Characterization and Chemical Speciation Modelling of Saline Effluents at Sasol Synthetic Fuels Complex-Secunda and Tutuka Power Station

by

Amon Nyamhingura

November 2009

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A thesis submitted in fulfilment of the requirements of the degree of Master of
Science in Chemistry in the Department of Chemistry
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Declaration

I declare that Characterization and Chemical Speciation Modelling of Saline Effluents at Sasol Synthetic Fuels Complex-Secunda and Tutuka Power Station is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references

Full Name: Amon Nyamhingura Nov 2009

Signed:

ABSTRACT

Chemical speciation and the evaluation of species distribution is the key to understanding the potential of brines to form scale or corrode the water circuit as well as the potential of mobility and release trends of the pollutants into the environment. It is important to identify highly soluble free ions in water chemistry because toxicity of ions is related to mobility and consequently bioavailability.

The chemical composition, character and chemical speciation modelling of saline effluents (brines) at Tutuka Power Station and Sasol Synthetic Fuels Complex in Secunda were studied. The form in which chemical species exist (chemical speciation) and the physical and chemical interactions of species in saline effluents at these two study sites is not fully understood. This study investigated how pH, temperature, alkalinity and chemical composition influenced chemical speciation, species distribution, scale forming and corrosion potentials of the different saline effluent streams at the two sites using computer programs PHREEQC and Aq.QA. Characterizations of the results were presented in Stiff and Piper diagrams generated by the Aq.QA computer software.

Chemical speciation modelling of the brines showed that scale-forming minerals aragonite, calcite, hematite, anhydrite and gypsum have positive saturation indices between 0 and 20 in mine water, RO brine at Tutuka and Sasol Secunda, EDR brine at Sasol Secunda and VC brine at Tutuka Power Station. The water types at Tutuka Power Station were found to be mainly Na-SO_4 water types and those at Sasol Secunda were a mixture of Na-Cl and Na-SO_4 water types. Water treatment chemicals play a major role in increasing the salt concentration in the treatment plants and in changing the character of water streams including introducing elements that were absent in the intake water. It was found that Sasol Secunda water streams are much more heavily contaminated than Tutuka water streams. The study also found that the mine water utilised at Sasol Secunda is two-fold more polluted than the mine water utilised at Tutuka although these sites are a mere 40 km apart. The sodium adsorption ratios showed that all the saline effluent streams at Tutuka and Sasol Secunda were unsuitable for irrigation, except for desalination product waters.

Chemical speciation showed that the predominant species in the most concentrated saline effluent (VC brine) at Tutuka were the free Cl^- ion at approximately 100 % with very minute quantities of $FeCl^+$ and $ZnCl^+$ and the predominant sodium species were the free Na^+ ion which existed at 85 %. Magnesium species had the predominant form as the ionic compound $MgSO_4$ at 73 % and the carbonates were mainly in the form of $NaCO_3^-$ (53 %), HCO_3^- (28 %) and CO_3^{2-}(7 %). The most concentrated brine analysed at Sasol Secunda was the TRO brine. PHREEQC did not predict the precipitation of $CaCO_3$ from the TRO brine at Sasol Secunda. The most abundant calcium species were Ca^{2+} (59 %) ions and $CaSO_4$ (40 %). The brine was at a pH of 5.76 with dissolved CO_2 at 73 % of the carbonate species.

Trace elements were evaluated and the toxic trace elements varied from 0.07 mg/L (As) to 26.75 mg/L (Sr) at Sasol Secunda. At Tutuka Power Station the toxic trace elements in brines varied from 0.02 mg/L (As/Se) to 16.85 mg/L (Sr). Sr and B were found to be the most highly concentrated toxic elements.

The major and trace ion chemistry, alkalinity, pH, sodium adsorption ratios, change in concentration of the water streams and the brine chemical composition after contact with ash was also evaluated. When saline effluents at Tutuka Power Station and Sasol Secunda are combined with ash, pH, Ca content and alkalinity of the resulting solution increased. The chemical composition of saline effluents can be influenced by the ingress of CO_2 from the atmosphere.

The study shows conclusively that brine composition and concentration is highly variable at these South African power utilities and processes such as RO, contact with ash and CO_2 ingress can have an impact upon the overall brine quality. Aq.QA was found to be a more accurate tool for classifying waters according to dominant ions than Stiff diagrams but Stiff diagrams still have the superior advantage of being a mapping tool to easily identify samples of similar composition as well as quickly identify what has been added or what has been removed from a water stream. Chemical speciation could identify effluent streams where CO_2 dissolution had taken place.

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ABBREVIATIONS

Abbreviation	**Explanation**
AC	Alternating current
DC	Direct current
DWAF	Department of Water Affairs
EDR	Electrodialysis reversal
EFC	Eutectic freeze crystallisation
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
IMS	Integrated membrane systems
MED	Multieffect distillation
MF	Microfiltration
MSF	Multistage flash distillation
NF	Nanofiltration
PCW	Process cooling water
PCWB	Process cooling water blowdown
RO	Reverse Osmosis
SAR	Sodium adsorption ratio
SRO	Spiral wound reverse osmosis
SWP	Specific daily water production
TCTA	Trans-Caledon Tunnel Authority
TDS	Total dissolved solids
TRO	Tubular reverse osmosis
TUAS	Texas University Agricultural Services
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VC	Vapour Compression

CHAPTER 1: GENERAL INTRODUCTION

1.1 Overview of Water Use and Treatment in South Africa

Increasing volumes of domestic, industrial and agricultural wastes are exerting huge pressure on water resources worldwide. Surface and underground water supplies are not plentiful especially in countries like South Africa (see Fig 1.1) where the average annual rainfall is half that of the world average (DWAF 1986). One of the obvious answers to conserving this precious resource is by recycling and reuse of domestic and industrial waste water. Water drawn from the Vaal supports 12 million consumers in Gauteng and surrounding areas (DWAF 2007). It is an important and already burdened water source. Together with changing legislation, continuous improvement of water treatment methods is vital for the sustainable continuation of coal mining activities in this region.

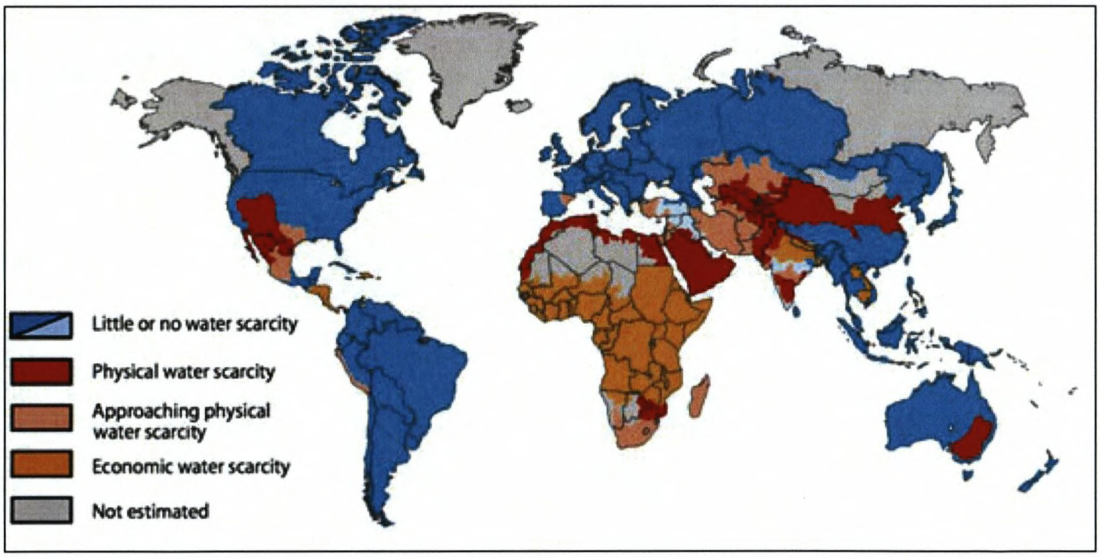


Figure 1.1: World water scarcity map (Foreign Policy Magazine 2009).

It has always been the South African government's priority that water users aim at enabling optimum management and protection of water resources and ensure sustainable development. The old South African Water Act (Act 54 of 1956) made it mandatory that effluent be treated to acceptable standards and returned to the water source from where it originated (Morrison et al.,. 2001).

- The Constitution of the Republic of South Africa (Act 108 of 1996) states that "South Africans have the right to have the environment protected for present and future generations".
- The National Water Act (No. 36 of 1998) mandates the Minister of Water Affairs and Forestry to ensure that water is protected, used, developed, conserved, managed and controlled in a sustainable and equitable manner for the benefit of all persons (DWAF 2009).

It has been this commitment to the environment by authorities that has seen some companies facing closure if they did not comply with government regulations. To counteract this, industries have embarked on wastewater discharge investigation as a tool for survival as the laws evolve with time.

The thermal power generating industry in South Africa consumes vast quantities of water as it is an essential part for its daily operations. Water is used to generate steam, and the steam is turned back to water by cooling water which flows in the turbine surface condensers (see Fig 1.3). Eskom's Tutuka Power Station and the Sasol Synthetic Fuels Complex in Secunda use thermal power to generate electricity as part of their operations. They have continuously restructured their water treatment methods with the objective to recycle water and achieve zero discharge to the environment. After the condensers, the cooling water will be carrying most of the heat from the steam and it is cooled in hyperbolic cooling towers by an upward natural draught. During the cooling process, evaporation takes place and pure water is lost to the atmosphere. "Make-up" water is used to replace the loss of cooling water due to evaporation. Raw water, cooling water blowdown and highly salty coal-mine water is used as make-up water at these two industrial sites. The use of raw water as make-up water has recently been limited due to improved recycling and treatment methods. If not treated, the make-up water can introduce large amounts of salts into the cooling water circuit. Salt deposits such as NH_4Cl and $FeCl_3$ will lead to corrosion and pre-mature failure of the plants (Alvisi and Lins 2007). On the other hand, deposition of insoluble salts such as $CaCO_3$ will lead to scaling and reduced heat exchange efficiencies in heat exchangers (DWAF 1996).

The salts in the effluents are removed by use of a combination of traditional and modern treatment technologies and the direct result is brine and reusable water. Desalination is the term used to describe the removal of salts from water. The earliest applications of desalination technology date back to the use of boiler condensate on early "steam-ships" (Glater and Cohen 2003). Water treatment at these plants is a continuous process which is essential in maintaining the salt levels in the cooling water circuits within acceptable limits. Brines generated in industrial applications such as power generation are pollutants which must be disposed of safely in a manner that protects the environment and abides by the principles of sustainable development.

1.2 Problem Statement and Hypothesis

The limited amount of water available in the Republic of South Africa (DWAF 1986) together with the government's environmental laws, has resulted in many power generating industries having to employ desalination measures in order to recover and reuse mine water as well as to reduce the volume of effluent requiring disposal by recycling the saline waste water produced. The desalination equipment is used either as an end-of-line effluent treatment process or as part of a closed loop recovery system. Fouling and scaling of heat or mass transfer surfaces is a common problem due to precipitation of salts resulting in low equipment efficiencies. This can lead to increased chemical consumption and effluent production as operators suppress precipitation through dilution or the use of scale inhibitors. Desalination equipment will thus become a point of entry of additional chemicals to be disposed into the environment.

The causes of unwanted precipitation are varied and they include alkalinity, pH, water composition or character and temperature. Chemical speciation is the term used to describe the nature of the individual components in solution. Chemical speciation modelling is required in order to better understand the chemistry of the water systems at power generating plants and the potential problems that may arise due to increased concentration of waste effluents. Chemical speciation provides the information needed to improve water treatment processes, reduce fresh water use and minimize the wastewater generated by:

(i) Determining the best pretreatment steps for desalination based on species in feed water and therefore it becomes possible to increase water recovery and minimize the volume of the saline reject stream.

(ii) Characterization of an effluent water by determining chemical species rather than total ion concentration and thus gaining an understanding of precipitation potentials of that water stream. This allows better understanding of the scales that may form and how they may be prevented or removed.

(iii) Modelling of water streams after different treatment stages to gain an understanding of the distribution of species and evaluate the effectiveness of the different treatment technologies in respect to the different forms of species in the feed water.

The hypothesis for this study can be generalized to give a statement for this thesis as follows;

This investigation demonstrated that the nature of individual components in saline effluents at Sasol Synthetic Fuels Complex in Secunda and at Tutuka Power Station is affected by pH, temperature, and chemical composition of the effluent stream.

After testing the hypothesis, the following research questions will be answered;

- To what extent does brine composition and concentration vary at the study sites and how is chemical speciation affected as a result of concentration?
- Are the types and quantities of major and minor elements in brines produced at Sasol Synthetic Fuels Complex in Secunda similar to those at Tutuka Power Station or is chemical composition site specific?
- What is the range of major species from intake mine water to the most highly concentrated brine at Tutuka Power Station and at Sasol Synthetic Fuels Complex at Secunda?
- Which are the scale forming minerals likely to precipitate from the water streams at Tutuka Power Station and at Sasol Synthetic Fuels Complex at Secunda?
- How do the saturation indices of the most common scale-forming minerals (i.e. calcium carbonate, calcium sulphate and iron oxide) vary with pH?
- Can coal ash be utilised to treat saline effluents as part of a remediation process?
- Does Aq.AQ software calculate saturation indices of calcite and aragonite comparably with PHREEQC?
- What are the similarities and differences between the two study sites?

1.3 Rationale

Chemical speciation is the term that is used to describe the nature of individual components or 'species' in water. It is an analytical approach which is a set of operations starting from the determination of total element content (using equipment such as ICP-MS) to quantifying single compounds and free ions in the water by use of computer-based programs such as PHREEQC and AQQA. Desalination activities at power generating plants produce saline effluents that can negatively affect the environment if not treated and disposed of properly. Treatment procedures have to be improved and developed, which prevent the discharge of metal and salt compounds into the environment. One of the most important prerequisite is adequate knowledge of the species existing in solution and their impact on water quality and waste water treatment technology. The behaviour of metals in water is directly dependent upon the physical and chemical properties of the species in which they occur (Davison 1999). Knowledge of chemical speciation in water is also of vital importance in understanding the availability of chemical species in a given water to biota (Davidson 1999), hence the need to characterize and speciate water streams at the study sites. The type of species in a water will influence the species available for absorption by organisms. The rationale of the study is to integrate chemical speciation into studies and models of mine water and brine treatment and generate knowledge to assist to alleviate disposal problems.

Chemical problems such as scaling occur in many industrial applications (Moller and Weare 1993). These problems for some operations can be handled with simple procedures during routine maintenance such as chemical cleaning. However for many large and important industries such as Tutuka Power Station and Sasol Secunda, scaling problems associated with brine chemistry may determine whether or not energy production operations are successful. As reported in some cases, scaling problems have been so severe that desalination plants have been abandoned even after considerable capital investment (Moller and Weare 1993). Characterisation and speciation help identify minerals likely to form scales and hence develop appropriate methods for scaling control.

1.4 Scope and Delimitations

Two industrial sites, Tutuka Power Station and Sasol Synthetic Fuels Complex in Secunda were investigated and chemical analysis data from 2006 to 2008 was analyzed. Historic chemical analysis data dating back to 1989 was obtained and analyzed for trends in some water streams where sampling and chemical analysis could not be carried out in the 2006 to 2008 period. Eskom's Tutuka Power Station and Sasol Synthetic Fuels Complex in Secunda practice desalination of coal-mine water to produce cooling water, boiler feed and brine. The sites both use brine to condition ash obtained from their coal-fired power generating units and therefore use ash as a salt sink. On both sites, the study covered all water streams: from the mine water intake up to the stage where brine is discharged after contact with ash. The sites were chosen for this study because of the large volumes of brine they produce as well as disposal problems due to their location in the Grootdraai catchment area. A map showing the towns of Standerton and Secunda (where Tutuka Power Station and Sasol Synthetic Fuels Complex are located respectively) is shown in Fig 1.2

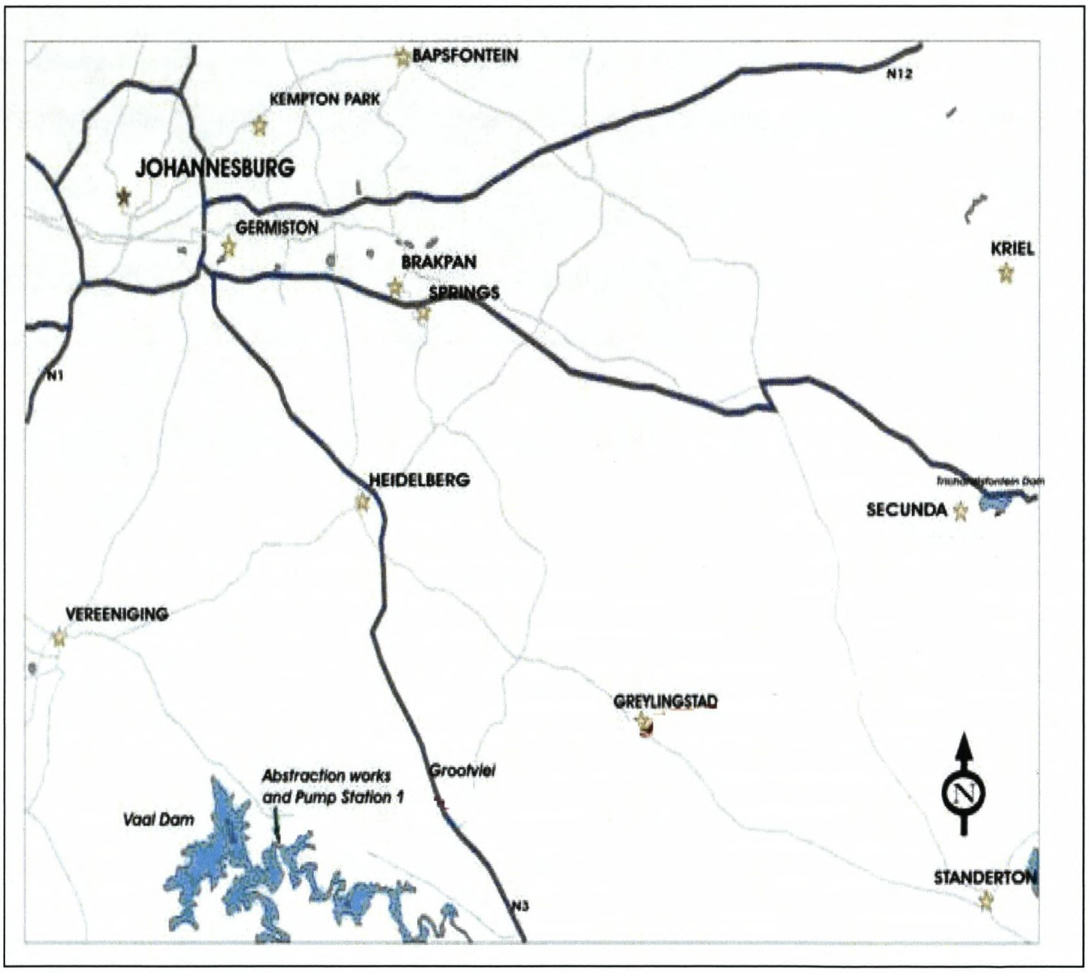


Figure1.2: A map showing the location of Standerton and Secunda and the Grootdraai catchment area (TCTA 2009).

1.4.1 Tutuka Power Station

Tutuka Power Station is located in the highveld between Standerton and Bethal, approximately 25 km from Standerton in Mpumalanga. It is about 160 km south east of Johannesburg and is owned by the electricity company, Eskom. Eskom is a large consumer of fresh water accounting for approximately 1.5 % of the country's total consumption annually (World Business Council for Sustainable Development, 2006). The main use of treated water is for cooling and Tutuka Power Station uses indirect wet-cooling (see Fig 1.3), which is cost effective to install but uses large amounts of water. The evaporation also results in high mineral concentrations in the cooling water which necessitates high blowdown rates and therefore high treatment costs, large volumes of make up water and large volumes of waste water (brine) to be handled. Tutuka Power Station is operated on Eskom's zero-effluent discharge philosophy whereby no liquid effluent is discharged into the environment. However, in May 2008, a trial was being conducted on disposing some of the brine into wells (aquifer re-injection) at the New Denmark Mine. The treatment plant process about 16.8 Ml per day of water which, after treatment is used as cooling water in the plant. This effluent feed water to the treatment plant is a 1:9 blend of the site's cooling tower blowdown to coal mine water. Due to water shortages and legislation forbidding the disposal of mine water into the Vaal River (Buhrmann et al., 1999), the power station constructed a spiral reverse osmosis (SRO) in 1998. This replaced the electrodialysis reversal (EDR) plant which had become costly to operate due to its age as well as its small capacity to handle the site's effluent (Buhrmann et al., 1999). At its inception in 1988, the treatment plant had a capacity of 12 Ml per day and it now stands at 16.8 Ml per day due to improvements made to the plant. Without new water treatment technologies, it meant the mine was to be closed down leaving the power station without a strategically situated coal supply. Accumulating mine water would have made further mining of coal impossible. The water treatment process is a combination of traditional treatment methods such as flocculation and clarification with the modern SRO plant in order to obtain good quality cooling water and achieve zero discharge. Brine obtained from the treatment process is combined with ash (to about 10 % moisture) for dust suppression during ash transportation to the ash dumps. Some of the brine is irrigated over the ash at the dumps for the same purpose.

