	**85**
FABr	120	161.83	47.38	**23**	12.59	196.62	**94**
CDSBr	30	206.10	3.11	**1**	195.42	13.80	**7**
CDSBr	60	183.28	25.93	**12**	184.65	24.57	**12**
CDSBr	120	169.94	39.28	**19**	147.56	61.66	**29**

4.6.2.6 Absorbent: brine ratio and contact time

Different ratios were explored when brine was reacted with adsorbents so as to see the removal efficiency of the adsorbent on the amount of brine added to the reaction as the amount of zeolite added was constant. Ratio 1:10 and 1:3 were used where 1g of an adsorbent: 10ml brine for 1:10 and 1g adsorbent: 30ml brine for 1:3 respectively. It can be seen that the amount of an adsorbent added to the reaction mixture as referred to as a ratio had an effect on the removal of ions of interest.

Generally, increasing adsorption time increased the removal efficiency. However, due to the complex multi component nature of the brine stream and competitive adsorption the removal efficiency could also decrease with time. This was found to be true for Na with fly ash removal (1:3 ratio), K with commercial Y and fly ash (1:3 ratio), Ca with commercial zeolite Y and for Mg for commercial zeolite Y and fly ash (1:3).

The effect of the absorbent: brine ratio was that generally the 1:10 ratio had higher removal efficiency after 120 min. This indicates that a high adsorbent: brine ratio is required to treat the brine.

CHAPTER 5

Conclusions and Recommendations

5.1 Introduction

This thesis has dealt with the use of adsorbents for the treatment of brine in term of major element removal. In South Africa due to the fact that most of the electricity produced is coal based there is a very high availability of fly ash, which is a waste product from coal power plant. The utilisation of this resource to benefit the environment by the treatment of brines was investigated. AMD is also a large environmental concern in South Africa. Therefore, the combination of fly ash and AMD, two waste products, to produce a low cost adsorbent that can be further used to treatment brine will be a great benefit to South African economy and environment.

5.2 Conclusions

The following conclusions were obtained in this thesis:

Zeolite P formation from solid residues obtained from AMD neutralisation with fly ash:

- Zeolite P was synthesised from the solid residues as confirmed by XRD, BET and FTIR.
- However, a pure zeolite P phase was not obtained as was identified by XRD. Quartz and mullite are also present resulting in a mixed crystalline and amorphous solid phase.

Brine treatment with fly ash, solid residues, zeolite P and commercial zeolite Y for the removal of major elements (Na, K, Ca, Mg, Si):

- Na was not removed from the brine by any of the absorbents except by fly ash. The low removal of Na could be ascribed to the high Na concentration in the brine and to the fact that Na is exchanged out of the zeolite during the uptake of more problematic species.

- Commercial zeolite Y and zeolite P had good removal efficiencies for K (69% at 120 minutes at a 1:10 ratio),
- Significant Si leaching was observed from the commercial zeolite Y, zeolite P and fly ash. Si is the major component of these absorbents and this could indicate some dissolution of these absorbents under the conditions tested.
- Commercial zeolite Y and zeolite P had good removal of Ca whereas fly ash and solid residues leached Ca. In the fly ash and solid residues this may be due to the high CaO present in the amorphous phase which can be readily dissolved into the brine.
- Zeolite P and fly ash had good removal efficiency for Mg.
- Zeolite P had similar or higher removal efficiency than the commercial zeolite Y for the removal of K, Ca and Mg,
- The effect of adsorption time was complex due to the complexity of the brine and competitive adsorption between the different elements.
- A high adsorbent: brine ratio is required for brine treatment.
- The zeolite P did not completely remove all the major elements from the brine and this is especially true for Na. However, the zeolite P did “clean up” the brine sufficiently to simplify the brine and allow for easier and less expensive further downstream processing.

The objectives that were set out initially for the study were achieved according to the results that have been discussed above. The following objectives were satisfied in this thesis:

- Solid residues resulting from neutralization of AMD using FA were used in a reaction with brine.
- Adsorbents like FA and zeolites were also reacted and compared for effectiveness in removing unwanted ions from brine.

- Zeolites were found to be the best candidates in stabilising brine as they could remove ions from the reaction mixture without some ions leaching out as compared to the other adsorbents used.