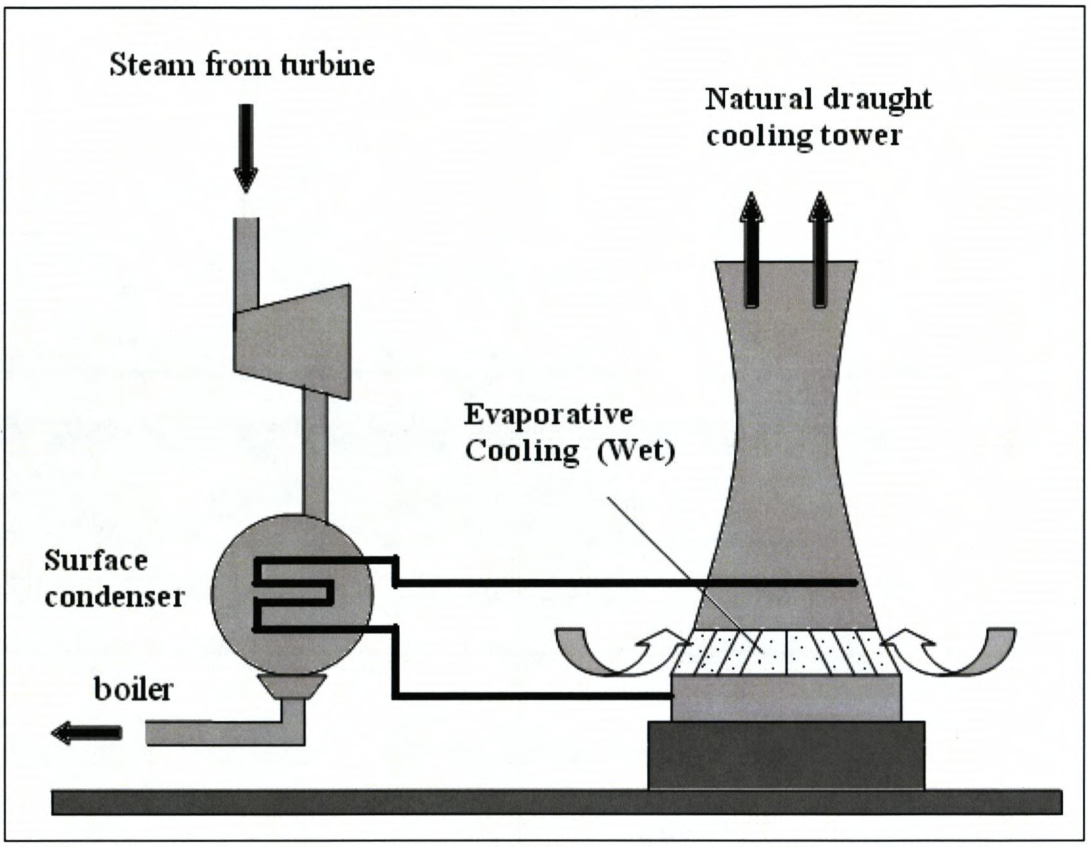


Figure 1.3: Indirect evaporative cooling system with surface condenser (GEA Aircooled Systems Pty Ltd), used at Tutuka Power Station and Sasol-Secunda.

1.4.1.1 Feed Water Quality and Plant Performance at Tutuka Power Station

The quality of feed water to the plant is extremely variable and contains high organic and biological loads (Buhrmann et al., 1999). The mine water is first stored in an open dam at the mine before being transported to the power station by a pipeline. The dam provides the ideal condition for the multiplication of organisms hence the high biological content in the feed water to the desalination plant. Clarification and microfiltration are the pre-treatment methods used to remove the biological load in the feed water. The feed water is saline (with approximately 4600 mg/L salt content). Some of the main contaminants are shown in Table 3.1

Table 1.1: Main Contaminants in Feed Water at Tutuka Power Station's SRO Plant (Buhrmann et al., 1999).

Ion	Concentration (mg/L)
Calcium	300
Magnesium	200
Sodium	1100
Chloride	700
Aluminium	400
Sulphate	1500
Copper	500
Iron	500
Barium	0.09

As previously mentioned in section 1.4.1, the plant has a current capacity of 16.8Ml per day (700 000 litres per hour) operating with five SRO units (approximately 208 m^3/hr per unit).

1.4.1.2 The Water Treatment Process

Below is Fig 1.4 which shows the process flow diagram at Tutuka power Station. The effluent blend consisting of cooling tower effluent, mine water and microfilter backwash is fed into the clarifier for softening by the addition of lime as well as for turbidity removal by the use of a flocculent and coagulant. A 50 % reduction in alkalinity and 93 % reduction in turbidity is achieved by this process alone (Buhrmann et al., 1999). The composition of the feed water to the clarifier fluctuates depending on plant needs and capacity but it is normally 90 % mine water and 10 % cooling water effluent. The clarified water is then chlorinated to stop biological activity and the pH is adjusted using sulphuric acid. The suspended solids are further removed by microfiltration (five units) which prevents solids contamination to the spherical reverse osmosis membranes. The filtered water is stored in a tank (filtered water tank) that supplies the SRO plant which consists of five units each equipped with a high pressure pump. The permeate from the five units is combined in a single product tank where it is returned to the cooling water circuit. The brine from the SRO is concentrated further by distillation using the vacuum compressor evaporator. The condensate from the evaporator is send back to the boiler/cooling water circuit and the brine concentrate is used to condition the ash. About thirty cubic metres per hour is returned to the mine for re-injection in 270 m deep wells.

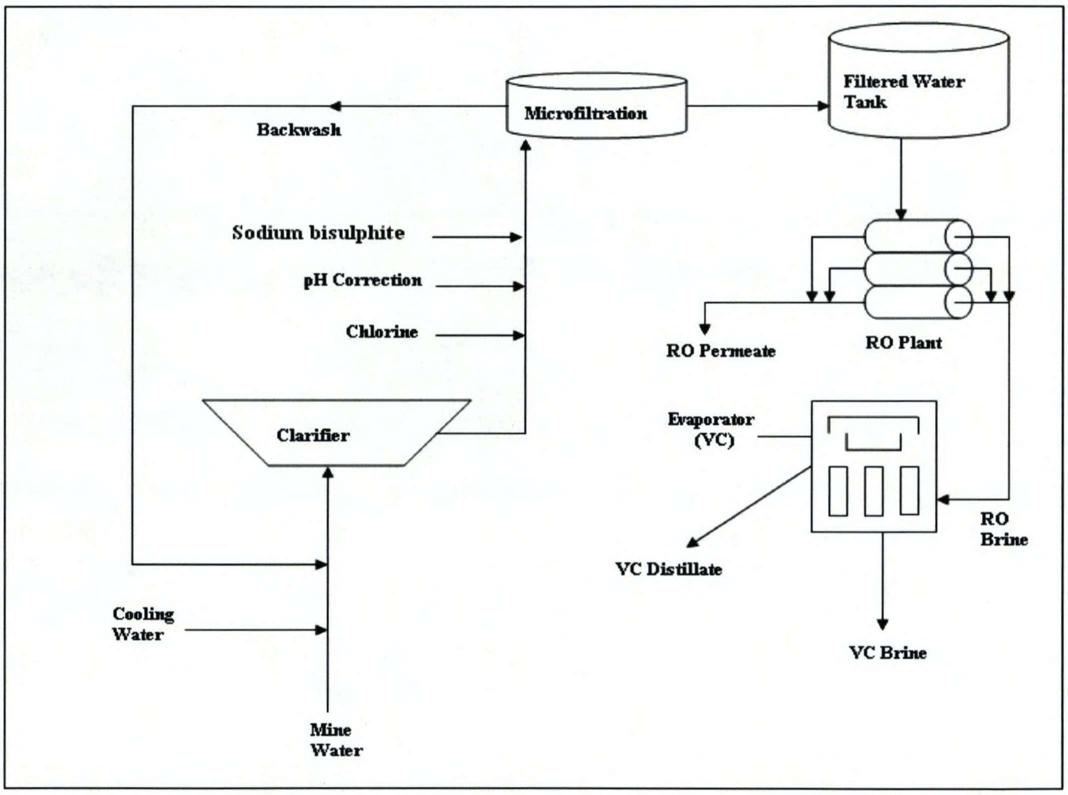


Figure 1.4: Tutuka Power Station Water Treatment Circuit (Buhrmann et al., 1999).

1.4.2 Sasol Synthetic Fuels Complex in Secunda

The Sasol Synthetic Fuels Complex is the largest synthetic fuels facility in the world. Sasol converts low-grade coal into value added synthetic fuels and chemicals through its proprietary Fischer Tropsch (FT) Technologies. It is located at Secunda, 145 km southeast of Johannesburg and was constructed between 1975 and 1982 in response to the international oil crisis of the mid 1970s (Phillips and du Toit 2002). The facility uses coal for gasification in synthetic fuel production as well as in generating electricity. As in any thermal power station, the power utilizes a large amount of water for cooling (evaporative wet cooling). To save water and minimize disposal of effluent into the environment, the facility adopted a concept of zero liquid discharge to surface water streams especially since the complex is situated in the upper catchment area of the Vaal Dam, an already overburdened major source of water for industrial, agricultural and domestic use. The company's engineers have adopted water-saving philosophies including maximum use of air cooling, total recycling of effluents and upgrading and re-using effluents. The main difference between the synthetic fuels facility and an ordinary thermal power station like Tutuka Power Station is that Sasol Secunda needs much more make-up water since steam is used as a reagent in the fuel production process and is not recovered as is the case in steam generated in boilers which is recovered as condensate. Therefore the quantities of effluent generated are much larger and contain organic contaminants from the synfuels production process to a larger extent than in ordinary thermal power stations.

1.4.2.1 The Feed Water Quality

One of the reasons why Sasol decided to install an Integrated Membrane System (IMS) was to prevent major polluting of the local river streams with mine water (von Gottberg et al., 2001). An IMS can be defined as a water treatment system combining two or more membrane processes or as a system combining a membrane process with other treatment processes. Table 1.2 describes the mine water quality

Table 1.2: Sasol Secunda Mine Water Composition (von Gottberg et al., 2001).

Ion	Concentration (mg/L)
Sodium	1115
Calcium	291
Magnesium	174
Potassium	6.5
Ammonia	0
Strontium	6.3
Barium	0.02
Chloride	280
Bicarbonate	112
Sulphate	3211
Total Dissolved Solids	5196

From the water quality given in the table above, the mine water has high quantities of calcium sulphate which is a big challenge in achieving high water recovery because calcium sulphate can easily form scale in membrane systems. At inception, the integrated membrane system produced water with 20 ppm TDS, ten times better than their raw water intake and achieved 70 % water recovery (von Gottberg et al., 2001).

1.4.2.2 The Water Treatment Process

The water distribution systems at Sasol in Secunda gave problems soon after start up in 1976 (Phillips and du Toit 2002). This was due to systems that did not perform according to design specifications as well as lower-than-expected evaporation rates in the evaporation ponds. Various approaches were taken to alleviate the challenges without much success. After some research, a decision was made to install a reverse osmosis system in 1996 made up of a primary tubular reverse osmosis (TRO) unit and a secondary spiral wound reverse osmosis (SRO) to treat about 14 Ml per day of clear ash effluent. This meant that some effluent streams had to be re-routed to accommodate the reverse osmosis plant. Coal used at Sasol Secunda comes from underground mines and one of the challenges came from the accumulation of contaminated mine water in the mines. Some of the water was used for dust suppression and coal washing and the rest had been stored in dams. To utilize this water, an Integrated Membrane System (IMS) was installed in 1997. The system consists of a clariflocculator (clarifier, reaction zone, and flocculation chamber built in one unit), sand filters (not shown in the diagram below), an electrodialysis reversal system and a spiral wound reverse osmosis system. Pre-treatment is necessary for the removal of suspended solids from the feedwater. Hypochlorite is also added to eliminate bacteria and a flocculant to promote coagulation and settling of the suspended solids. The clarification process and the sand filters which are packed with anthracite/sand remove the solids. The pH of the water is adjusted to between 5.5 and 6.5 to minimize hydrolysis of the cellulose acetate membranes. Anti-scalants are also added to inhibit scaling by gypsum.

The EDR removes most of the minerals. The permeate is used as boiler feed water and it has a design capacity of 0.9 Ml per day (Phillips and du Toit 2002). Installation of an evaporator-crystallizer followed due to problems in handling the significant volumes of brine produced from processing mine water.

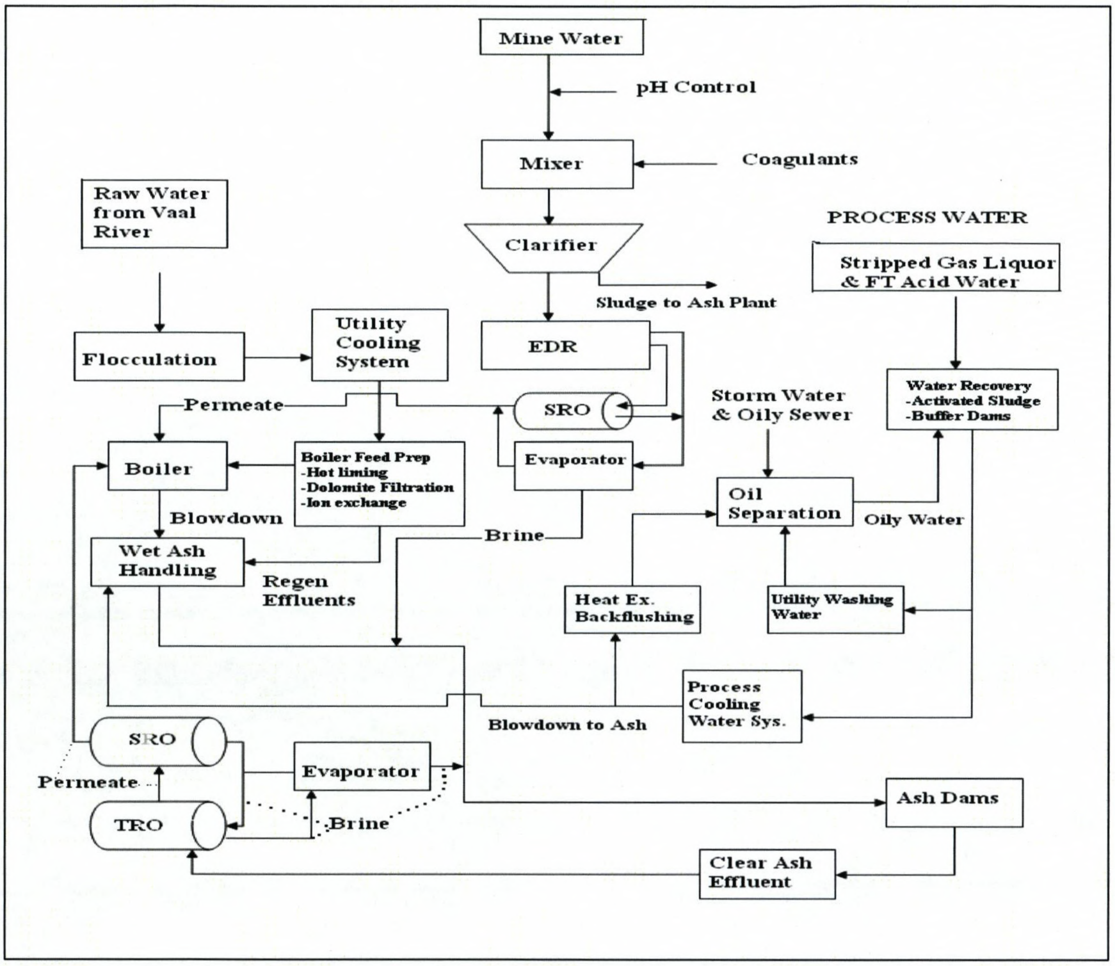


Figure 1.5: Schematic Diagram of Sasol Synthetic Fuels Complex at Secunda (Phillips and du Toit 2002).

Improvements have been made on the treatment technologies since inception and Table 1.3 shows the current design capacities as well as average daily water usage.

Table 1.3: Water usage and design capacities at Sasol Synfuels Complex-Secunda.

Effluent streams	**Design [Ml/d]**	**Actual daily average [Ml/d]**
Mine water intake	8.4	8.3
Brine Discharge of TRO's	20.7	24.8
Process cooling supply	4320	5400
Process cooling blow down	12	14
Design capacities	**Design feed [Ml/d]**	**Design permeate/condensate[Ml/d]**
U67 - TRO	15.3	6.9
U67 - SRO	6.6	3.6
U69 TRO	20.9	9.4
Falling film evaporators	9.1	8.6
EDR (Polish mode)	8.4	4.4
Evaporator Crystalliser	3.2	2.9

1.4.3 Delimitations

In the current study, the following will be investigated:

- Chemical composition of saline effluents;
- The characterization of saline effluents;
- The nature of individual components in saline effluents;
- The effect of pH and temperature on the nature of individual components in saline effluents;
- The scale-forming minerals likely to precipitate from saline effluents.

In this study, the following areas were not investigated:

- Other power stations in South Africa and around the world due to time constraints;
- Species percent distribution of minor elements due to time constraints and the enormous amount of data that had to be handled;
- Bioavailability studies of species as it was beyond the scope of this study;
- Methods of immobilization and clean-up of species in the waste as it was beyond the scope of this study;

- Determination of carboxylic acids in brines due to the absence of a suitable analysis method to be used during field measurements;
- Considerations, development and design of desalination technologies and remediation measures based on chemical speciation results due to time constraints.

1.4.4 Thesis Outline

The rest of the thesis will unfold in the following way:

Chapter 2: *The Origins, Disposal, Chemical Composition, Analysis Classification and Environmental Impacts of Brines: A Literature Review*

The literature reviews the evolution of saline water, classification methods and available treatment technologies. This chapter also discusses current disposal methods, available speciation software and the effects of brine on biota and the environment.

Chapter 3: *Experimental*

Chapter 3 details the sampling procedures employed in testing the hypothesis, sample preservation methods used and the analytical methods applied. Analytical parameters and modelling input parameters are also fully set out in this chapter.

Chapter 4: *Results and Discussion*

Analytical results obtained from the methods set out in the experimental section are presented in this chapter. The evolution of water streams, their compositions, historical data, trends, species distributions and brine interaction with ash are fully discussed here.

Chapter 5: *Conclusions and Recommendations*

This chapter is comprised of conclusions drawn from the study, the contributions the thesis has made (successes), failures and prospects for future research and/or directions.

References

This section is made up of a list of references used within the text of this thesis, in full and in alphabetical order.

Appendices

This section contains detailed analytical results obtained from the experimental procedures in chapter 3. Historical data and tables of minerals likely to precipitate from some of the water streams sampled at Tutuka Power Station are found in this section.

CHAPTER 2: THE ORIGINS, DISPOSAL, CHEMICAL COMPOSITION, CLASSIFICATION AND ENVIRONMENTAL IMPACTS OF BRINES

2.1 Introduction

About 68 % of energy consumed in South Africa is coal based (Energy Information Administration 2000). The mining of coal has led to deterioration of water quality and a significant negative impact on the environment. During mining, minerals in rocks are oxidized due to exposure to moisture and oxygen. This results in the release of sulphates, metals, generation of acidity, carbonates and other chemicals. The co-existence of carbonates with acidity derived from oxidized pyrites (FeS_2) explains why many coal mine waters are not necessarily acidic but often high in dissolved salts (Usher 2003). The coal mining activities carried out to support power generation by power stations (such as Tutuka Power Station) and synthetic fuel plants (such as Sasol Synthetic Fuels Complex in Secunda), introduce many environmental problems and produces huge amounts of wastes. Brine, coarse ash and fly-ash are some of the wastes produced in power generation.

2.2 Origins of Brines: Globally

2.2.1 Introduction: General Global Aspects

Salinity in water comes from different sources. These sources are either natural or caused by human intervention. Natural brines are commonly found deep into the earth whereas industrial brines are a product of industrial applications where desalination activities take place. Brines can contain extremely high concentrations of dissolved elements, ions and molecules. They are generally considered more saline than sea water and may contain up to 5 times the salt content of average sea water which has a salinity of 35000 mg/L (Water Condition & Purification 2005). The following table shows the classification of water according to salinity, which is a measure of the amount of salt in a water sample.

Table 2.1: Water classification by salinity level (The Engineering Toolbox 2009).

Water Class	Fresh Water	Brackish Water	Saline Water	Brine
Salinity (mg/L)	<500	500-35000	35000-50000	>50000

Due to their high salt content, brines are of commercial value. They are useful in the production of table salt and other salts (Turek et al., 2005). Despite being useful, they can cause a lot of trouble when they leak into water supplies consumed by humans, plants and animals. Worldwide, brines have historically been dumped into pits and would gradually "evaporate" and disappear. In actual fact, they would be seeping into the ground and slowly contaminate the local aquifer. In most places groundwater moves very slowly, probably several millimetres a year (Dasch and Hoyle 2009). Thus several years may pass before a nearby water supply is contaminated and the lawsuits then follow.

Salinity of water is an ecological factor of considerable importance (Mantyla 1987), influencing the types of plants and organisms that can grow in such a water or on land irrigated by it. In inland areas, the need to dispose of brine is the major limiting factor to the installation of desalination plants whereas in coastal areas, the solution is normally to pump it into the sea. This practice is also not sustainable as it disturbs the environment.

2.2.2 Chemical Evolution of Natural Groundwater

Water vapour condenses to form pure water with a neutral pH. As it falls through the atmosphere, it comes into contact with carbon dioxide (CO_2) gradually forming carbonic acid (H_2CO_3) and reaching a pH of about 5.7 (Murray 2009). In industrial areas, the pH can be much lower after coming into contact with atmospheric sulphur dioxide (SO_2) and nitrogen oxides (NO_x). Rain also comes into contact with gases such as oxygen, nitrogen and argon. By the time rain reaches the ground, it is a slightly to moderately acidic, oxidizing solution that can quickly change the chemical composition of soils, organic matter and minerals through which it moves. Therefore the chemical composition of the groundwater itself also changes with time. Carbon dioxide produced from decaying organic matter (equation 2.1) combines with water to form H_2CO_3 which dissolves minerals such as albite ($NaAlSi_3O_8$) and calcite ($CaCO_3$).

$NaAlSi_3O_8 + H_2CO_3 + 9/2\ H_2O \rightarrow Na^+ + HCO_3^- + 2H_4SiO_4 + \frac{1}{2}\ Al_2Si_2O_5(OH)_4$
Albite Kaolinite

……………………………………………………………………………………………Equation 2.1

$CaCO_3 + H_2CO_3 \rightarrow Ca^{+2} + 2HCO_3^-$……………………………………………Equation 2.2
Calcite

Oxidation of pyrite (FeS_2) to form sulphuric acid is another source of soil acidity

$8H_2O + 4FeS_2 + 3\ O_2 \rightarrow 8H_2SO_4 + 2Fe_2O_3$…………………………………Equation 2.3

Shallow water has lower total dissolved solids (TDS) than deeper water in the same system meaning that ground water composition evolves chemically with residence time. At the end of such an evolution, the groundwater has a composition similar to that of sea water (Murray 2009). The evolution of such waters is normally characterized by changes in dominant anion species also known as the Chebotarev Sequence, often interpreted in terms of large sedimentary basins (Murray 2009). The sequence, which is made up of three zones is shown below.

$HCO_3^- \rightarrow HCO_3^- + SO_4^{-2} \rightarrow SO_4^{-2} + HCO_3^- \rightarrow SO_4^{-2} + Cl^- \rightarrow Cl^- + SO_4^{-3} \rightarrow Cl^-$

Increase in distance with increase in residence time or age

→

The upper zone is characterized by rainfall flushing through the zone of aeration comprised of shallow groundwater rich in HCO_3^- and is low in total dissolved solids (TDS). In the intermediate zone which is characterized by slower rate of groundwater flow and higher TDS than the upper zone, sulphate becomes the dominant anion.The lower zone has very slow rates of groundwater migration.It is characterized by large amounts of soluble minerals because very little groundwater flushing has occurred (Murray 2009).This zone is typified by high Cl^- concentrations and high TDS.

Bicarbonate content in groundwater is high in the top soil due to the availability of carbon dioxide generated from organic matter. Sulphate comes from gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$).

$H_2O + CaSO_4.2H_2O) \rightarrow Ca^{2+} + SO_4^{2-} + 3H_2O$……………………………Equation 2.4

The chloride is primarily derived from dissolution NaCl (halite) or sylvite (KCl) which are the dominant and soluble chloride minerals. Below is a conceptual model

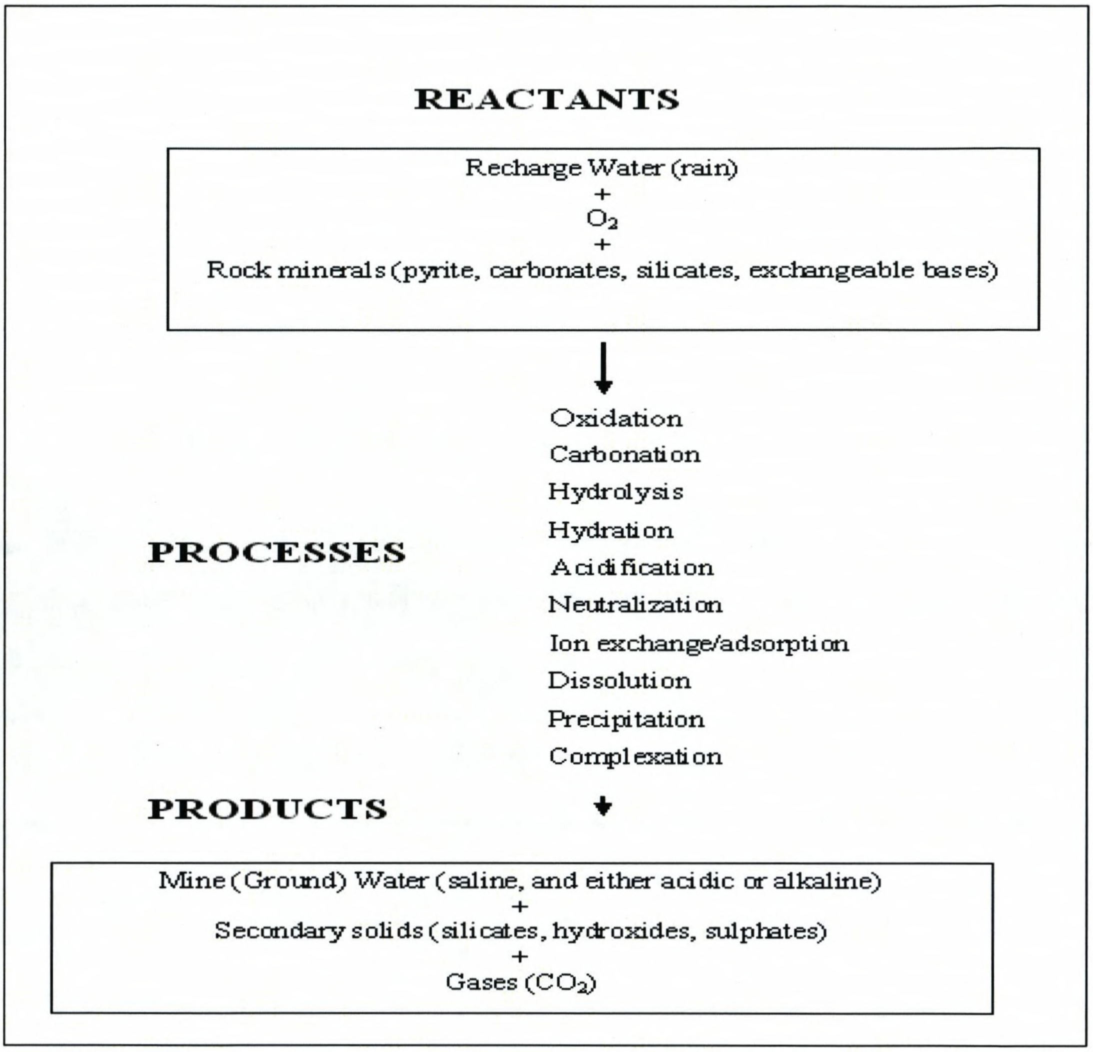


Figure 2.1 Conceptual model for the geochemical evolution of groundwater (Azzie 2002).

2.2.3 Electrochemical Evolution of Natural Groundwater

Due to exposure to atmospheric oxygen, rain water has a high redox potential when it reaches the ground. Oxidation of organic matter in the top soil removes most of the oxygen. This reduces the redox potential as the water moves deeper into the ground. Oxygen depletion will depend on the amount of organic matter, its distribution in the soil, porosity and permeability of the soil, depth of the water table, the amount and frequency of precipitation and the temperature (Murray 2009).

2.2.4 Formation of Natural Brines

2.2.4.1 Evaporation

This is more common in shallow water or margins of the sea. The sun's rays evaporate the water resulting in the solution becoming more concentrated. The process is called evaporite formation and the result is a sediment called an evaporite (Dasch and Hoyle 2009). Ground water can become saline due to circulating through evaporates (Svensson 2005).

2.2.4.2 Sea Ice

Another process by which ocean brines arise is through the formation of sea ice. As sea water begins to solidify, some of the saltier, denser water (brine) drains to underlying water. As the ice thickens, the brine can become trapped in pores known as brine pockets. This effect further concentrates the brine. Brine pockets are typically less than half a millimeter in diameter, but can extend downward into the ice for some distance (Dasch and Hoyle 2009).

2.2.4.3 Connate Water

Connate water is water that was trapped in sedimentary rocks during their formation and has become naturally saline due to water-mineral interactions. It is also known as ancient water and saline intrusion of connate water to overlying fresh water is possible, for example if there is excessive pumping (Svensson 2005).

2.2.4.4 Soil Salinisation

Soil salinisation is the continuous accumulation of salts due to quick evapotranspiration of rain or irrigation water. It can also be due to capillary rise of shallow saline groundwater. Salts can accumulate from agricultural activities during artificial fertilizer application. Saline soil causes salinisation of underlying groundwater aquifers. Soil salinisation can be minimised by setting up run-off control systems (Svensson 2005).

2.2.4.6 Coastal Saline Water Intrusion

Coastal saline water intrusion is a situation whereby sea water displaces or mixes with fresh water in an aquifer due to hydrogeological changes. It is partly natural due to the drying up of fresh water aquifers, or partly human due to excessive exploitation of wells in low lying coastal regions. It can even be caused by overpumping groundwaters further inland that have a hydraulic connection with sea water. Global warming will increase the area of dry land and raise the sea level in relation to the level of fresh water tables, increasing saline intrusion (Svensson 2005).

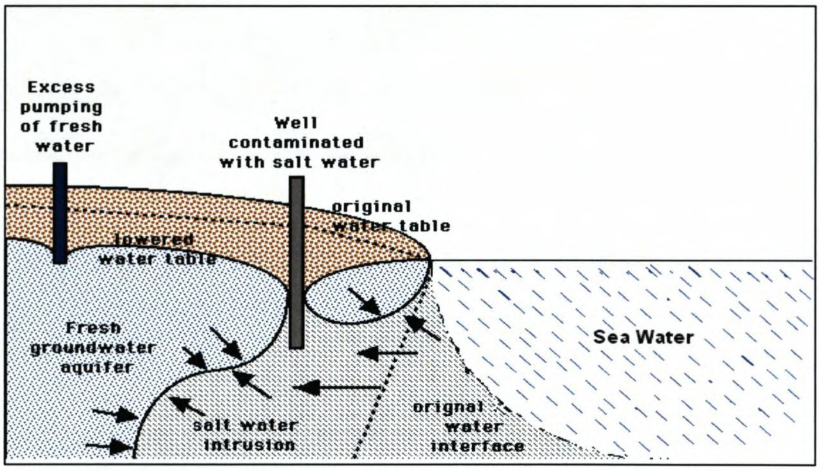


Figure 2.2: Coastal saline intrusion (Svensson 2005).

Saline intrusion is not limited to coastal areas only. It takes place in inland areas too. The difference is that in coastal areas, saline intrusion is due to the horizontal movement of water whereas in inland areas it is the vertical movement of underlying connate water. Population growth and industrialization have led to an increase in the problems of saline intrusion due to increased use of water resources in both coastal and inland areas

Saline intrusion can be managed by using the following methods (Svensson 2005).

(i) Injection barrier wells

These are wells where fresh water is injected to maintain the fresh water table at a higher level, thus preventing the sea water movement towards the fresh water body.

(ii) Extraction barrier wells

These are wells in which sea water is extracted to lower its level in relation to the water table of the fresh water. The water extracted is normally brackish and is pumped back into the ocean.

(iii) Subsurface barriers

These are physical barriers vertically mounted to stop movements of saline water. These can be steel sheets or concrete walls.

(iv) Aquifer management

Managing aquifers can be achieved by monitoring pumping activities along the coast and relocating wells where necessary. This maintains the level of the freshwater and prevents saline intrusion.

2.2.5 Artificial Brines

Discharge from desalination activities in industry into deep wells, landfills, rivers and oceans is one of the causes of salinity in water. Excessive pumping of fresh water can also induce saline intrusion as described in section 2.2.4.6.

2.3 Composition, Characterization and Classification of Brines

2.3.1 Introduction

Mankind has been concerned with water quality for a very long time. The simplest way to determine the suitability of water for drinking was by taste. With this in mind, the very early classification systems classified water into fresh, brackish and saline. This classification system has been used up until today. The use of this classification system however depends on geological locations. A person who has been drinking river water of for example 200 mg/L salinity will describe groundwater (of say 700 mg/L salinity) as highly brackish. On the other hand a desert dweller might find water at a salinity of 1500 mg/L as fresh water.

As agriculture developed, many classification systems were devised for agricultural purposes. They focused on water of salinity lower than 3000 mg/L (El-Manharawy and Hafez 2002). Industrial development in the last six decades has required new classification approaches. Highly saline water from desalination and oil and gas production plants has become a valuable natural resource that can be used in various industrial applications such as salt production and brine shrimp farming.

The growth of these industries also found the growth of problems such as metal corrosion and inorganic scale formation in their processes. With these problems, the use of describing words for classification (such as “extremely saline”) is inadequate to give an accurate chemical identification of a specific water type. Accurate chemical identification is critical in reverse osmosis desalination for the purposes of membrane selection, a water’s inorganic fouling and scaling capability as well as for the proper pre-treatment method selection. El-Manharawy and Hafez (2002) proposed a water classification system based on the grouping of natural waters that acquire similar chemical characteristics in relation to chloride concentration in mMol/kg. This system will be briefly described in section 2.3.2. In this study, the characterization of the waters shall be done using hydrochemical diagrams and Aq.QA software. Hydrochemical diagrams are aimed at facilitating interpretation of evolutionary trends in water samples. A trilinear diagram to describe water chemistry was first drawn up by Hill (1940) and was later perfected by Piper (1944). A new diagram was introduced by Durov in 1948 (Azzie 2002). The Piper diagram is widely used to study the similarities and differences in the composition of waters and to classify them into different chemical types. They show the major ion compositions in the samples. Like any other trilinear diagrams, the Piper diagram has the drawback of being incapable of showing the actual ion concentration. However this shortcoming does not lessen the usefulness of the Piper diagram (see Fig 2.4) and Durov diagram (see Fig 2.4) in the characterization of water trends.

2.3.2 Classification in Relation to Chloride Ion Concentration

El-Manharawy and Hafez (2002) proposed a system of classification in relation to increasing chloride concentration. It has four major water classes which are divided into 14 water types (Table 2.2). Low chloride water in the lower classes possesses higher dissolving capacity and can readily cause mineral leaching (El-Manharawy and Hafez 2002). However, this system of classification is relatively complicated for industrial use and it shall have limited application in this study. Nevertheless, it can be valuable in accurately describing and characterizing water samples

Table 2.2: Chemical classification system of natural waters based on chloride molar concentrations (mMol/kg) (El-Manharawy and Hafez 2002).

Class	Type	Proposed Name	Chloride (mMol/kg)	Major ions (mg/kg)						
				Ca	Mg	Na	K	SO_4	Alk[a]	TDS[b] Range (mg/kg)
Class D: Very high Chloride	14	Brine	>800	>20	>100	>800	>30	>70	<5	>60000
	13	Sub-brine	700-800	<20	<100	<800	<30	<70	<5	50000-60000
	12	Very salty seawater	600-700	<20	<80	<600	<15	<60	<5	40000-50000
	11	Seawater	500-600	<20	<60	<500	<10	<50	<5	30000-40000
Class C: High Chloride	10	High salty	200-500	<25	<35	<400	<10	<40	<10	15000-30000
	09	Medium salty	100-200	<30	<20	<200	<6	<30	<15	1000-15000
	08	Low salty	50-100	<25	<15	<100	<4	<25	<20	7000-10000
Class B: Medium Chloride	07	High Brackish	25-50	<20	<10	<70	<3	<20	<30	4000-7000
	06	Medium brackish	10-25	<10	<6	<40	<1.5	<10	<25	2000-4000
	05	Low brackish	3-10	<5	<5	<20	<1	<5	<20	1500-2000
Class A: Low Chloride	04	High fresh	1.5-3.0	<3	<2	<10	<0.5	<2	<15	1000-1500
	03	Medium fresh	1.0-1.5	<2.5	<1.5	<5	<0.4	<1.5	<10	600-1000
	02	Low fresh	0.5-1.0	<2	<1	<3	<0.3	<1	<8	300-600
	01	Very low fresh	<0.5	<1	<0.5	<1.5	<0.2	<0.5	<4	<300

Alk[a]: is the sum of alkalinity ions (= $OH^- + CO_3 + HCO_3^-$)

TDS[b] in mg/kg are estimated for guidance purposes

One advantage of classifying waters by the chloride ion concentration is that chloride is very conservative chemically. The total ion concentration does not change with reactions involving other ions. It is therefore a good water tracer, unlike sulphate, for example, which is depleted by reactions (Ghanem 2005).

2.3.3 Other Classification Systems

The following classification systems are also used in the health, agriculture and industrial applications:

2.3.3.1 World Health Organization Water Classes

In 1988 the World Health Organization published the chemical and biological guidelines for drinking water quality and they classified natural potable waters according to salinity in mg/L as follows

Table 2.3: Classification of drinking water according to salinity in mg/L (WHO, 1988).

Class	Salinity (mg/L)
Excellent	< 300
Good	300 – 600
Fair	600 – 900
Poor	900 – 1200
Unacceptable	> 1200

2.3.3.2 The Texas University Agricultural Services Water Classes

In 1996 The University of Texas Agricultural Services set guidelines for water quality to be used in irrigation and fields of economically valuable foliage and flowering plants as given in the table below.

Table 2.4: Classification of irrigation water (TUAS, 1996).

Class	TDS (mg/L)	Na (% of TDS)	SAR[a]	pH
Excellent	< 175	< 20	< 3	~ 6.5
Good	175 - 525	20 - 40	3 - 5	6.5 – 6.8
Permissible	525 - 1400	40 - 60	5 - 10	6.8 - 7
Doubtful	1400 - 2100	60 - 80	10 - 15	7 - 8
Unsuitable	> 2100	> 80	>15	> 8

SAR[a] = Sodium Adsorption Ratio = sodicity = $Na \div \sqrt{[(Ca + Mg) \div 2]}$
The concentration of Na, Mg and Ca is in meq/L

2.3.3.3 The United States Geological Survey (USGS, 2000) Water Classes

The US Geological Survey (USGS) classified natural waters in 2000 based on the total salinity measured as TDS in mg/L. The following table shows the categories in which natural waters can fall.

Table 2.5: Classification of natural waters according to salinity in mg/L (USGS, 2000).

Class	TDS (mg/L)
Fresh	< 1000
Slightly saline	1000 - 3000
Moderately saline	3000 - 0000
Highly saline	10000 - 35000

2.3.4 Characterization of Water Chemistry

2.3.4.1 Water Type Characterization Using Aq.QA Software

Aq.QA is software developed for water chemists by the geological company Rockware Incorporated in the United States of America. The water type, for example $Na\text{-}SO_4$ or $Ca\text{-}HCO_3$ is determined by obtaining the predominant inorganic cation and anion in the sample based on electrical equivalents. In determining the water type, Aq.QA accounts whenever possible for carbonate speciation in solution using the sum of equivalents of the CO_3^{2-} and HCO_3^- concentrations to represent carbonate. The software also calculates, if pH is given, the free ion concentration of H^+ and OH^-, and accounts for these species when assigning a water type. For example, an acidic water sample might be categorized as H-SO_4 or an alkaline one as Ca-OH.

2.3.4.2 Characterization by Hydrochemical Diagrams

Graphing water analyses is an important part in the interpretation of data obtained from field samples. Early efforts are discussed in Section 2.3.1. Graphing data provides an easy way of visualizing trends, but "*graphing of water analyses is a study technique and not an end itself*". This is an important concept by Hem, 1985.

(i) Stiff Diagrams

Stiff diagrams show the composition of a single sample in terms of common cations and anions. The concentrations are represented in meq/L and are plotted on four parallel horizontal lines. Concentrations of up to four cations and anions can be plotted, one each to the left or right of the centre zero axis. The resulting points are connected to give an irregular polygon pattern. Stiff diagram patterns can be a relatively distinct method of showing water-composition similarities and differences. They can also show what has been added or removed from a water.

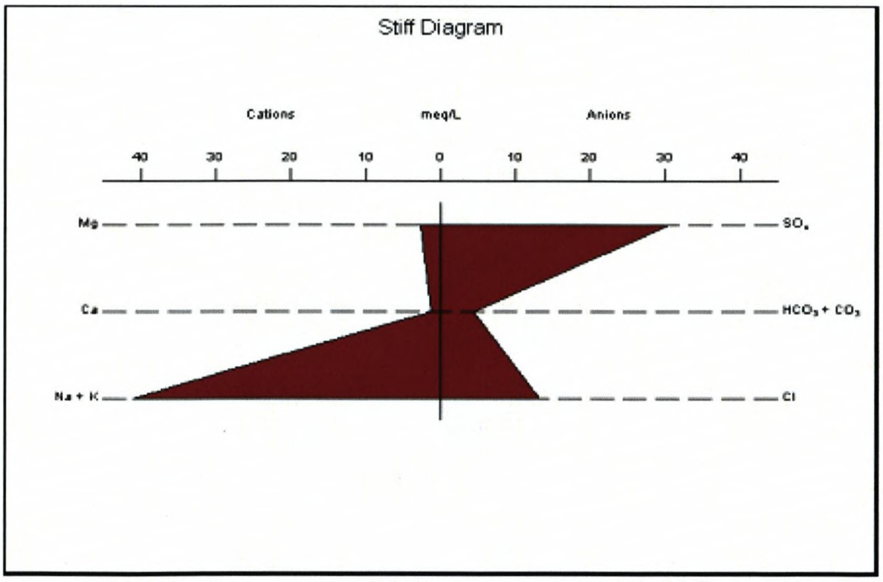


Figure 2.3: The Stiff diagram of a Tutuka Power Station water sample.