It can therefore be seen that the main objective of the study of treating the effluent to recycle the effluent and use it again in the power plant as a way of addressing the issues facing the mining industry and coal fired power stations with respect to their waste minimization and waste disposal and to develop methods to treat water effluent that are cost effective also not time consuming.

5.3 Recommendations

I would like to recommend the following for future work on the treatment of brines:

- Future work to be done on the study looking at anions as they could not be analysed with type of instrument used in the study
- Samples to be analysed as soon as possible to avoid precipitation and other sample changes.
- Solids that were reacted with the brine sample be kept for further analysis and mass balance calculations
- Analysis should be done in duplicate or even triplicate and also explore other ratios as the results differ based on the ratios used and an optimum should be found.
- Further investigation into producing pure zeolite P phase from the solid residue is required.

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Appendices

Appendix 1: pH and EC measurements for a co-disposal reaction of Navigation AMD and Arnot FA.

Time (Min)	pH	EC(mS/cm)
10	4.06	5.93
20	4.05	5.73
30	4.90	7.64
40	5.02	7.49
50	5.36	7.45
70	5.57	7.36
80	5.65	7.20
90	6.07	7.07

Appendix 2: pH and EC against contact time of brine and commercial zeolite Y at a ratio 1:3.

ZeoBr	**1:3:120**	
Time(Min)	**pH**	**EC**
10	5.57	18.46
20	5.52	18.48
30	5.56	18.44
40	5.53	18.44
50	5.55	18.41
60	5.55	18.38
70	5.56	18.01
80	5.50	18.38
90	5.51	18.22
100	5.50	18.24
110	5.50	18.25
120	5.51	18.24

Appendix 3: pH and EC measurements for a reaction of brine and commercial zeolite Y at a ratio of 1:10.

ZeoBr	**1:10:120**	
Time(Min)	**pH**	**EC**
10	4.92	16.75
20	4.93	16.61
30	4.96	16.39
40	4.98	16.23
50	4.97	15.96
60	4.98	15.82
70	4.94	15.71
80	4.99	15.36
90	4.99	15.22
100	4.98	14.97
110	5.00	14.85
120	5.02	14.60

Appendix 4: pH and EC measurements for a reaction of brine and fly ash at a ratio of 1:3.

FABr	**1:3:120**	
Time(Min)	**pH**	**EC**
10	9.76	>20
20	9.79	>20
30	9.95	>20
40	9.98	>20
50	9.66	>20
60	9.77	>20
70	9.77	>20
80	9.78	>20
90	9.85	>20
100	9.87	>20
110	9.91	19.56
120	9.82	18.98

Appendix 5: pH and EC measurements for a reaction of brine and fly ash at a ratio of 1:10.

FABr	**1:10:120**	
Time(Min)	**pH**	**EC**
10	10.74	>20
20	10.86	18.63
30	10.93	18.14
40	11.07	17.84
50	11.15	17.54
60	11.15	17.17
70	11.09	16.82
80	11.11	16.64
90	11.14	16.21
100	11.20	15.88
110	11.19	15.58
120	11.16	15.39

Appendix 6: pH and EC measurements for a reaction of brine and solid residues at a ratio of 1:3.

CDSBr	**1:3:120**	
Time(Min)	**pH**	**EC**
10	8.61	>20
20	8.58	>20
30	8.64	>20
40	8.73	>20
50	8.72	>20
60	8.69	>20
70	8.68	>20
80	8.75	>20
90	8.75	>20
100	8.75	>20
110	8.75	>20
120	8.82	>20

Appendix 7: pH and EC measurements for a reaction of brine and solid residues at a ratio of 1:10.

CDSBr	**1:10:120**	
Time(Min)	**pH**	**EC**
10	8.63	19.77
20	8.79	19.68
30	8.80	19.41
40	8.80	19.04
50	8.73	19.17
60	8.77	18.79
70	8.79	18.74
80	8.78	18.54
90	8.74	18.71
100	8.75	18.69
110	8.75	18.50
120	8.76	18.53

Appendix 8: pH and EC measurements for a reaction of brine and zeolite P at a ratio of 1:3.