(ii) Piper Diagrams

The Piper diagram helps water chemists to display groupings of water types. Major ions are plotted as cation and anion percentages in meq/L in two base triangles. Total ions are set to equal 100 %. Data points in the two base triangles are then projected to a central diamond allowing the comparison of a large number of samples. It shows the clustering of samples and the water types involved. A water sample that is a mixture of two samples will lie in a straight line between the two end members on all three parts of the Piper diagram. However this concept has drawbacks in that post-mixing reactions such as dissolution, ion exchange and precipitation may obscure the mixing trend and therefore must be used with caution.

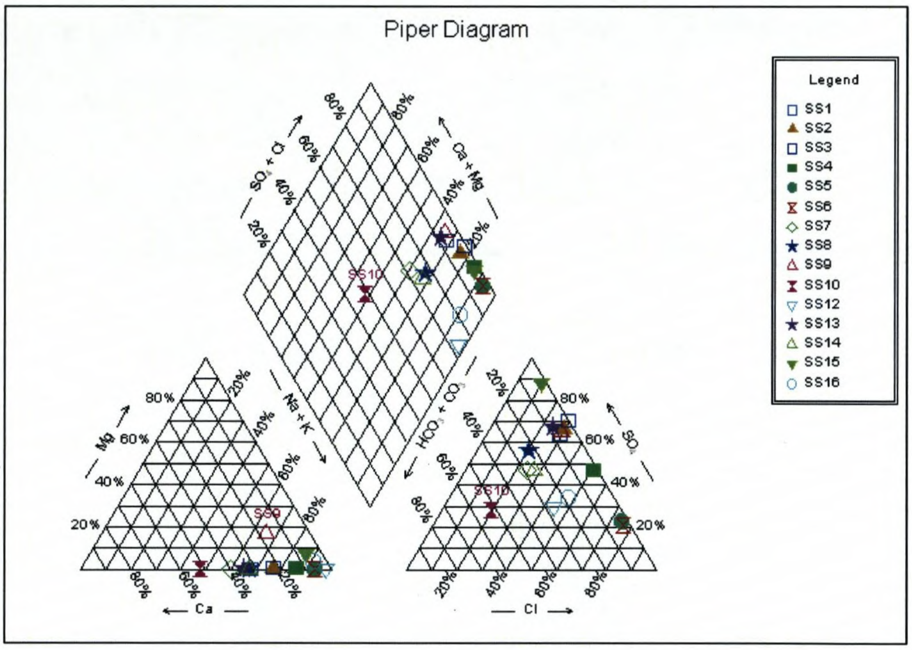


Figure 2.4: The Piper diagram showing samples from Sasol Synfuels Complex in Secunda.

(iii) Durov Diagrams

Durov diagrams are an alternative to the Piper diagram. This type of diagram plots the major ions as percentages of milli-equivalents in two base triangles. The total cations and the total anions are set equal to 100 % and the data points in the two triangles are projected into a square grid which lies perpendicular to the third axis in each triangle. TDS and pH can also be plotted in two separate rectangles as shown the in Fig 2.5 below. This type of plot reveals useful properties and relationships for large sample groups. The major use of this diagram is to show clustering of data points to indicate samples that have similar compositions.

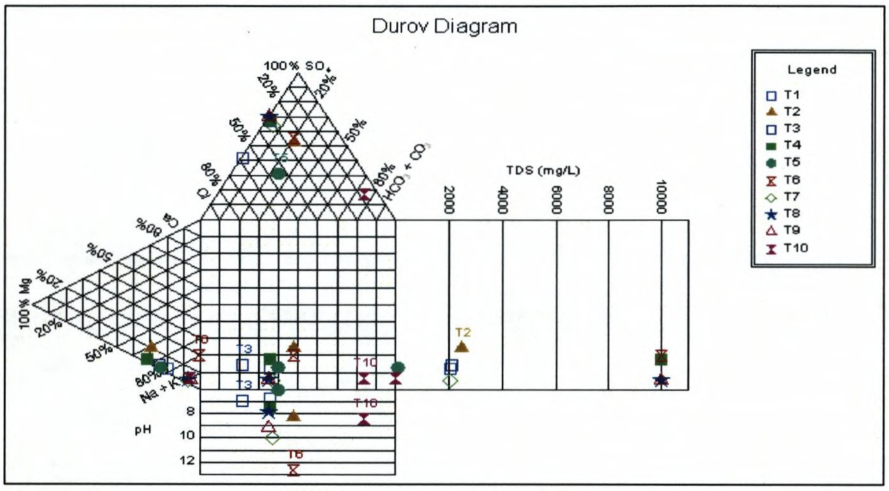


Figure 2.5: The Durov diagram showing samples from Tutuka Power Station.

2.3.5 Composition of brines

Brines contain various cations and anions depending on their origins as discussed earlier. They generally contain calcium, magnesium, sodium, potassium, bromide, iron, silica, chloride, ammonia, bicarbonate, nitrate, sulphate, fluoride, trace elements and a pH of approximately 7.5. Some brines may also contain heavy metals and even organic contaminants.

2.4 Uses of Brines

The traditional approach to deal with saline effluent has been to treat it as a waste disposal problem. However, a number of opportunities have been opened after realizing that these effluents are a resource. Saline effluents can be used in agriculture, forestry, fauna, algae and mineral production. A few of these processes are reviewed in this subsection.

2.4.1 The SAL-PROC Process

This is a process in which chemical products in crystalline, slurry and liquid forms are extracted from inorganic saline waters. It involves multiple evaporation and/or cooling aided by mineral and chemical processing. No hazardous chemicals are added during processing and the closed fluid flow circuits are simple with minimal waste discharge requirements. It is also a process that has seen more than 10 years of technological development and is capable of treating large amounts (Ahmed et al., 2003) of effluent to produce commercially valuable chemical products while achieving zero liquid discharge to the environment.

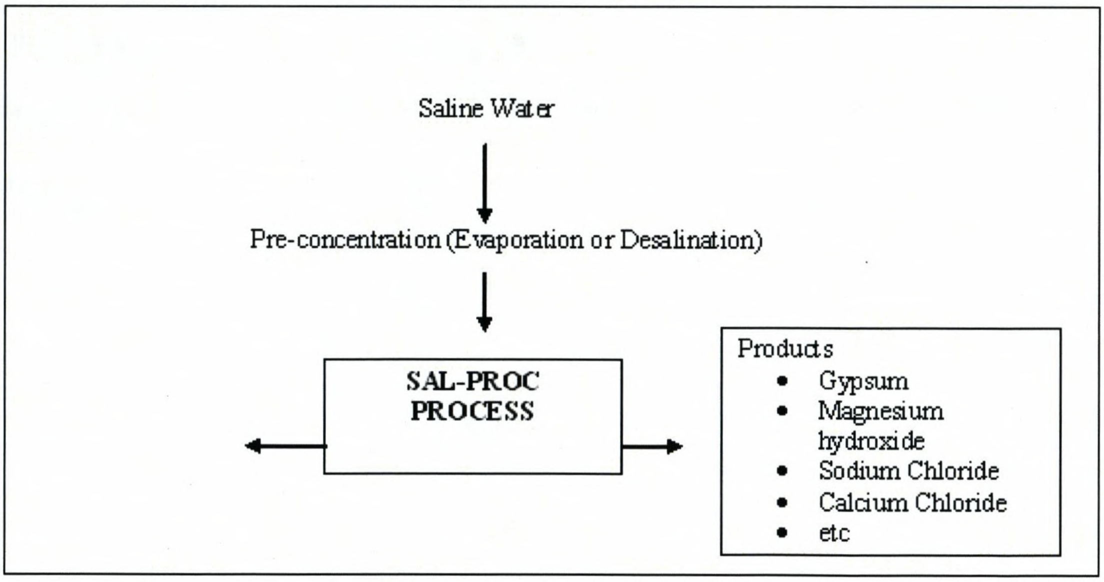


Figure 2.6: A typical SAL-PROC process.

Chemicals produced by this process are of high quality and in demand as shown in Table 2.6.

Table 2.6: List of commercial products that can be recovered depending on the composition of the feed water (Svensson 2005).

Products	**Physical features**	**Application areas**
Calcium carbonate, $CaCO_3$	Fine grain, crystalline	Paper coating pigment, Filler for paper manufacturing rubber and paint
Calcium chloride, $CaCl_2$	Concentrated solution	Dust suppressants Sodic soil remediation Construction industry Cement, concrete stabilizer Road stabilizers
Caustic soda, NaOH		Many industrial applications pH buffering Feedstock for chemical processes
Gypsum, $CaSO_4$		Manufacturing of building products Sodic soil remediation Evaporation pond liners
Gypsum and magnesium $CaSO_4.2H_20 + Mg(OH)_2$	Slurry or powder	pH buffering Soil conditioner Wastewater treatment
Halite, NaCl	Crystalline salt	Chlor-alkali production Bulk salt supply for industries Food and industrial processes
Magnesium carbonate $XMgCO_3$.	Fine grain, crystalline	Magnesium metal production Filler for paper manufacturing rubber and paint Fire retardants
Magnesium hydroxide, $Mg(OH)_2$	Slurry or powder	Animal stock feed Fire retardants Acid neutralization Magnesium metal production Water, wastewater treatment
Soda ash, Na_2CO_3		Chemical industry Water treatment
Sodium chlorate, $NaClO_4$		Paper bleaching Chemical industries
Sodium hypochlorite, $NaOCl_4$		Chemical industries Disinfection Pool chlorine
Thenardite, Na_2SO_4		Detergents, glass and surfactants manufacture

2.4.2 Re-use for Agriculture

2.4.2.1 Irrigation

Saline effluents can be used to irrigate some plants. The main considerations to be made are that the plants are salt-tolerant and that the chemical concentrations in the effluent will not contaminate the soil and groundwater. The chemical content allowable should be dictated by vegetation tolerance and underlying groundwater salinity. One factor to consider if using it for irrigation is that there should be an alternative use for the brine or an alternative disposal method during periods of sufficient or more than sufficient rainfall. The criteria for using brine for irrigation should therefore be site selection, pre-treatment method, land requirements, loading rates, vegetation tolerance and runoff control (Svennson 2005).

2.4.2.2 Fish Culture

Brine can be disposed of in evaporation ponds and to reduce costs, productive activities such as fish farming can be set up. Fishes like Red Snapper, Barramundi, Black Bream, Milk fish, Mullet and Tilapia (Svensson 2005) can thrive in highly saline water.

2.4.2.3 Algae Production

Algae is used in the production of commercial grade beta-carotene and it can grow in saline water in excess of 200 mg/L salinity (Svensson 2005).

2.4.2.4 Brine Shrimp Production

Brine shrimp and fish production can be synergized as the shrimp can utilize the nutrients produced by the fish and excess shrimp can be fed to the fish. Saline effluent ponds are ideal for shrimp because the salinity is high and no predators or other competitors can survive and it becomes a monoculture (Ahmed et al., 2001).

2.4.3 Electricity and/or Heat Generation

Salinity gradient solar ponds can be used with evaporation ponds as yet another synergy. These collect solar energy and store it for a long time. They can provide thermal energy ranging from 50 to 90 degrees Celsius or electricity (Walton et al., 2001). The pond has three zones or layers. The first layer at the surface of the pond is known as the upper convective zone (UCZ) and the water in this zone contains 1-4 % salt by weight (Walton et al., 2001). The thickness of this layer should be around 0.3m as increasing it reduces the ability to store heat (Ahmed et al., 2001). The middle layer is called the non-convective zone (NCZ) and is the insulating layer as the salinity gradient goes from higher to lower concentrations as you approach the surface (Walton et al., 2001).The thickness of this layer can be between 0.5 – 1.5 m (Ahmed et al., 2001). The lower zone is called the lower convective zone (LCZ) and contains near saturated or saturated brine with about 26 % salt by weight (Walton et al., 2001).

The energy from the sun that reaches the lower (LCZ) can only escape by conduction. The conductivity in water is low and if the insulating layer has an optimal thickness, the heat loss from the LCZ will be very low. Due to the high heat capacity of water, a large volume of water in the pond and the insulating non-convective zone (NCZ), the pond can collect energy and store it for a long time. For electricity generation, the generator requires a temperature of above 85 ^{o}C (Walton et al., 2001) to run efficiently. However the thermal efficiency is affected by the clarity of the saline effluent, the thickness of the zones, the salt gradient, the pond area and maintenance of the vertical salt gradient (Svensson 2005). A 10000 m^2 solar pond in Victoria (Australia) produced 200 000 kWh of electricity per year (Ahmed et al., 2001). Solar ponds evolved from the conceptual zero-discharge desalination plant as shown in the schematic diagram below.

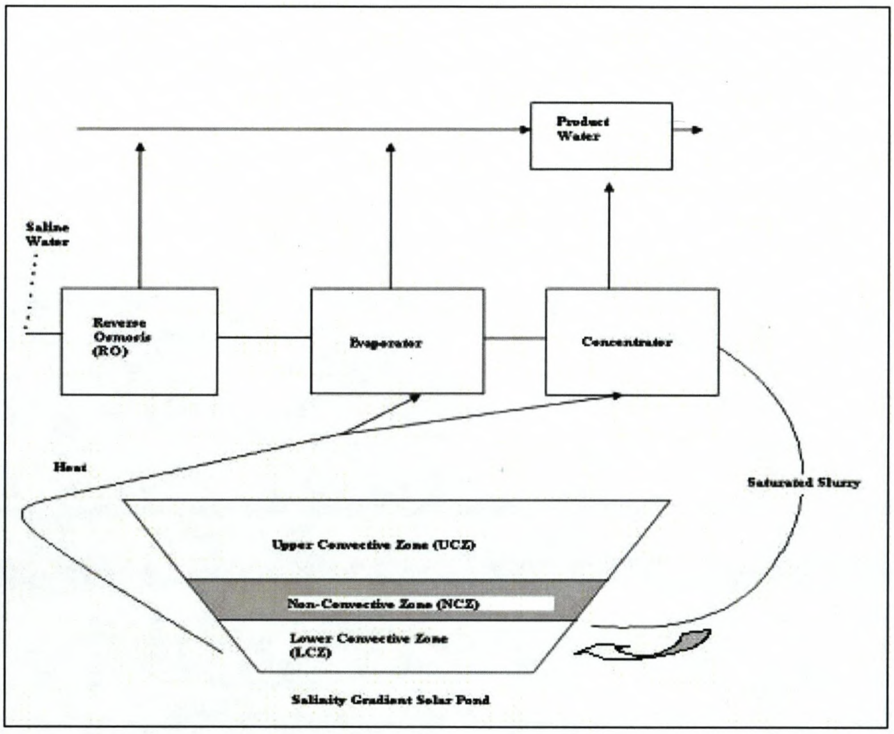


Figure 2.7: Schematic diagram showing solar ponds in zero-discharge desalination (Rife 2002).

2.5 Brine Disposal Methods

Desalination plant engineers have to consider several issues before the plant can be set up to operate in a way that can safeguard the environment. The most important environmental issues are the location of the plant, brine disposal methods and energy considerations (Tsiourtis 2001). The location should obviously be within an economical distance from the feed water source and the energy supply. For the disposal of the brine, the methods to be used are a very important consideration. The main scenarios regarding brine disposal are inland located plants and coastal located plants. Coastal located plants have the simplest and least costly (Svensson 2005) way of disposal, i.e. by discharging back into the sea. In inland locations, alternative methods have to be used that will decrease the economical and environmental impacts of desalination. The major ways of disposing brine at inland sites are; 1.

Deep well injection 2. Evaporation ponds 3. Zero liquid discharge. Several other methods have been proposed but many of the approaches are limited. Some of these approaches have been discussed under the uses of brine and some will be briefly discussed here.

2.5.1 Disposal in Inland Desalination Sites

As discussed earlier, the use of inland brackish water in desalination as a process for water recovery is increasing but the major bottleneck for an inland plant has been the disposal of the resulting brine. There are numerous recognized ways of disposing the brine and some are being investigated but they are all site-specific. A brief review of various brine disposal methods follows.

2.5.1.1 Deep Well Injection

This method of disposal has been used worldwide (Glater and Cohen 2003). It involves injecting the brine into deep wells containing non-drinkable water. It is only practical where wells with consolidated aquifers are available. This method presents a considerable uncertainty of the environmental impact. It is also a very expensive procedure (Svensson 2005).

2.5.1.2 Aquifer Re-injection

This involves returning the brine into the same source of feed water to the desalination plant. It is therefore applicable to smaller plants and the impact of salinity increase in the feed water can be minimized by re-routing some of the brine to other disposal methods or uses. Tutuka Power Station in South Africa has started using this method where some of their saline effluent is re-injected into the nearby New Denmark Coal Mine where mine water used as feed for their desalination plant emanates. However, the important considerations in this method are the size of the aquifer, salt concentration in the aquifer and the predicted total salt load that is returned (Svensson 2005). It is also important that the intake well and the re-injection well should have an adequate distance between them in order to restrict feed water quality deterioration.

2.5.1.3 Discharge to Wastewater Treatment Plants

This is a viable method if the desalination plant is located near a wastewater treatment plant. The most important consideration will be the effect of the brine on equipment, piping, filtration processes, environmental regulations and the composition of the brine.

2.5.1.4 Discharge to Sewage System

This is suitable to smaller plants or where it is part of several disposal options. It has the advantage of having a dual purpose of dilution. It however can make the mixed wastewater undesirable for irrigation (Ahmed et al., 2000).

2.5.1.5 Discharge to Open Land

The brine is simply pumped onto an open land "natural pond". This method will lead to the contamination of groundwater.

2.5.1.6 Discharge to Inland Surface Water

Disposing brine into rivers and lakes is not an environmentally viable option and is not permitted in South Africa.

2.5.1.7 Evaporation Ponds

These have been around for centuries as they have been used to generate salt. For brine disposal purposes, the ponds are used to concentrate the brine until precipitation of salts occur at the attainment of solubility limits. The factors that determine the costs of evaporation ponds are land costs, earthwork, lining, operation and maintenance and seepage monitoring. It is more economical (Svensson 2005) to build a number of smaller ponds connected to each other by pipes than one big one to minimize wave damage to levees and the smaller ones are easier to manage. High salinity in the brine decreases the evaporation rate (Ahmed et al., 2000), therefore the more saline the effluent, the more land is required. The evaporation rate can be enhanced by increasing the temperature. This can be done by introducing dyes into the brine. Using Naphthol green dye at a concentration of 2 ppm can increase the evaporation by 13 % (Ahmed et al., 2000). An algae species can also be grown in the pond which will cause the colour of the pond water to turn green (Svensson 2005). This colour change will also improve the evaporation rate. Aquasonics is a company that has developed and patented another method to enhance evaporation. The brine is sprayed through nozzles at high velocities creating drops of specific shapes and sizes with evaporation taking place inside milliseconds (Svensson 2005). This is due to increased surface area exposure to the atmosphere. The rate of evaporation depends on the size of the drops, velocity of the drops and atmospheric conditions and the brine concentration. During evaporation, the salts are flashed out leaving crystal flakes and water vapour which is collected. This technique can be used at saturated brine levels (25 % salinity) (Svensson 2005).

2.5.1.8 Zero Liquid Discharge

Zero liquid discharge is brine treatment in which only a dry end product is recovered with no liquid being discharged into the environment. The use of technologies like the SAL-PROC process discussed earlier in this chapter is one way of achieving zero discharge. Spray evaporation is another. The disposal of the dry end product is much more economically viable than disposing a liquid. Disposing this dry waste is normally done by depositing it into approved salt sinks or sites, in mines or the sea.

2.5.2 Disposal in Coastal Desalination Sites

Discharge into the sea is the disposal method almost used by all desalination plants near or at the coast. The main consideration is that there should be enough distance between the intake point and the outlet point to avoid feed water deterioration. Marine life is also affected by disturbances that occur in the area surrounding the brine outlet (see section 2.7.1).

2.5.3 Disposal at Tutuka Power Station and Sasol Secunda: Local Scenario

At Tutuka Power Station, brine is disposed of onto dry ash dumps. Tutuka Power Station has recently (by April 2008) started dumping brine into deep wells (about 270m deep) at the nearby New Denmark Coal Mine. The brine is also used to condition ash prior to transporting it to the ash dumps to prevent dust problems. The cementing properties (pozzolanic properties) of the ash are thought to enable the salts in the brine to be bound in the ash preventing rapid leaching of the salts, a practice that has not yet been proven to be sustainable. The volumes of brine produced are large. For example, Tutuka Power Station treats 16.8 Ml/day of water of which about 15 % becomes brine. Tutuka Power Station therefore has to dispose 2.52 Ml/day of brine from Tutuka Power Station.

The Sasol Synthetic Fuels Complex handles its brine in a slightly different manner. The brine and the ash are mixed to form a slurry (with 20 % solids) which is pumped into ash dams. The ash settles and the brine percolates into clear effluent dams where the salty water is recycled back to TRO treatment. Sasol Secunda discharges 20.7 Ml/day of brine from the TRO plant.

2.6 The Treatment of Brines

Water treatment is the alteration of water of a certain quality in order to achieve a quality that meets specified applications. Brine contains different contaminants, depending on their origin, which must be removed before it can be used for any beneficial industrial application. Getting rid of the by-product of brine treatment is costly because of its make-up and also because of the large amounts that may need to be handled, depending on the size of the treatment plant.

2.6.1 Desalination Technologies

Desalination is a process that separates high salinity water into a more concentrated stream and a less concentrated stream. A number of technologies have been developed for desalination including reverse osmosis (RO), nanofiltration (NF), distillation and electrodialysis reversal (EDR).

Figure 2.8: The Desalination Process.

2.6.1.1 Reverse Osmosis (RO) and Nanofiltration (NF)

Pressure driven membrane techniques have become economical and they compete successfully with traditional thermal applications such as distillation (Vavra and Petriciolet 2004). However, where the membrane techniques are to be used, a thorough investigation is supposed to be undertaken to evaluate the contaminants in the feedwater for that particular site. This information is critical for the choice of the most suitable membrane technology to be used for optimal performance and the pre-treatment methods to be employed. This also gives the idea of the service life of the plant in general and guidance on optimal processing parameters. The feedwater contaminants will end up in the brine concentrate unless removed.

In reverse osmosis, feedwater is pumped at high pressure through semi-permeable membranes, separating salts from the water. Nanofiltration is a similar process that works at lower pressures. The feed water is pre-treated by use of pre-treatment methods such as ultrafiltration (UF) and microfiltration (MF) to remove suspended solids, organics, bacteria and metals that may oxidize or precipitate and clog the membranes. The reverse osmosis membrane permits the passage of water molecules but it is a barrier to most of the dissolved salts. The quality of the produced water depends on the pressure, the concentration of salts in the feedwater and the salt permeation constant of the membranes (Buros et al., 1987). Product water quality can be improved by adding a second set of membranes whereby the product from the first membrane set is fed into the second set. Reverse osmosis systems can remove most dissolved substances (von Gottberg et. al 2001). On the other hand, nanofiltration systems mainly remove divalent ions and organics. Another advantage of reverse osmosis is that it is an absolute barrier to bacteria and pathogens. It is therefore ideal for treating water for direct consumption.

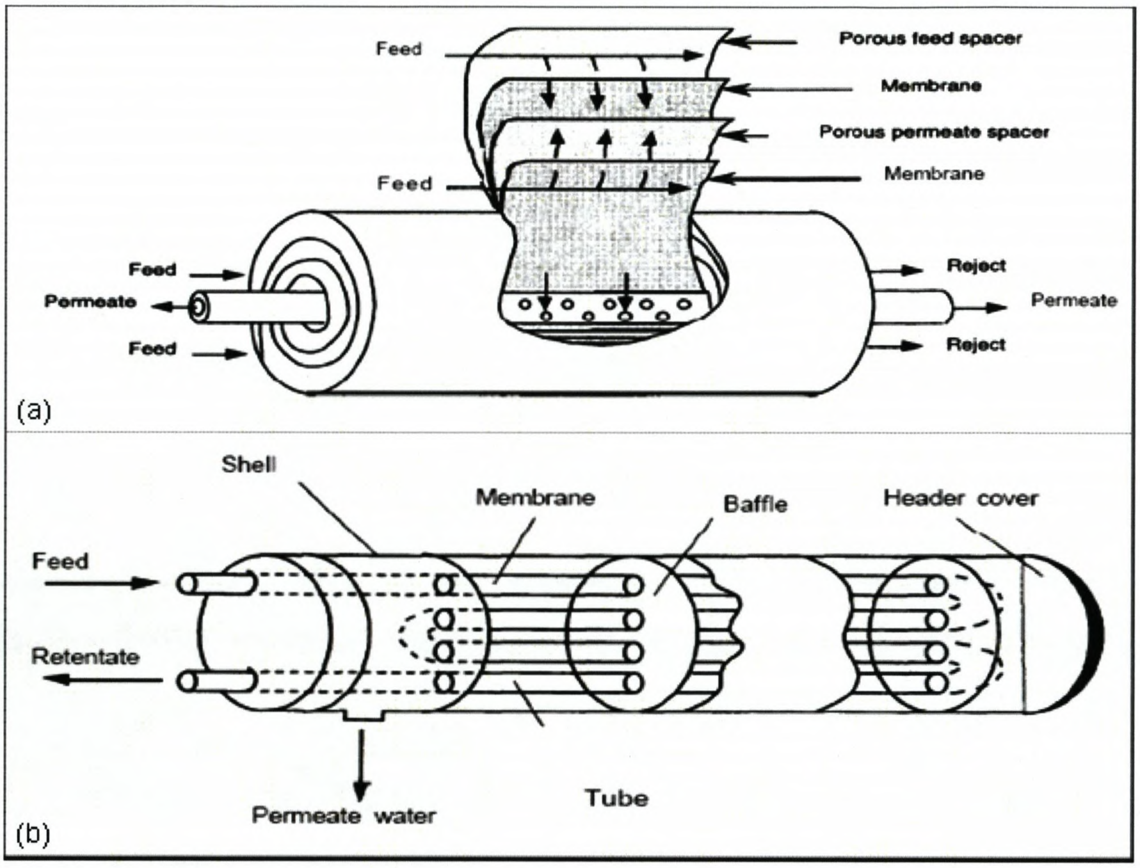


Figure 2.9: RO membranes; (a) Spiral wound and (b) Tubular (USEPA 1996).

The most common types of membranes used in reverse osmosis are the spiral-wound (SRO) and the tubular (TRO). The spiral type [see Fig 2.9 (a)] uses a sandwich flat sheet membrane and supports, wrapped spirally around a collection tube. The feed flows in against one end of the rolled spiral support and along one side of the membrane sandwich. The support layers are designed to minimize pressure drop and allow a high packing density. They can be designed to promote turbulence and therefore increase mass transfer across the membrane (USEPA 1996) or provide uninterrupted flow path to decrease membrane fouling (USEPA 1996). Spiral reverse osmosis membranes offer greater packing densities than tubular reverse osmosis membranes but they require regular maintenance (USEPA 1996).

Tubular reverse osmosis membranes [see Fig 2.9 (b)] have their membranes supported within the inner part of tubes. The operators of a plant utilizing tubular reverse osmosis can easily service feed and permeate (product water) channels to remove fouling layers. They are to a certain extent resistant to fouling when operated with a turbulent feed flow which may be attained by the larger flow channels than those in the spiral type. However the drawbacks with the tubular membranes are the high energy requirements for pumping large volumes of water at high velocity for turbulent flow, high capital costs and low membrane surface area per unit volume of module or column.

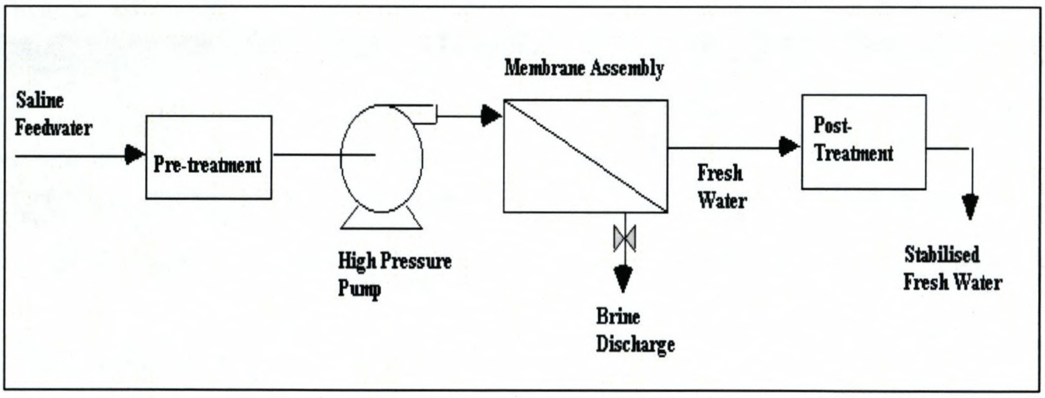


Figure 2.10: Flow Diagram of a reverse osmosis system.

2.6.1.2 Distillation

In the distillation process, the saline feed is heated and then evaporated to separate out dissolved salts and recover water. The most common methods of distillation include multistage flash (MSF), multiple effect distillation (MED) and vapour compression (VC).

(i) Multistage flash distillation

In multistage flash distillation, the feedwater is heated and the pressure is lowered so that the water "flashes" into steam. This process constitutes one stage of a number of stages in series, each of which is at a lower pressure than the preceding stage.

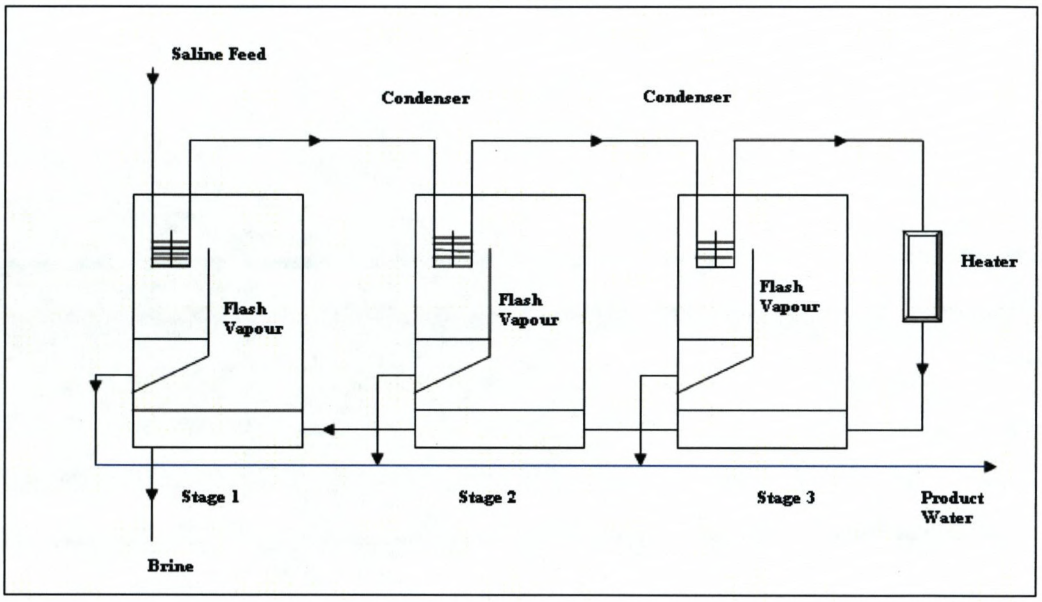


Figure 2.11: Multistage flash distillation (Clayton 2006).

(ii) Multiple effect distillation

In multiple effect distillation, the feedwater passes through a number of evaporators in series. Vapour from one series is subsequently used to evaporate water in the next series.

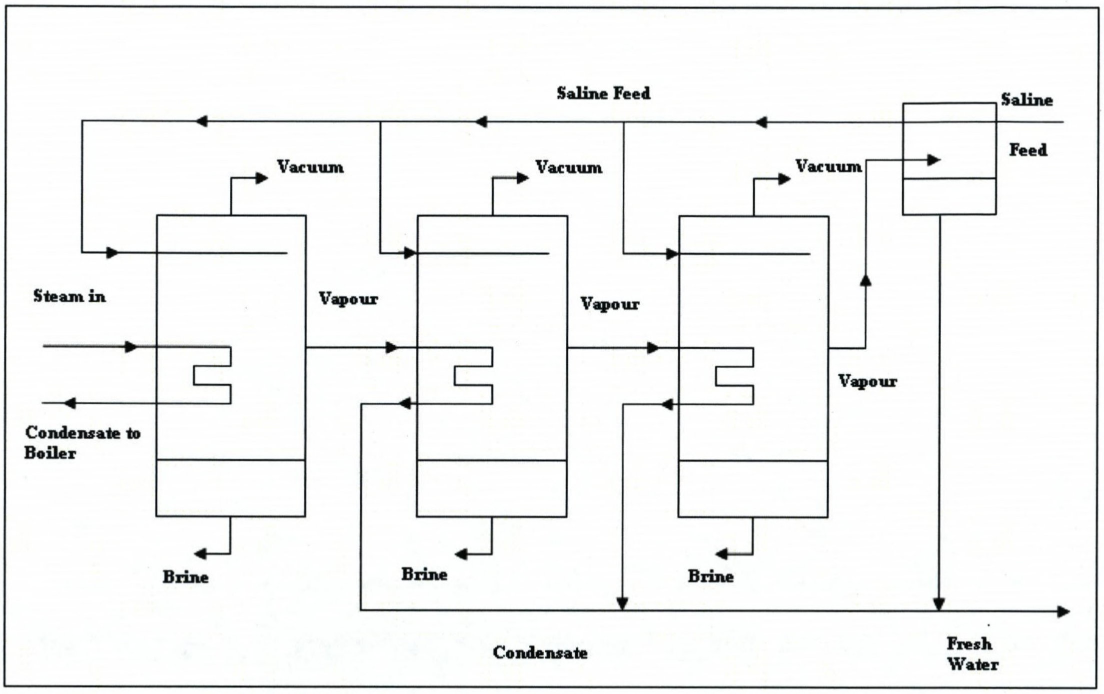


Figure 2.12: Multiple effect distillation (Clayton 2006).

(iii) Vapour Compressor (VC)

The vapour compressor involves evaporating the feedwater, compressing the vapour, and then using the heated compressed vapour as a heat source to evaporate additional feedwater.

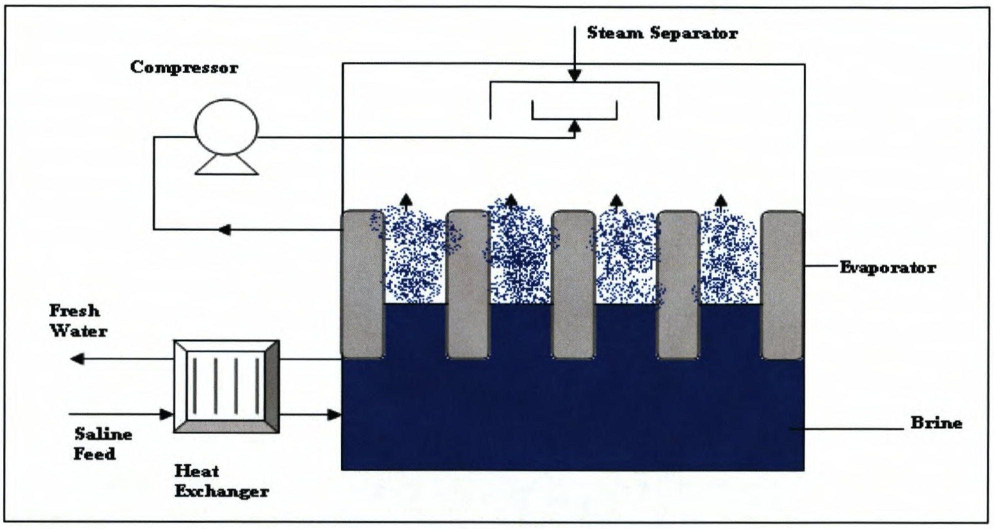


Figure 2.13: Vapour Compression distillation (Clayton 2006).

2.6.1.3 Electrodialysis Reversal (EDR)

Electrodialysis is an electrically-driven process that uses an electrical difference to drive charged ions through a semi-permeable membrane, reducing the TDS in the feedwater. This process uses alternating, semi-permeable cation and anion transfer membranes in a direct-current (DC) voltage potential field. Feedwater flows between the cation and anion membranes. Spacers are used to create pathways for the feedwater, support the membranes and create turbulent flow. The DC voltage potential creates movement of cations to the anode through the anionic membrane and anions to the cathode through the cationic membrane. The system periodically reverses the polarity and consequently the product and brine compartments. This helps flush scale forming ions off the membrane surface and minimizes membrane fouling (von Gottberg et al., 1998). EDR is typically used on hard-to-treat, hard, lower salinity waters (from 200-5000ppm TDS) (von Gottberg et al., 2001).It can handle higher saturation levels of precipitating compounds allowing it to achieve higher water recoveries than reverse osmosis, (up to 95 % recovery with 90 % salt recovery has been achieved) (von Gottberg et al., 2001).Electrodialysis reversal is also tolerant to residual chlorine of 0.5 mg/L (von Gottberg 2001). Electrodialysis has been practiced in South Africa since 1958 but its energy demands are a limiting factor except where such energy is abundant (Mason 1957).

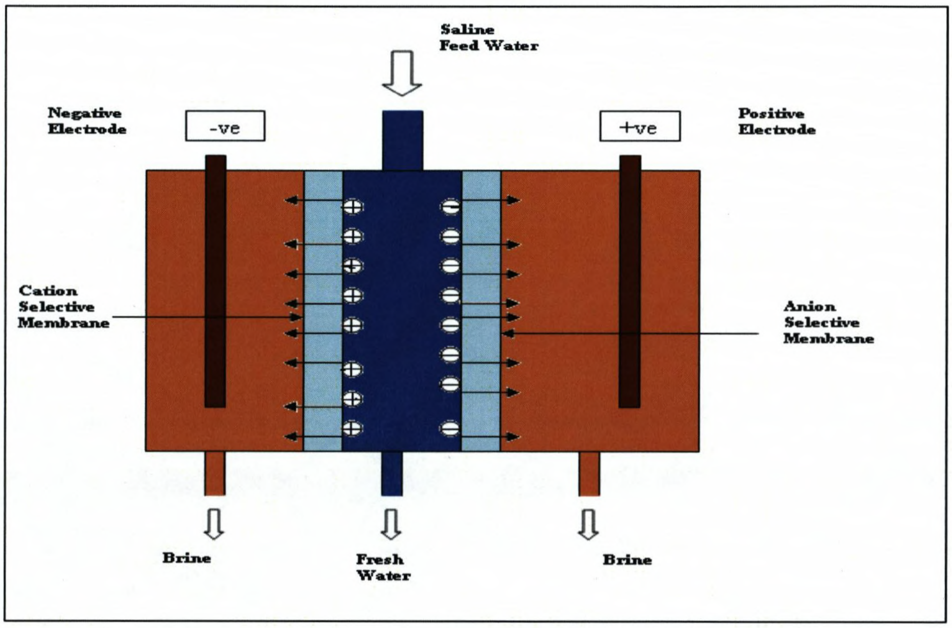


Figure 2.14 Electrodialysis Reversal Desalination.

2.6.1.4 Eutectic Freeze Crystallisation

Eutectic freeze crystallisation (EFC) is an alternative to evaporative crystallisation for separating salts from solutions. Evaporation of water is costly due to the amount of heat required. Eutectic freeze crystallisation is one of the desalination technologies that have received very little attention recently. The principle of EFC is explained in Fig 2.15.

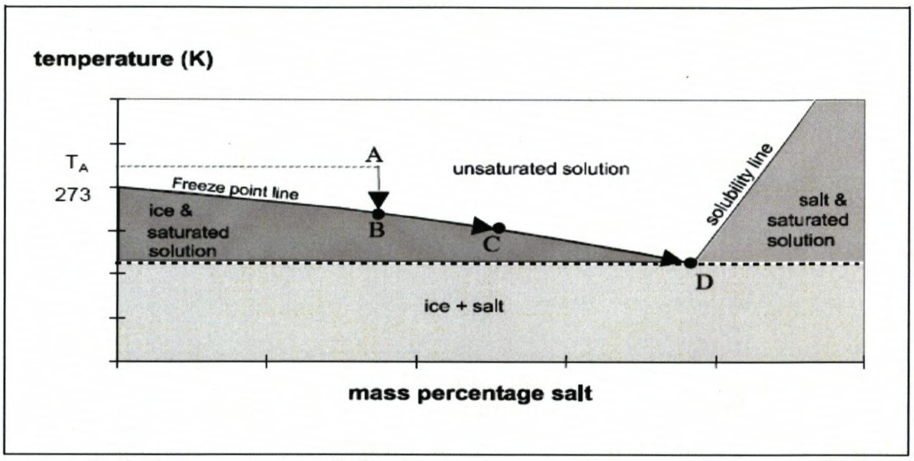


Figure 2.15: The principle of eutectic freeze crystallisation (Seckler et al., 2002).

If a solution indicated by point 'A' in Fig 2.15 is cooled below 265K, ice starts to form at point B. If cooling continues, more ice is formed and the solution becomes more concentrated. The composition then moves from B to C until it reaches D (the eutectic point). At D the solution is saturated and further cooling leads to formation of pure ice and salt as separate crystals. The density difference between ice and a salt is typically about 1000 kg m^{-3}. It is therefore possible to separate the two solids simply by gravity. Fig 2.16 shows a schematic diagram of eutectic freeze crystallisation.