ZeoCDSBr	**1:3:120**	
Time(Min)	**pH**	**EC**
10	9.91	17.32
20	9.73	17.38
30	9.86	17.25
40	9.91	17.12
50	9.92	17.08
60	9.84	17.00
70	9.71	17.12
80	9.81	16.96
90	9.84	16.81
100	9.87	16.71
110	9.86	16.62
120	9.87	16.52

Appendix 9: pH and EC measurements for a reaction of brine and zeolite P at a ratio of 1:10.

ZeoCDSBr	**1:10:120**	
Time(Min)	**pH**	**EC**
10	10.37	16.91
20	10.45	16.52
30	10.51	16.26
40	10.52	15.78
50	10.53	15.61
60	10.54	14.96
70	10.57	14.68
80	10.59	14.28
90	10.58	13.97
100	10.58	13.68
110	10.46	13.58
120	10.53	13.32

ICP-MS data

Values in ppm

	QC std			**Brine**	**ZeoBr**	**ZeoBr**	**ZeoBr**	**ZeoBr**	**ZeoBr**	**ZeoBr**	**ZeoCDSBr**	**ZeoCDSBr**	**ZeoCDSBr**	**ZeoCDSBr**
	Certified	**Analysed**	**% RSD**		**1:03:30**	**1:3:60 AM**	**1:3:120 AM**	**1:10:30**	**1:10:60 AM**	**1:10:120 AM**	**1:03:30**	**1:3:60 AM**	**1:3:120 AM**	**1:10:30**
K	1984.00	2001.00	0.86	126.86	82.67	69.43	77.92	46.50	49.40	38.79	80.12	83.85	73.51	53.36
Si	0.00	0.00	0.00	48.89	106.96	96.01	86.44	58.03	119.90	90.29	65.79	70.72	62.60	111.42
Ca	9.80	9.87	0.69	135.79	46.80	33.13	44.06	78.58	22.68	34.00	49.63	54.30	48.81	38.48
Mg	0.10	0.10	7.80	209.22	99.44	69.26	89.63	128.19	38.85	57.99	85.30	84.18	69.84	14.28
Na	0.10	0.09	4.40	4603.55	4874.81	3652.11	4538.47	4720.03	4620.65	3584.76	4667.08	4982.70	4284.57	5044.42
Fe	95.70	106.80	11.60	3.28	1.02	1.38	1.37	3.61	2.16	2.13	9.01	9.92	7.12	14.73
B	92.00	99.22	7.85	1.44	1.18	0.97	1.10	1.13	1.07	0.88	1.03	1.03	0.84	0.90
Al	138.33	137.30	0.74	3.12	48.40	44.39	35.08	16.47	57.49	37.71	12.37	12.67	10.77	18.28
Sr	315.20	326.50	3.59	4.66	1.42	1.12	1.30	2.56	0.57	0.98	2.63	2.68	2.24	1.62
P	0.00	0.00	0.00	1.66	1.11	1.11	1.32	1.15	1.22	1.14	2.02	2.26	1.97	3.35
Be	13.64	12.93	5.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Li	17.00	17.29	1.71	0.40	0.33	0.26	0.30	0.30	0.28	0.23	0.97	1.06	0.93	1.16
Ti	0.00	0.00	0.00	0.26	0.08	0.12	0.09	0.08	0.18	0.08	1.68	1.82	1.37	2.43
V	36.93	37.68	2.03	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.03	0.03	0.02	0.06
Cr	19.90	20.45	2.76	0.34	0.13	0.11	0.13	0.13	0.12	0.14	0.41	0.42	0.42	0.47
Mn	38.02	38.47	1.18	0.33	0.07	0.09	0.08	0.12	0.08	0.08	0.37	0.37	0.29	0.50
Co	26.40	26.54	0.53	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.03	0.02	0.03
Ni	60.89	61.31	0.69	0.33	0.22	0.20	0.22	0.22	0.19	0.17	0.37	0.37	0.35	0.38
Cu	22.20	22.20	0.00	0.53	0.33	0.28	0.34	0.14	0.11	0.12	0.25	0.27	0.19	0.30
Zn	76.50	74.27	2.92	0.25	0.29	0.20	0.27	0.20	0.13	0.21	0.90	0.62	0.73	1.28
As	58.98	59.57	1.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Se	11.68	11.62	0.51	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mo	118.50	124.70	5.23	0.09	0.07	0.06	0.06	0.05	0.04	0.04	0.08	0.08	0.07	0.08
Cd	6.41	6.49	1.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	531.00	519.60	2.15	0.19	0.04	0.04	0.05	0.10	0.06	0.07	0.47	0.50	0.38	0.62
Pb	19.15	18.85	1.57	0.11	0.01	0.01	0.01	0.01	0.01	0.02	0.10	0.11	0.09	0.13

ZeoCDSBr 1:10:60 AM	ZeoCDSBr 1:10:120 AM	FABr 1:03:30	FABr 1:3:60 AM	FABr 1:3:120 AM	FABr 1:10:30	FABr 1:10:60 AM	FABr 1:10:120 AM	CDSBr 1:03:30	CDSBr 1:3:60 AM	CDSBr 1:3:120 AM	CDSBr 1:10:30	CDSBr 1:10:60 AM	CDSBr 1:10:120 AM
45.85	39.21	80.42	82.10	92.78	96.27	78.54	73.42	107.00	99.19	90.19	99.44	93.17	74.54
100.78	152.27	68.55	67.71	76.36	33.70	42.17	51.94	78.79	40.11	38.47	19.10	18.32	15.27
28.56	45.50	185.81	216.99	263.68	377.26	339.90	387.15	537.24	468.45	448.33	1082.17	1027.19	845.86
9.58	15.59	137.82	147.63	161.83	40.84	31.73	12.59	206.10	183.28	169.94	195.42	184.65	147.56
4448.08	3494.18	3424.15	3538.02	3936.76	4153.05	3344.66	3093.94	4687.42	4295.59	3981.91	4373.70	4037.11	3267.39
9.38	20.94	2.08	5.35	10.00	2.75	6.11	6.69	12.06	4.29	7.35	3.43	3.94	3.27
0.74	0.52	1.30	1.31	1.57	1.27	1.15	1.58	1.37	1.25	1.18	1.61	1.48	1.17
12.54	28.10	20.92	10.71	13.85	7.30	12.58	16.62	22.83	6.79	8.90	3.38	3.40	3.21
1.20	1.70	4.03	4.46	5.02	5.69	4.83	5.42	5.61	6.03	5.71	7.34	7.02	5.39
2.29	3.41	1.63	1.81	3.54	2.17	2.22	3.42	3.05	2.20	2.70	1.90	2.02	1.84
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.09	0.96	0.31	0.31	0.35	0.55	0.40	0.35	0.33	0.29	0.26	0.32	0.29	0.22
1.63	3.84	0.15	0.79	1.07	0.51	0.99	0.91	1.71	0.45	0.65	0.19	0.19	0.18
0.05	0.06	0.20	0.23	0.31	0.37	0.29	0.45	0.09	0.05	0.08	0.05	0.05	0.04
0.46	0.43	0.19	0.23	0.28	0.39	0.35	0.52	0.17	0.12	0.14	0.14	0.13	0.12
0.35	0.62	0.13	0.27	0.30	0.12	0.24	0.23	0.59	0.26	0.32	0.20	0.20	0.16
0.02	0.03	0.01	0.03	0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.02	0.02	0.01
0.33	0.33	0.16	0.17	0.19	0.19	0.17	0.17	0.22	0.19	0.19	0.19	0.23	0.27
0.17	0.19	0.34	0.30	0.28	0.11	0.10	0.06	0.30	0.25	0.21	0.19	0.17	0.13
0.60	0.65	0.30	0.30	0.21	0.28	0.35	0.23	0.50	0.34	0.33	0.31	0.28	0.29
0.01	0.01	0.06	0.07	0.09	0.05	0.03	0.09	0.03	0.02	0.03	0.02	0.02	0.02
0.01	0.01	0.03	0.05	0.04	0.10	0.09	0.10	0.02	0.02	0.02	0.02	0.03	0.02
0.07	0.06	0.08	0.09	0.10	0.14	0.12	0.15	0.09	0.08	0.08	0.11	0.10	0.08
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.43	0.93	0.30	0.48	0.62	0.69	0.69	0.84	0.93	0.63	0.71	0.78	0.92	0.77
0.13	0.12	0.15	0.06	0.02	0.01	0.03	0.01	0.02	0.01	0.02	0.01	0.01	0.01