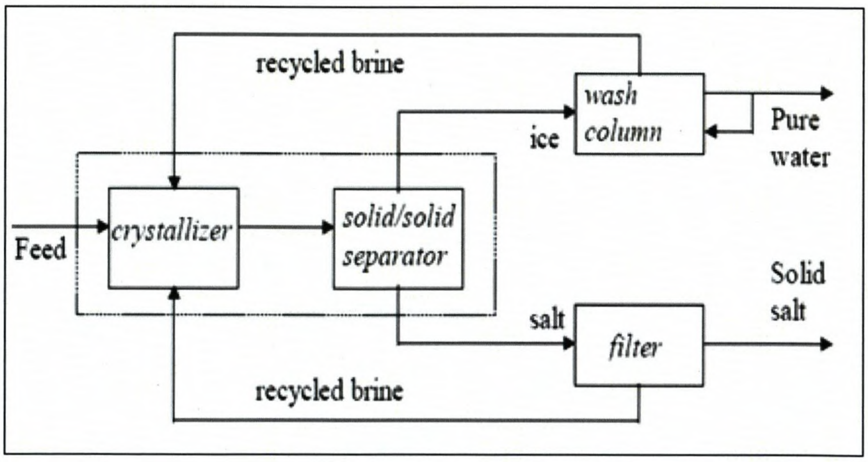


Figure 2.16: A schematic diagram of eutectic freeze crystallisation (Seckler et al., 2002).

The waste product or retentate from these processes is a solution with very high salt concentration. Distillation plants produce high quality product water ranging from 1.0 to 50 mg/L TDS, while RO plants produce a product water ranging from 10 to 500 mg/L TDS (Pantell 1993). If produced for domestic consumption, post-treatment may be employed to ensure that the water meets the health standards for drinking water as well as the recommended aesthetic and anti-corrosive standards.

2.7 Brines and the Environment

Constituents of brines from desalinations plants depend on the desalination technology used, the quality of water produced, the pre-treatment methods used, the cleaning and flushing methods used, the quality of the feed water available etc. The environmental considerations of desalination plants are shown in the table below (Mohammed et al., 2004).

Table 2.7: Environmental considerations of desalination plants.

Category	Impact
Energy: Burning fossil fuels to generate power for desalination plants	Human health, Climate change, Noise level
Land use	Land degradation, Affects soil properties
Desalination reject brine	Affects marine life, Affects animal and human life, Affects plants, Contaminates groundwater

2.7.1 Effects of Brine on Marine Organisms

Where ocean disposal is practiced, marine disturbances in the area surrounding the brine outlet occur. Brine is denser than sea water and therefore sinks to the bottom of the ocean in the form of a plume. There is always an osmotic balance between marine organisms and their surroundings (Svensson 2005). A salinity gradient can have a great effect on plankton as it can cause dehydration of cells and eventually death

(Einav et al., 2003). The extent, to which salinity gradient affects marine organisms, varies from species to species and the age of the affected organism. Species with long abdomen are more sensitive than species with short abdomen (Einav et al., 2003). Younger organisms are obviously more sensitive than their older counterparts. Brine introduces turbidity to sea water preventing the penetration of sunlight thereby reducing the rates of photosynthesis. Brine disposed into the ocean also increases the temperature of the sea water resulting in a reduction in dissolved oxygen. Corrosion of equipment at the outlet introduces heavy metals such as copper and nickel which can be toxic to marine organisms (Qdais 1999).

2.7.2 Effects of Brine on Soil Properties

High concentration of sodium has an adverse effect on the permeability and tilth of the soil. They reduce the permeability especially in clayey soils (Svensson 2005). This generally leads to reduced aeration. As mentioned earlier in section 2.3.3.1, the Sodium Adsorption Ratio (SAR) is an important index used in classifying waters used in irrigation. When the water has a high salinity, calcium and magnesium salts may precipitate to form barriers that block the movement of water in the soil.

2.7.3 Effects on Plants

Depending on the salt tolerance of plant species, salinity generally reduces plant growth (Svensson 2005). The most tolerant crops include sugar beet, sugar cane and cotton while the least tolerant crops are beans, onions, strawberries, carrots and almonds (Svensson 2005). Symptoms of salinity overdose are darkening of the leaf colour followed by leaf tip and/or edge burning (Svensson 2005).

2.7.5 Effect of Brines on Life

Brines can end up contaminating groundwater and eventually find their way to communities who use untreated or under-treated ground water from wells. Some brines can contain nitrates which when consumed reduce the ability of red blood cells to carry oxygen. Nitrate is reduced to nitrite in acidic conditions like those found in the stomach. The nitrite combines with haemoglobin to form methaemoglobin which is incapable of transporting oxygen (Usher 2006). In most adults and children, these red blood cells rapidly return to normal. However in infants 0 to 6 months of age (Usher 2006), it can take much longer for the blood cells to return to normal. Infants who consume water with nitrates can develop a serious health condition called methemoglobinemia or "blue baby syndrome". The WHO standard nitrate limit in drinking water is 50 mg/L (Nettnin 2005). Nitrates also cause eutrophication when in excess, which is a process where the population of plants in water multiplies rapidly. The plants consume all the dissolved oxygen in the water and die. The result is stagnant water bodies with rotting plant material. Some phosphate based antiscalants used in desalination can cause the same effect (Svensson 2005). Brines contain other dissolved salts normally found in sea water but at a higher concentration. Brines can contain salinity of 46 000 mg/L to 80 000 mg/L compared to the 35 000 mg/L in typical sea water (Mohammed et al., 2004). Nettnin (2005) reported the health problems associated with drinking saline water in Gaza. It was found out that "*50 per cent of Gaza's children have a parasitic infection; children and adults suffer from diarrhoea; high chloride levels causes kidney disease; consumption of saline water leads to salt levels in humans that causes kidney dysfunction, heart failure, neurological symptoms, lethargy, and high blood pressure; excessive levels of fluoride are toxic, causing gastritis, ulcers, kidney failure, bone fluorisis (bone fractures and crippling), and teeth fluorisis (black lines around gums and tooth decay*" and of course as mentioned above, high nitrate levels causes "blue baby" syndrome. Excessive fluoride causes mottling of tooth enamel. The teeth may become brittle because the fluoride affects tooth density. Many children in Gaza have been found to have this defect (Ghanem 2005). Other health effects caused by some heavy metals are detailed in the table below

Table 2.8: Health effects of some heavy metals (Lenntech, 2009).

Metal	Effect on Health
As	Most toxic element that can be found. Irritation to stomach, decreased production of red and white blood cells, skin changes, lung irritation, infertility, miscarriages in women, brain damage, DNA damage.
B	Affect stomach, liver, kidneys, brains and eventually death
Cr	Skin rash, upset stomach and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, death
Cu	Irritation of nose, mouth and eyes, headaches, stomach-aches, dizziness, vomiting, diarrhoea, liver and kidney damage, death
Mo	Highly toxic. Gout, liver dysfunction, pains in the knees, hands/feet/articular deformities, erythema and edema of the joint areas
Ni	Lung cancer, nose cancer, larynx cancer, prostate cancer, sickness, dizziness, lung embolism, respiratory failure, birth defects, asthma & chronic bronchitis, heart disorders
Se	Brittle hair, deformed nails, rashes, swelling of the skin, severe pains, burning of eyes, death
Pb	Neurotoxic, causes headaches, irritability, mental impairment in children, damages,brain, liver and kidneys
Sr	Disruption of bone development, can cause cancer
V	Bronchitis, pneumonia, irritation to lungs, throat, eyes and nasal cavities, cardiac & vascular disease, inflammation of stomach & intestines, damage to the nervous system, bleeding of liver & kidney, rashes, severe trembling, paralyses, nose bleeds, throat pains, weakening, sickness, dizziness, behavioural changes, headaches
Zn	Stomach cramps, skin irritations, vomiting, nausea, anaemia, pancreas damage, respiratory disorders, disturb protein metabolism
Cd	Cancer in animals, Damage to liver

2.8 Chemical Speciation Modelling

The composition of natural groundwaters and waste waters such as brines is affected by a wide variety of chemical interactions between the solution, solid and gas phases. It is, in most cases, impossible to predict the impact of these interactions on the water composition without a realistic knowledge of the type of chemical reactions that occur in such waters. Computer models perform complex calculations in milliseconds, an operation which would not be accomplished timeously without computers. The most important calculations include the listing of chemical forms in which elements, ions and compounds exist in the water (speciation), oxidation-reduction reactions and minerals that would deposit at the bottom (precipitate). Conceptual models are a combination of the knowledge of the type of chemical reactions taking place and a computer code capable of calculating the reactions that impact on the mass transfer between the phases in the water. They can be developed based on these processes using computer software such as PHREEQC and the site-specific analytical data. Chemical speciation modelling is therefore a powerful tool for characterizing environmental site contaminants and predict or forecast environmental impacts or responses of the system to a change in conditions. It is applicable in real-world environmental problems such as acid mine drainage, nuclear waste disposal, brine disposal and landfill leachates.

Chemical speciation or the form in which chemical species exist is important because different chemical species control chemical reactions differently. For example, Cu^{2+} reacts differently to complexed Cu. Chemical speciation controls bioavailability i.e. free ions are more bioavailable to some organisms than complexed ones. Toxicity also depends on the form in which chemical species exist.

Some chemical speciation models that are available for use are;

(i) MINTEQ by the United States Environmental Protection Agency (USEPA)

MINTEQ is a program capable of computing equilibria among dissolved, adsorbed and gaseous chemical species. It can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The limitation of MINTEQ that has been identified are errors in solutions that include metal-organic complexes (Reddy and Lewis 2006).

(ii) PHREEQC by the United States Geological Survey (USGS)

PHREEQC is a computer program for speciation, batch-reaction and one dimensional transport among other useful geochemical calculations. The limitations of PHREEQC are that it cannot account for the non-ideality of aqueous solutions in the concentration range of sea water and above. It also lacks internal consistency in the data provided in the two databases (*phreeqc.dat* and *waterq4f.dat*). Careful selection of aqueous species and thermodynamic data is left to the user of the software (USGS 2009).

(iii) Analyser from OLI Systems Inc

OLI software uses a speciation-based thermodynamic model to calculate speciation, chemical equilibria, and phase equilibria for multi-component aqueous systems. The limitations (Reddy and Lewis 2006) of using the OLI software program are;

- It lacks a separate activity coefficient model
- Vapour critical parameters are correlated to find a fugacity coefficient

(v) Aq.QA

Aq.QA is a program that is limited to the predicting of carbonate among the three carbonate species, HCO_3^-, CO_3^{2-} and CO_2 as well as mineral saturation indices for the

$CaCO_3$ minerals calcite and aragonite. Saturation indices indicate the saturation state of a water with respect to a given mineral.

2.9 Summary of Literature Review

Saline effluents or brines can be of natural origin or as a result of human activities. They are highly saline and their chemistry is highly complex. Brine disposal is a major challenge. Man-made brines are mainly as a result of desalination activities that are carried out mainly to save and recycle water. The pollutants in brines can end up contaminating groundwater and eventually be consumed by plants and biota. The health problems that may be associated with toxic elements present in brines are numerous and these include pneumonia, lung cancer, disruption of bone development, severe pains, feet deformities, skin rashes, infertility etc (see Table 2.9). Brines can affect the soil tilth and permeability of soils and the salinity that results generally reduces plant growth. Where disposal of brine into the ocean is practised, a salinity gradient around the brine outlet is created which has adverse effects on marine organisms.

Although brine disposal is a major challenge, saline effluents can be used as a resource. The SAL-PROC process harnesses useful chemical products such $CaCO_3$ from saline effluents. No hazardous chemicals are added during processing. Other uses of brine include shrimp, algae and fish production, electricity and heat generation and irrigating salt tolerant plants. Disposal methods of brine that have been in use are deep well injection, aquifer re-injection, discharge to sewage and/or wastewater treatment plants, discharge to open land, discharge to evaporation ponds and discharge into the ocean.

The most common commercially available brine treatment technologies can be divided into two main categories, namely; membrane technology and evaporation. Membrane technologies include nanofiltration, reverse osmosis and electrodialysis.

Nanofiltration and reverse osmosis are pressure driven while electrodialysis is electrically driven and both require high energy input. The brine may be pre-treated by ultrafiltration and microfiltration before treatment using the aforementioned membrane technology. When two or more membrane technologies are combined in one operation, the combination becomes known as an integrated membrane system (IMS). Distillation technologies have been practised for decades and they include multistage flash distillation (MSF) multiple effect distillation (MED) and vapour compression (VC). One disadvantage of distillation technologies is that they utilise high energy. New technologies that are not yet widely used are adsorption desalination, vacuum freezing and eutectic freeze crystallization.

CHAPTER 3: EXPERIMENTAL

This chapter states the background to analytical techniques, materials and methods, sampling procedures, experimental procedures and analytical methods used in this study to characterize brines.

3.1 Background to Analytical Techniques

3.1.1 pH

pH is the most common measure of the acidity/alkalinity balance in a solution. It is a measure of the availability in solution of hydrogen ions (H^+). It is also defined as the negative algorithm (to base 10) of the hydrogen ion activity (in moles/L) and values normally fall between 0 and 14 and they are reported without units. The process that rules the proton balance and therefore the pH of pure water is the dissociation of the water molecule.

$H_2O \leftrightarrow H^+ + OH^-$...Equation 2.5

When the concentrations of the protons and hydroxide ions are equal, the logarithm of the molar hydrogen ion concentration yields a value of 7. A pH of 7 therefore indicates water which is neither acidic nor alkaline and is portrayed as having a neutral pH. In practice, few waters have a pH of exactly 7. Waters with a pH of between 6.5 and 8.5 are referred to as circum-neutral (Younger 2006). Those below 6.5 can be described as acidic. In acidic water, little OH^- is present in solution whereas H^+ is abundant. This normally happens where major anions are not balanced by an equivalent concentration of major cations. Dissociation of water then occurs, releasing protons into solution to maintain electroneutrality. Most rainwater and many groundwaters are at least slightly acidic (pH 5-6) due to the tendency of atmospheric carbon dioxide in rainwater to form carbonic acid. As discussed in section 2.2.2, reaction of acidic rainwater with minerals and organic matter raises pH to around 7. However, where rainwater infiltrates without encountering any reactive minerals (for example, in a soil composed of mainly quartz sand) then the resultant groundwater can be expected to have a pH of 6 or less. On the other hand, waters with a pH above 8.5 are considered alkaline. In these cases, the dissolved concentration of OH^- greatly exceeds those of H^+. This normally occurs when the meq/L concentration of major cations in solution exceeds that of the major anions. In order to maintain the overall neutrality of the water, the water molecules then dissociate to release sufficient hydroxide ions to balance the positive charge exerted by the major cations. However, very few natural geological settings yield strongly alkaline water. It is important to note three aspects of pH value interpretation in water analysis results.

(i) The pH is logarithmic. A unit change in pH corresponds to ten fold change in proton concentration. Therefore a change in pH needs to be evaluated with a due sense of proportion.

(ii) The balance of dissolved cations and anions determines the degree to which water molecules must dissociate in order to maintain electroneutrality. Since the strongly ionizing cations or anions can affect the H^+ /OH^- balance; pH is only regarded as one of the components of the total acidity of a given water sample. While ambient pH is surely the most useful single index of the acidity-alkalinity balance, the small atomic mass of H^+ in comparison with the dissolved metals means that it tends to make a rather modest contribution to the total dissolved mass of acidity-generating ions. This means that pH is not the same parameter as acidity.

(iii) The rates of many geochemical and physical reactions are strongly pH-dependent. For instance, dissolution of carbonates and silicates occurs much more rapidly at low pH than at high pH. Adhesion of most cations to mineral surfaces occurs much more rapidly at circum-neutral to moderately alkaline pH than at aicidic pH. Therefore pH is a “master variable” in many geochemical environments. To know pH is to be able to predict many aspects of solution chemistry (Younger 2006).

3.1.2 Electrical Conductivity (EC)

Electrical conductivity is a measure of the ability of a substance to conduct electricity. It can be used to estimate the concentration of total dissolved solids in water. The ability of a given water to conduct electricity is directly proportional to the concentration of dissolved, charged i.e mobile species (ions) which it contains. It is very easy to measure the conductivity of water using the robust inexpensive hand-held electronic meters. The units of measurement are microsiemens (μS/cm) per centimetre or for more saline waters in millisiemens per centimetre (mS/cm). In a conductivity meter, the sensor simply can consist of two metal electrodes that are about 1.0 cm apart and protrude into the water. A constant voltage (V) is applied across the electrodes. An electrical current flows through the water due to this voltage and is proportional to the concentration of dissolved ions in the water - the more ions, the more conductive the water resulting in a higher electrical current which is measured electronically. Distilled or deionized water has very few dissolved ions and so almost no current flows across the gap (low EC). The relationship between ionic content and conductivity is linear at low concentrations. The sum of the meq/L cation concentrations in a water multiplied by 100 approximate (to ± 10%) the conductivity of the water expressed in μS/cm (Younger 2006). Following the principle of electroneutrality, the same calculation can be done using the sum of meq/l anion concentration.

Conductivity is temperature dependent. In metals, conductivity decreases with temperature and in non-conductors it increases with temperature. In water, electrical current flow increases with temperature and conductivity meters are normally equipped to automatically correct values to 25 degrees Celsius giving the specific electrical conductivity. The temperature compensation for most naturally occurring waters is about 2%/°C but however can range from 1 to 3%/°C (Younger 2006). The approximate relationship between conductivity and the total dissolved solids is given in equation 3.2 (Younger 2006)

TDS (mg/L) = 0.64EC (uS/cm)…………………………………………..Equation 2.6

The total dissolved solids (TDS) values (in mg/L) can also be determined from the analytical results by adding the anion and cation concentrations (in mg/L).

3.1.3 Total Dissolved Solids

Total dissolved solids refers to the total amount of all dissolved substances – including minerals, salts, metals, cations or anions –within a given water sample (Younger 2006). Sources of TDS include agricultural run-off, urban run-off, industrial wastewater, sewage, and natural sources such as leaves, silt, and rocks. Piping may also release metals into the water. While TDS is not considered a primary pollutant, higher TDS values normally indicate that the water is more polluted and may lead to scale build up in pipes, reduced efficiency of water filters and aesthetic problems in drinking water such as a bitter or a salty taste. The United States Environmental Protection Agency (USEPA) recommends that drinking water be treated when TDS concentrations exceeds 500mg/L. As discussed in chapter one, TDS can be used as a basis for classifying waters. There are two main ways of testing for TDS in water samples. An electrical conductivity test provides an estimate of TDS concentration levels and the relationship is shown by equation 3.2 .The second way of determining TDS levels is by gravimetric methods and this is the most accurate method. It involves evaporating a known volume of filtered water and then obtain the mass of the residue by difference using an analytical balance.

3.1.4 Alkalinity

Alkalinity of a water is the capacity to neutralize acid to a specific endpoint. Total alkalinity or methyl orange alkalinity end point is pH 4.5 while phenolphthalein alkalinity endpoint is at pH 8.3. (Younger 2006)

Alkalinity is usually expressed in terms of carbonate or bicarbonate because several species dominate (Younger 2006). For circum-neutral water, the concentration of HCO_3^- in water (in mg/L) may be calculated using the equation below.

$$HCO_3^- = \frac{\text{Total alkalinity (as } CaCO_3)}{0.8202} = \text{Total alkalinity} \times 1.22 \text{ ....Equation 2.7}$$

3.1.5 Eh (Redox)

Eh is a measure of the status of reduction and oxidation reactions in a water sample. It is also known as the redox potential of the water sample. Redox refers to the gain and loss of electrons by reacting ions. Since it is essentially a measure of the status of electron distribution between potentially interacting ions, Eh is an electrical potential and is measured in millivolts. Most geochemists find Eh difficult to deal with, and it is not the least problem that this parameter is extremely difficult to measure accurately in practice (Younger 2006). Eh measurements values obtained cannot be interpreted in strictly quantitative terms. The best interpretation is generally that well-oxygenated water in which most cations are in their most highly charged forms (e.g. with iron present as Fe^{3+} rather than as Fe^{2+} tend to display high values of Eh. In water without dissolved oxygen, in which cations are in their least charged form, Eh tends to be low or even negative (Younger 2006).In the same manner that pH indicates the activity of H^+ ions in a solution, a parameter known as "pe" represents the theoretical electron transfer potential of a solution. Unfortunately it cannot be measured directly as free electrons do not occur as a solution. It can be calculated from Eh values and other parameters.

3.1.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a very sensitive, element selective detection system, which when used with a separation module such as HPLC or GC becomes a versatile tool for speciation analysis. Inductively coupled plasma mass spectroscopy was developed in the 1980s, combining the easy sample introduction and quick analysis of ICP technology with the accurate and low detection limits of a mass spectrometer. This resulted in an instrument capable of trace multielement analysis (often at parts per trillion levels). ICP-MS has been applied in different fields including drinking water, wastewater, natural water systems, soil science, mining/metallurgy, food sciences and medicine (Kvech and Worley 2000).

The ICP-MS technology was constructed on the same principle as that used in atomic emission spectrometry. Samples are decomposed to neutral elements in a high temperature argon plasma and analyzed based on their mass to charge ratios. An ICP-MS operates in four main stages which are; sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination and the detection.

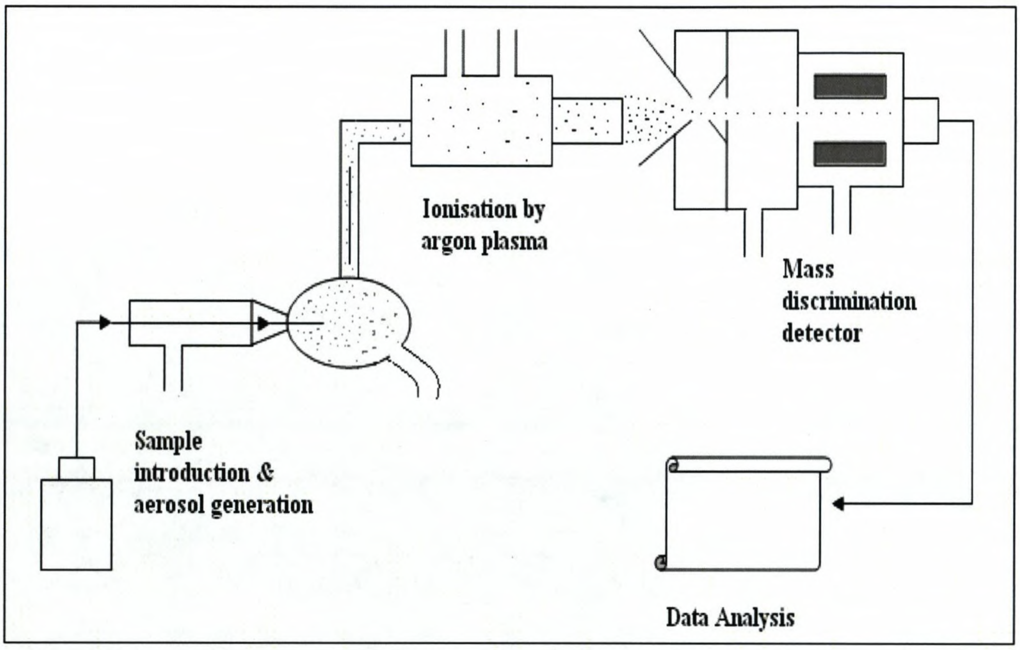


Figure 3.1: Schematic diagram of ICP-MS (Kvech and Worley 2000).

ICP-MS can accept solid as well as liquid samples unlike an atomic emission spectrometer. Solid samples are introduced into the ICP via a laser abalation system which is usually acquired as an accessory. Aqueous samples are introduced by way of a nebuliser which aspirates the sample with high velocity argon, forming a fine mist. The aerosol then passes into a spray chamber where larger droplets are removed via a drain (Jarvis et al., 1992). Normally only 2% of the original mist passes through the spray chamber (Olesik 1996). This process is necessary to produce droplets small enough to be vaporized in the plasma torch. In the nebuliser, the partially desolvated sample is now an aerosol which moves into the torch body and is mixed with more argon gas. A coupling coil is used to transmit radio frequency to the heated argon gas, producing an argon plasma "flame" located at the torch (Jarvis et al., 1992). This hot plasma removes any remaining solvent and causes sample atomization followed by ionization. Sample atoms are ionized and excited in the hot plasma, a principle that is also used in ICP-atomic emission spectroscopy. Since atomization/ionization occurs at atmospheric pressure, the interface between the ICP and and the mass spectrometer components becomes crucial in creating a vacuum environment for the mass spectrometer system. Ions flow through a small orifice, approximately 1mm in diameter into a pumped vacuum system. Here a supersonic jet forms and the sample ions are passed into the mass spectrometer system at high speeds expanding in the vacuum system (Jarvis et al., 1992). The whole mass spectrometer system must be kept in a vacuum so that ions are free to move without collisions with air molecules. The ICP is at atmospheric pressure and therefore a pumping system is required to continuously pull a vacuum inside the spectrometer. To effectively reduce the pressure, several pumps are normally used to gradually reduce pressure to about 10^{-5} mbar before the ion stream reaches the quadrupole.If only one pump were used, the size would be too big to reduce the pressure immediately upon entering the mass spectrometer. In the first stage of the mass spectrometer, ions are removed from the plasma by a pumped extraction system. An ion beam is produced and focused further into the actual unit. There are several different types of mass analyzers that can be used to separate isotopes based on their mass to charge ratio. Quadrupole analyzers are compact and easy to use but offer lower resolutions when dealing with ions of the same mass to charge ratio. Double focusing sector analyzers offer better resolution but are larger and have higher capital cost. The quadrupole mass filter is made up of four metal rods. A combined DC and AC electrical potential is applied to the rods with opposite rods having a net negative or positive potential. Ions enter into the path between all of the rods. When the DC and AC voltages are set to certain values only one particular ion is able to continue on a path between the rods and the others are forced out of this path. This ion will have a specific mass to charge ratio (m/z). Many combinations of voltages are chosen which allows an array of different m/z ratio ions to be detected. These quadrupole rods require periodic maintenance and cleaning due to the accumulation of ions which are removed during the discrimination process. The most common type of ion detector found in an ICP-MS system is the electron multiplier. This cone or horn shaped tube has a high voltage applied to it opposite in charge to that of the ions being detected. Ions leaving the quadrupole are attracted to the interior cone surface. When they strike the surface, additional secondary electrons are emitted which move further into the tube emitting additional secondary electrons. Even more electrons are formed as the process continues, resulting in as many as 10^8 electrons at the other end of the tube after one ion strikes at the entrance of the tube (Jarvis et al., 1992). The importance of cleaning and maintenance is similar to that of the quadrupole rods. ICP-MS has one great advantage over other methods and this is its ability to achieve extremely low detection limits for a wide variety of elements. Table 2.10 shows some common detection limits by element. It also offers a rapid multielement analysis for all metals avoiding a multi-technique approach when using traditional techniques where more than one instrument is needed to conduct a full analysis (Agilent 2005)

Table 3.1: Common detection limits (Kvech and Worley 2000).

Element	Detection Limit (Parts per trillion)
U, Cs, Bi	Less than 50
Ag, Be, Cd, Rb, Sn, Sb, Au	10 - 50
Ba, Pb, Se, Sr, Co, W, Mo, Mg	50 - 100
Cr, Cu, Mn	100 - 200
Zn, As, Ti	400 - 500
Li, P	1 – 3 pbb
Ca	Less than 20ppb

The ICP-MS used in this study was equipped with an Octopole Reaction System (ORS). The ORS offers an off-axis reaction cell, which effectively removes spectral interferences in even the most complex sample matrices (Agilent 2008). The ORS is designed to handle highly complex matrices and elements that suffer from significant plasma based (Ar-based) interferences such as Fe, Se, As etc.

3.1.6 Ion Chromatography

Ion chromatography is a type of liquid chromatography where retention is predominantly controlled by ionic interactions between the ions of the solute and counter ions that are situated in or on the stationery phase (Scott 2009). It can be used for almost any kind of charged molecules including large proteins, small nucleotides and aminoacids. The solution to be injected is known as the sample and the separated components are called analytes. It is often used in protein purification, water analysis and quality control. Ion Chromatography retains analyte molecules based on coulombic (ionic) interactions. The stationery phase surface displays ionic functional groups (R-X) that interact with analyte ions of the opposite charge. The stationery phase may also include an additional neutralizing stripper or suppressor column to remove background element ions. Cation exchange chromatography retains positively charged cations because the stationery phase displays a negatively charged functional group.

$\text{R-X}^{-}\,\text{C}^{+} + \text{M}^{+}\text{B}^{-} \leftrightarrow \text{R-X}^{+}\text{M}^{+} + \text{C}^{+} + \text{B}^{-}$ ....Equation 2.8

Anion exchange chromatography retains anions using positively charged functional groups:

$\text{R-X}^{+}\text{A}^{-} + \text{M}^{+}\text{B}^{-} \leftrightarrow \text{R-X}^{+}\text{B}^{-} + \text{M}^{+} + \text{A}^{-}$............................Equation 2.9

The ion strength of either C^{+} or A^{-} in the mobile phase can be adjusted to shift the equilibrium position and thus retention time.

Ion methods have been in use since the 1850s when H. Thompson and J.T Way of England treated clays with ammonium sulphate or carbonate in solution to extract the ammonia and release calcium. The first zeolite mineral column was used in 1927 to remove interfering calcium and magnesium ions from solution in order to determine the sulphate content of water. In the 1970s, the Dow Chemical Company developed ion chromatography to be used in automated analysis. Dionex (Dow Ion Exchange) Corporation was later formed as a separate business for its new ion chromatography products. Ion chromatography is a powerful technique for the determination of low concentrations of ions and is especially useful in environmental and water quality studies among other applications. However, ion chromatography has generally been found to be one of the most difficult types of chromatography to exploit and is most often used for analysis of anions for which there are no other quicker analytical methods.

3.2 Sampling Procedures

Sampling was done at the two sites described in section 1.4. Water samples were collected at various locations which will be identified in the next chapter. The grab sampling method was employed throughout the entire study. A grab sample is a single sample collected at a particular time and place that represent the composition of the water. Sampling was carried out each year from 2006 to 2008 in the winter months of May, June or July. The main reason for choosing the winter months instead of summer was to avoid sample dilution from rain during sample collection. Grab sampling was chosen for this study because it allows for the unstable parameters i.e. pH, temperature, conductivity and total dissolved solids (TDS to be measured immediately after sample collection.

3.2.1 Sample Preservation

The aim of sample preservation is to prevent reduction or loss of target analytes. Analyte loss can occur between sample collection and laboratory analysis because of physical, chemical and biological processes that can lead to precipitation, adsorption, oxidation, reduction, ion exchange, degassing or degradation (Radtke 2002). However, preservation stabilizes analyte concentrations for only a limited period of time, depending on the analyte in question and the preservation method employed. Some analytes require a shorter holding time than others. In this study, all samples were preserved by filtration through 0.45um filters at the site. This was followed by dilution and acidification (of samples prepared for cation determination only) using nitric acid at the laboratory on site. Alkalinity titrations were carried out on aliquots of the filtered samples.

Generally, the procedure followed was that for anion analyses, filtered samples were diluted using ultrapure water to a point where the electrical conductivity was less than 1 mS/cm. For the cation analysis, pure nitric was added to a pH of about 1 after dilution to less than 1 mS/cm electrical conductivity.

3.2.2 Sample Storage

Immediately after preservation, samples were chilled at 4 ^{o}C or below without freezing until analysed. Samples were kept chilled for a period ranging from one to three weeks before analysis. While in transit by plane or by road, samples were kept chilled by the use of ice packs. Prior to analysis all samples were refrigerated at 4^{o}C.

3.3 Analytical Methods

3.3.1 pH

The pH of all samples was measured using a potable Hanna HI 991301 pH meter fitted to a pH/TDS/EC/Temperature probe. Calibration of the pH meter was done using pH 4.0 and pH 7.0 every time before measurements were taken.

3.3.2 Temperature

Temperature is very easy to measure accurately within ± 0.1 degrees Celsius using electronic sensors. These sensors are generally so robust that they rarely require calibration and are therefore very suitable for field measurements where they can be left turned off for long periods of time. Knowledge of water temperature is important for the correct interpretation of solution chemistry, especially for assessing the tendency for minerals to dissolve in, or precipitate from a given water sample. Temperature was measured using the probe described in section 3.2.1 coupled with the portable Hanna HI 991301 pH meter.

3.3.3 Electrical Conductivity

Electrical conductivity was measured during sample collection on site and in the laboratory using the Hanna HI 991301 and the probe described in section 3.2.1. The probe was calibrated using a 12.88 mS/cm standard at room temperature.

3.3.4 Total Dissolved Solids (TDS)

TDS was measured using a Hanna HI 991301 TDS meter and the probe described in section 3.2.1.

3.3.5 Total Alkalinity

Total alkalinity was determined by titration with 0.1M Hydrochloric acid to an end point of pH 4.5 with the aid of a standardized pH meter. Alkalinity was calculated using the equation below and reported in mg/L $CaCO_3$

$$\text{mgCaCO}_3/\text{L} = (T \times M \times 50 \times 1000)/S \quad \text{......................................Equation 3.1}$$

Where;

T = standard acid titre in millilitres

M = standard acid molarity

S = volume of sample in millilitres

$$HCO_3 = \frac{\text{Total alkalinity}}{0.8202} = \text{Total alkalinity} \times 1.22 \quad \text{..................................Equation 2.7}$$

3.3.6 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Cations were analysed for using ICP-MS. All samples were filtered through a 0.45µm filter and diluted using demineralised water to EC values of less than 1mS/cm.

Preservation was by addition of nitric acid and chilling at the laboratory on site. Major and trace elements were determined using ICP-MS (Agilent 7500ce with ORS).

3.3.7 Ion Chromatography

Anions were analysed for using ion chromatography. Samples were filtered through a 0.45µm filter and diluted to EC of less than 1 mS/cm using demineralised water. They were then preserved by chilling before analysis using the specified conditions below. The period between sampling and analysis ranged from one week to three weeks depending on logistics.

Machine Model: Dionex ICS-1000 Ion Chromatograph
Column: Ion Pac AS14
Guard Column: AG14
Eluent: $Na_2CO_3/NaHCO_3$

3.3.8 Modelling and Chemical Speciation of Brines

3.3.8.1 Chemical speciation using Aq.QA

The following parameters were used to formulate the input files for Aq.QA

(i) Equilibrium solution pH
(ii) Total concentration of cations and anions specified in ppm
(iii) Equilibrium solution temperature

3.3.8.2 Chemical speciation using PHREEQC

The following parameters were used to formulate the input files for PHREEQC;

(i) Equilibrium solution pH values
(ii) Total concentration of cations and anions specified in ppm

(PHREEQC requires total alkalinity to be in mg/L HCO_3^{2-})

(iii) Equilibrium solution temperature

(iv) The software's default *pe* (4.0)

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter outlines and discusses all the results obtained by the experimental techniques described in Chapter 3. Detailed chemical analyses are presented in the Appendices section. Speciation modelling was carried out on results obtained in 2008 as they had better analytical consistency than previously obtained results. This is shown by the ion balance results under the Appendices section. Factors behind the lack of consistency in analytical results can be many and this may include sampling handling methods, sample preservation and equipment used. In 2008, care was taken to immediately take measurements of all unstable parameters and fill all sample containers to the brim to exclude as much air as is possible. Carbon dioxide in air can be interact with brine to give results that do not represent the original sample. All modelling parameters used are presented with the results and discussion. Major ion chemistry, cations (calcium, magnesium, sodium and potassium) and anions (chloride, and sulphate) have been used as tracers to easily recognize chemical input or withdrawal from a water stream (Connected Water 2009).

The major ionic species obtained from the chemical analyses are projected graphically on Stiff diagrams and Piper diagrams. The stiff method uses four parallel horizontal axes extending on each side of a vertical zero axis. The concentration of cations and anions are plotted to the left and right of the vertical zero axis. The resulting points are then connected to give an irregular polygon shape or pattern which shows water composition differences or similarities. The width of the pattern is an approximate indication of total ionic content. The chemical data on Stiff diagrams is expressed in milli-equivalents per litre. They are an excellent mapping tool.

The Piper diagram shows the percentage composition of different ions. The cations and anions are plotted in left and right triangles as a single point. These points are then projected into the central diamond-shaped area parallel to the upper edges of the central area. All the points in the diamond-shaped area represent the total ionic distribution. For each water sample, a single point is obtained in the diamond-shaped area, which represents the total ionic distribution. Piper diagrams are useful in identifying the mixing of waters. Aq.QA software was used to generate the Piper diagrams in this study with the intent to identify inorganic signatures of the samples. One disadvantage in using Stiff and Piper diagrams is that they do not accommodate waters where other cations and anions may be significant. For example, the ultrapure water Stiff diagram (Fig 4.1) does not show that silicone is the dominant cation in that water.

4.2 Chemical Composition of Water Streams at Tutuka Power Station

4.2.1 Introduction

Sampling at Tutuka Power Station was done once a year during the winter months of May, June or July from 2006 to 2008. Sampling points are shown in Fig 4.12. Winter was chosen simply because of the dry weather conditions in the region during winter and therefore avoiding sample dilution from rains. The detailed results are given in the Appendices A1, A2 and A3. Cations (such as calcium, magnesium, sodium and potassium) and anions (such as chloride, bicarbonate and sulphate) have been used as tracers (Connected Water 2009) to determine the evolution of water streams and trends along the water treatment flow paths. Major ions data was presented in graphical format, of which the most useful plots are the Piper diagrams that show the total major anion or cation composition. These diagrams have the advantage for showing a large number of analyses in one plot to define distinct populations or trends. The Stiff diagram format was also used to illustrate the composition of samples.

4.2.2 Major Ion Chemistry

The most concentrated brine from the vapour compressor obtained during the sampling period was found to contain 0.5 g/L of calcium, 22 g/L of sodium, 25 g/L of chloride and 77 g/L of sulphate. The high sulphate content is attributed to the high rejection of sulphate by RO and the low calcium is due to pre-treatment of the feed water before RO. Fig 4.2 shows the major ion chemistry of samples from Tutuka Power Station presented in a Piper diagram. Sample identification can be found in Appendices A1-A3 and in Fig 4.12. The least polluted water sample was the vapour compressor product which had 0.23 mg/L calcium, 1.81 mg/L sodium, 0.54 mg/L chloride and 3.56 mg/L sulphate from the 2008 results. All the samples have sodium as the dominant cation and sulphate as the dominant anion with the exception of RO water and vapour compressor product which are Na-Cl and Na-HCO_3 water types respectively. The water types change in these two waters because a large amount of salts have been withdrawn by reverse osmosis from the preceding water, while in the other streams, the salts have either been concentrated by evaporation and filtration or precipitated and/or absorbed after contact with ash.

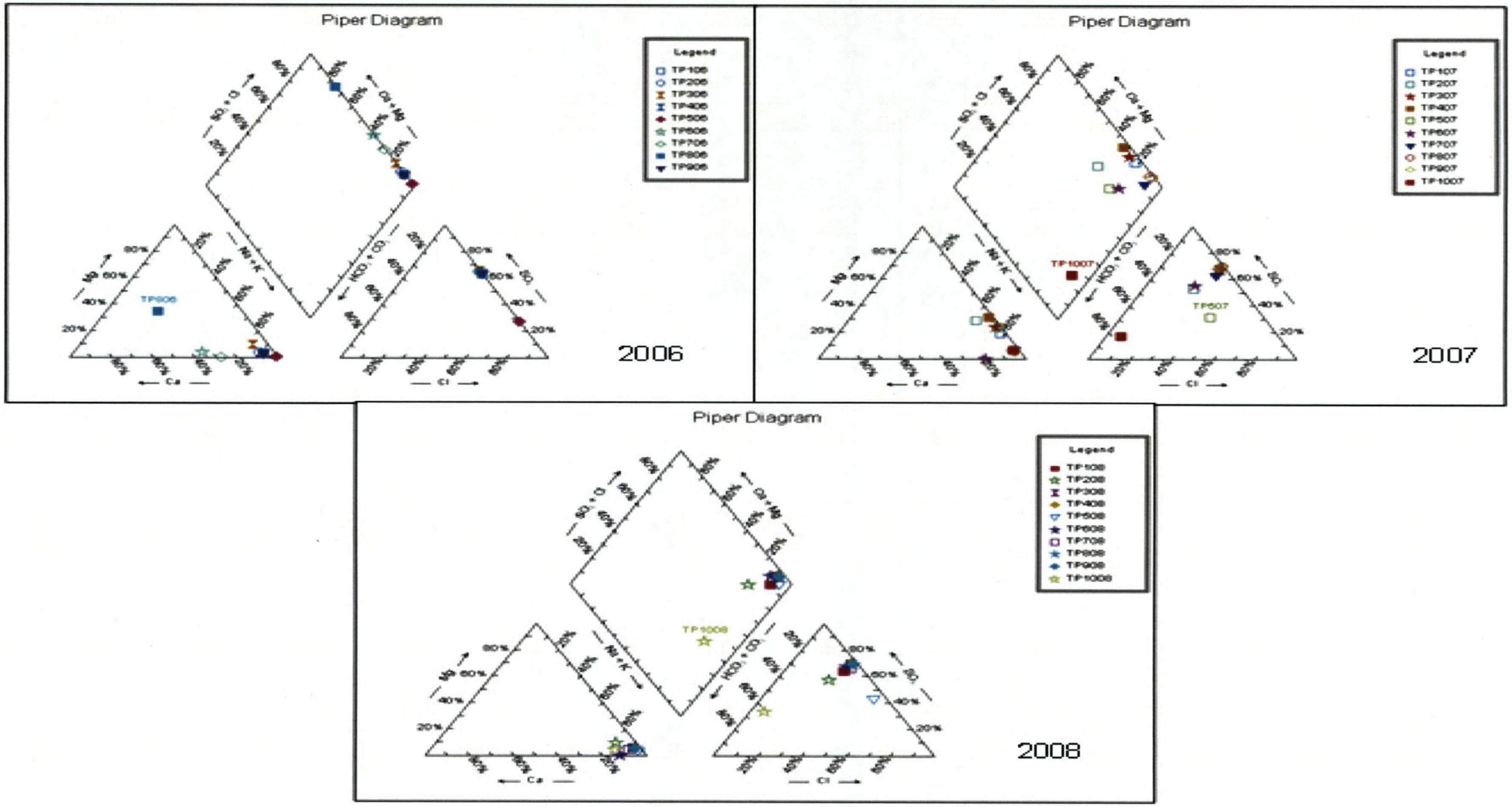


Figure 4.1: Piper diagrams showing major ion chemistry of Tutuka Power Station samples taken in 2006, 2007 and 2008.

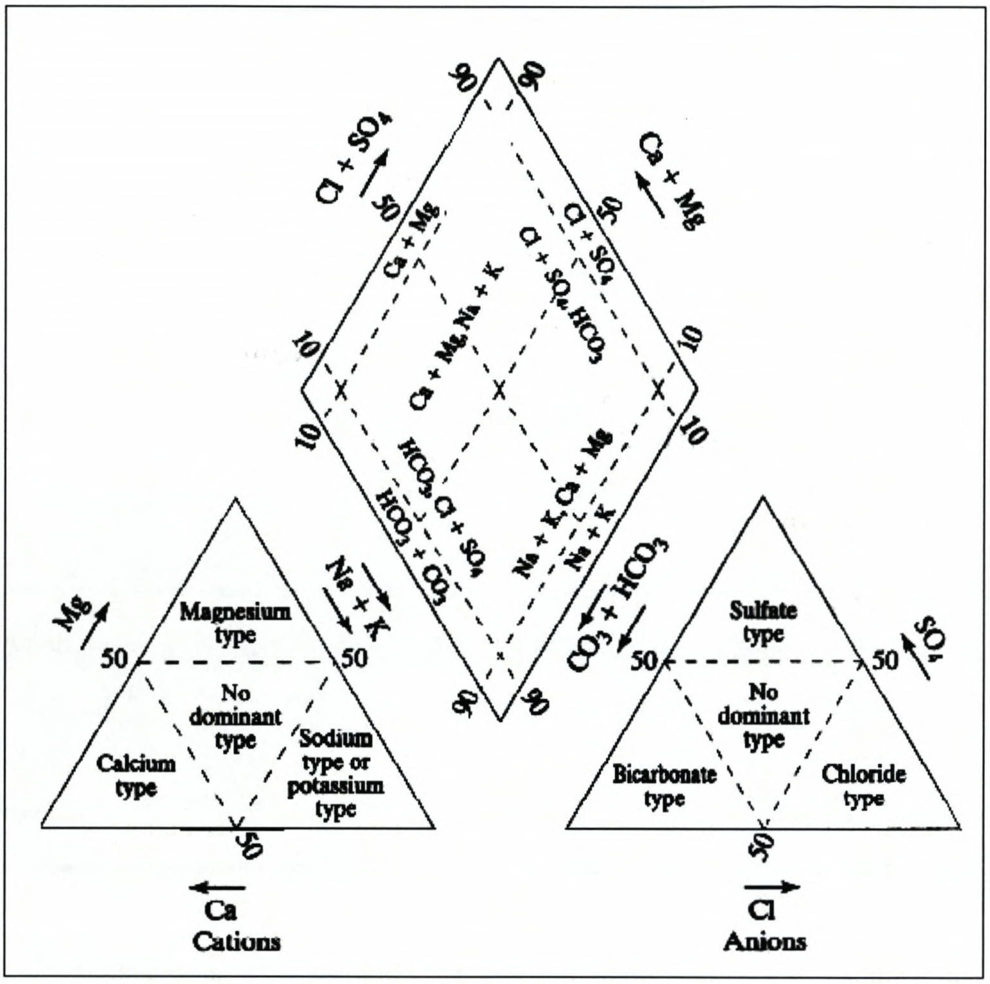


Figure 4.2: Classification of hydrochemical facies from the Piper plot (Kehew 2001).

To illustrate how the water samples from Tutuka Power Station were characterised, Fig 4.3 (Kehew 2001) has been included in this section. Superimposing Piper diagrams in Fig 4.2 onto Fig 4.3 reveals the water types found at Tutuka Power Station. This diagram confirms Aq.QA software calculation (Appendices A1-A3) that most of the waters sampled from 2006 to 2008 have sodium as the dominant cation and sulphate as the dominant anion. The data points are clustered in the sodium corner of the cation triangle and above the 60 % mark in the sulphate corner of the Piper diagrams in Fig 4.2. Possible source waters, or end members, are identified on Piper diagrams by water samples that plot at the extreme edges of the sample distribution (USGS 2009). Waters that are mixtures between two end members are identified as samples that plot on lines connecting the end members (USGS, 2009). The Piper diagrams in Fig 4.2 show samples in line and this is due to the fact that the samples are from different stages of the water treatment circuit which utilises a single water source. If both anion and cation compositions plot in the middle of the two triangles, then the waters would be referred as mixed cation-mixed anion types (Kehew 2001). From the samples analysed, this type of water was not identified at Tutuka Power Station. Even the RO water and the vapour compressor product have dominant cations and anions.

Fig 4.3 shows the major ion chemistry at Tutuka Power Station in the 2008 samples. Data values showing the minimum and maximum major ion content have been included. For example, calcium varied from 0.23 mg/L to 469.32 mg/L in the samples analysed. This can be seen in the table of analyses (Appendix A1) that sodium is the dominant cation among the samples and the dominant anion is sulphate. At Tutuka Power Station, major ions are mainly removed by reverse osmosis and by the vapour compressor as shown through sample TP508 and TP1008 respectively in Fig 4.4. Detailed percentage reduction/increase in major ion concentration at each sampling point in relation to the starting water is given in section 4.3.7 of this chapter.

In Fig 4.5(a), 4.5(b) and 4.5(c), the water samples drawn in 2008 from Tutuka Power Station were characterised using the Stiff diagram. The samples are identified in Appendix A3 and the positions of the sampling points are as indicated on the circuit diagram in Fig 4.12. All samples have the same shape except TP1008 because they originate from the same water. TP1008 has most of the salts removed completely by the vapour compressor but still contains an alkalinity level of 6.8 mg/L as $CaCO_3$ and exhibits a different shape from the other water streams. This could be due to dissolved carbon dioxide. Besides being an excellent mapping diagram, Stiff diagrams are a vital tool in identifying additions and removal of major ions from waters as they evolve or proceed along a flow path. TP608 is brine after contact with ash. Its precursor is TP908 (VC brine) and it can be clearly seen that magnesium has been removed in TP608 during contact with ash in the Piper diagram presented.

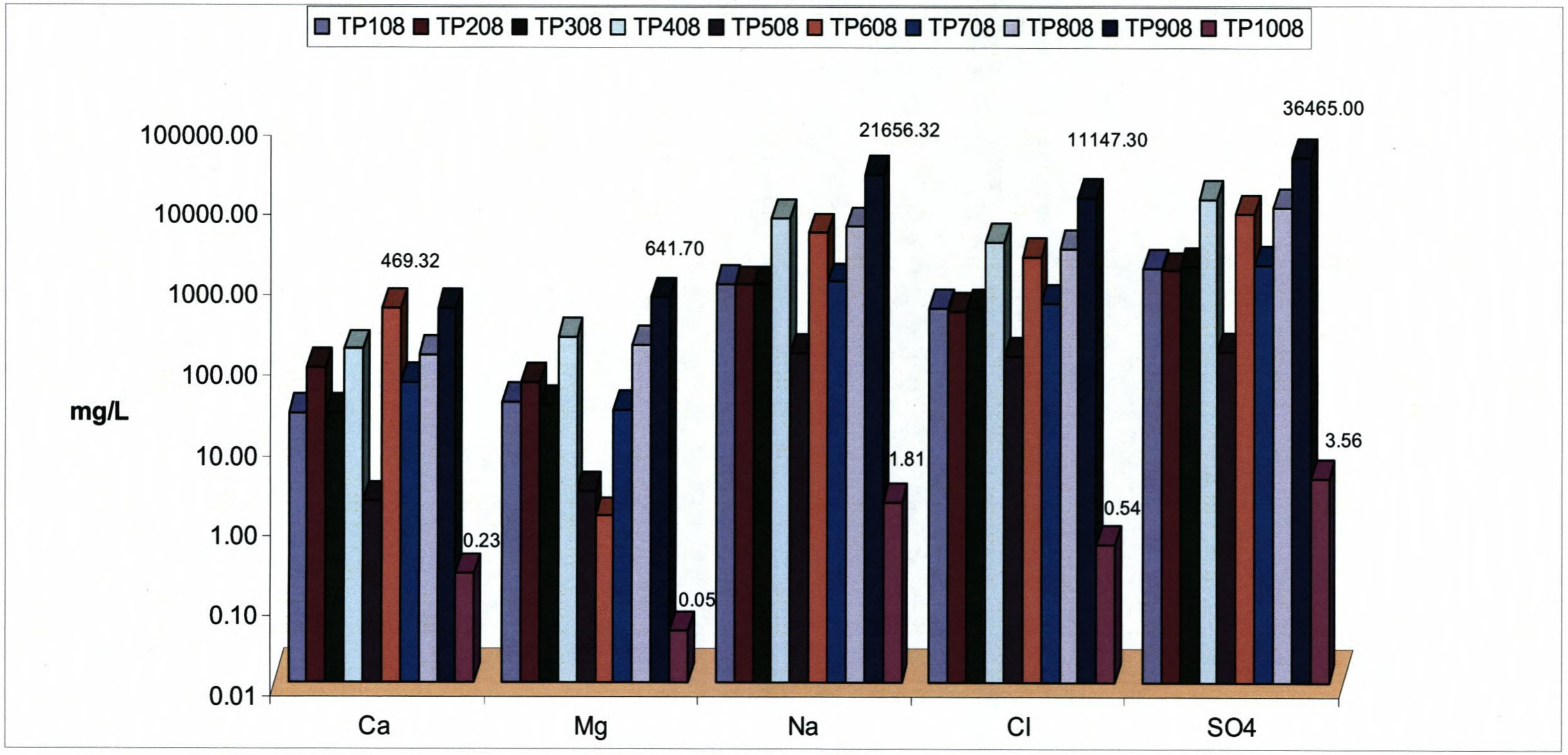


Figure 4.3: Major ion chemistry at Tutuka Power Station in 2008 samples.

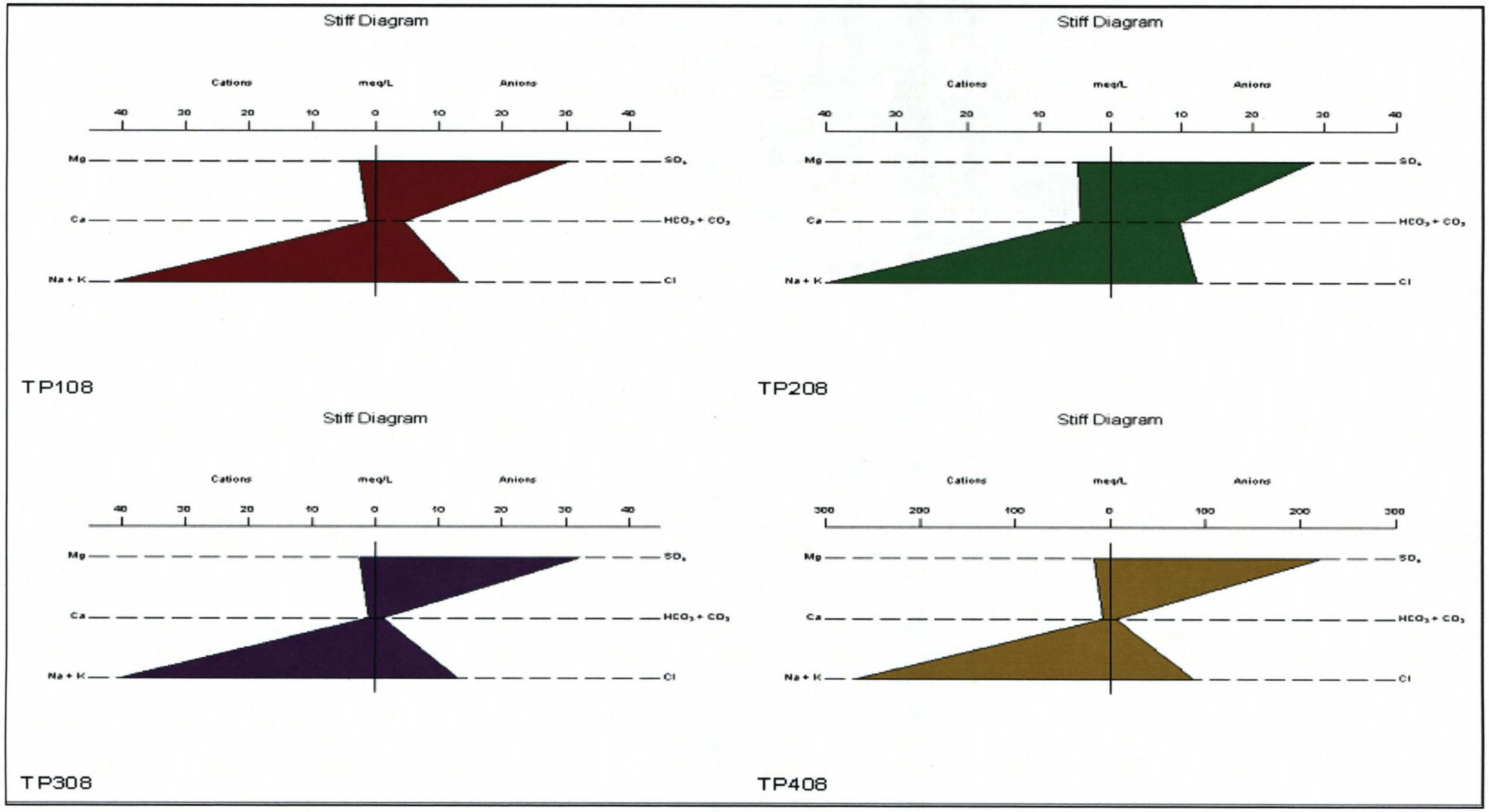


Figure 4.4(a): Stiff diagrams for Tutuka Power Station 2008 samples.

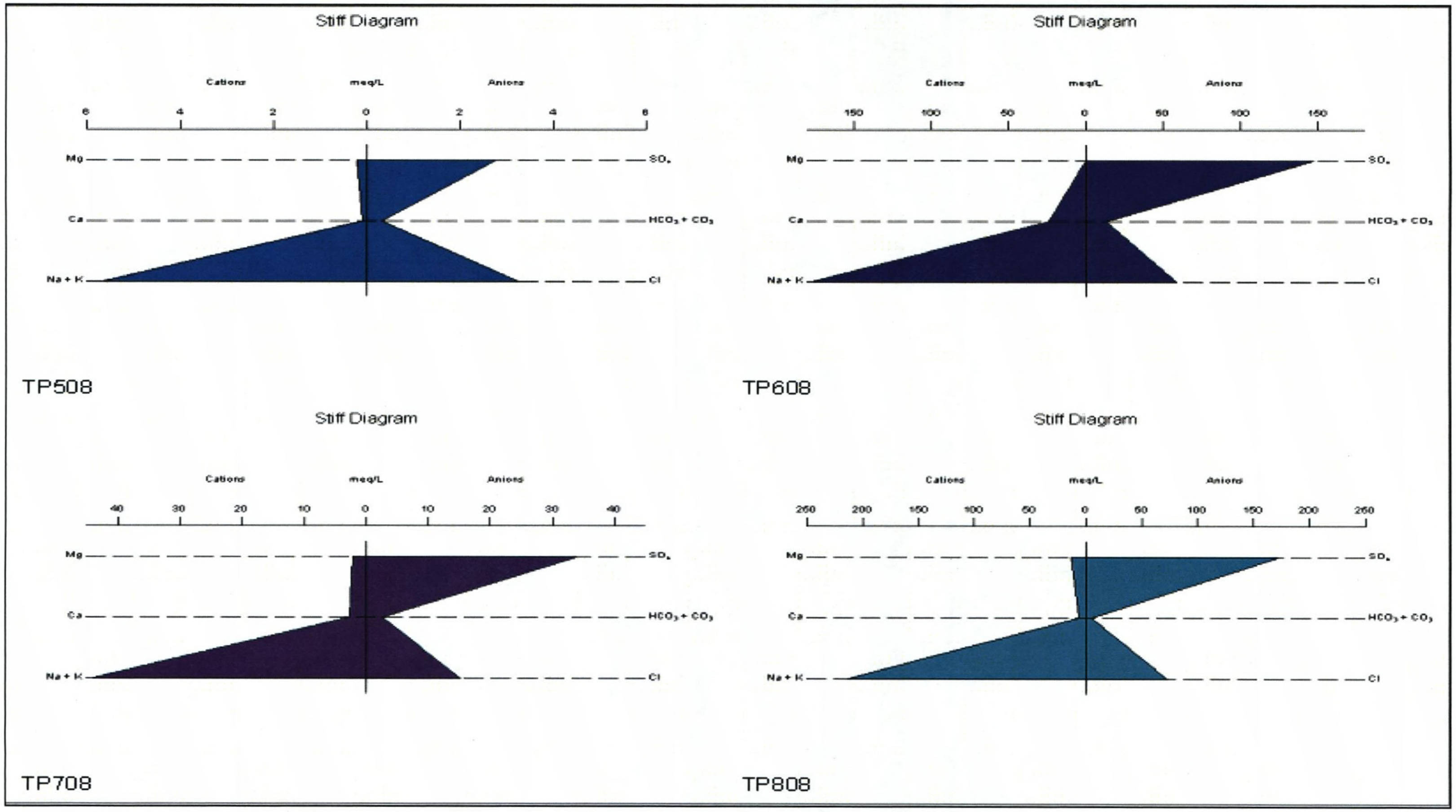


Figure 4.4(b): Stiff diagrams for Tutuka Power Station 2008 samples.

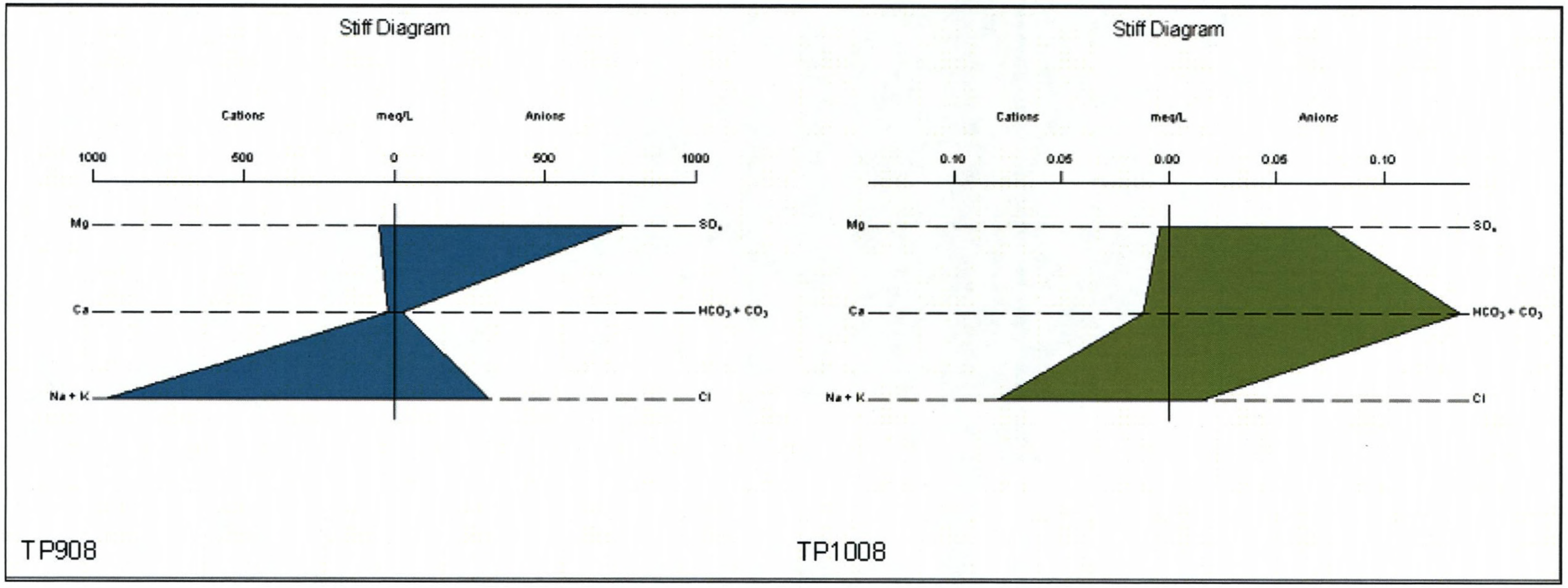


Figure 4.4(c): Stiff diagrams for Tutuka Power Station 2008 samples.

4.2.3 Trace Elements

Trace elements are commonly present at low levels in nature. Many trace elements such as iron, manganese, molybdenum and zinc are essential micronutrients in very small quantities, but the concentration range between deficiency and toxicity is narrow (Tanji and Kielen 2002). Trace elements of concern in drainage water include: arsenic, boron, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, strontium, uranium, vanadium and zinc (Tanji and Kielen 2002). For insight into their effects on health, refer to Table 2.9 However, some trace elements such as nitrate might have been considered non-toxic but may lead to methaemoglobinemia in infants (Usher 2006). Fig 4.6 shows the concentration of nitrates in mine water (main intake input) which was 5.00 mg/L and the concentration of nitrates in VC brine (the last reject brine) which was 38.33 mg/L.

Fig 4.6 shows all the trace elements detected in the 2008 samples at Tutuka Power Station. Sample T508 is RO permeate and it shows a significant reduction in the concentration of trace elements. In sample TP1008 (vapour compressor product), only 7 out of 25 original trace elements are detected. Detailed percentage reduction/increase in major and trace elements at each sampling point relative to the starting water will be discussed later under section 4.3.7.

It is quite difficult to note any trends with all the trace elements from all the samples on one graph (see Fig 4.6). The trace elements were therefore split into two groups; namely the toxic ones (Tanji and Kielen 2002) and the non-toxic ones. To further simplify the graphs, only mine water, RO permeate, brine after contact with ash, vapour compressor brine and vapour compressor product waters were considered. The reason for this choice was because mine water is the main input into the

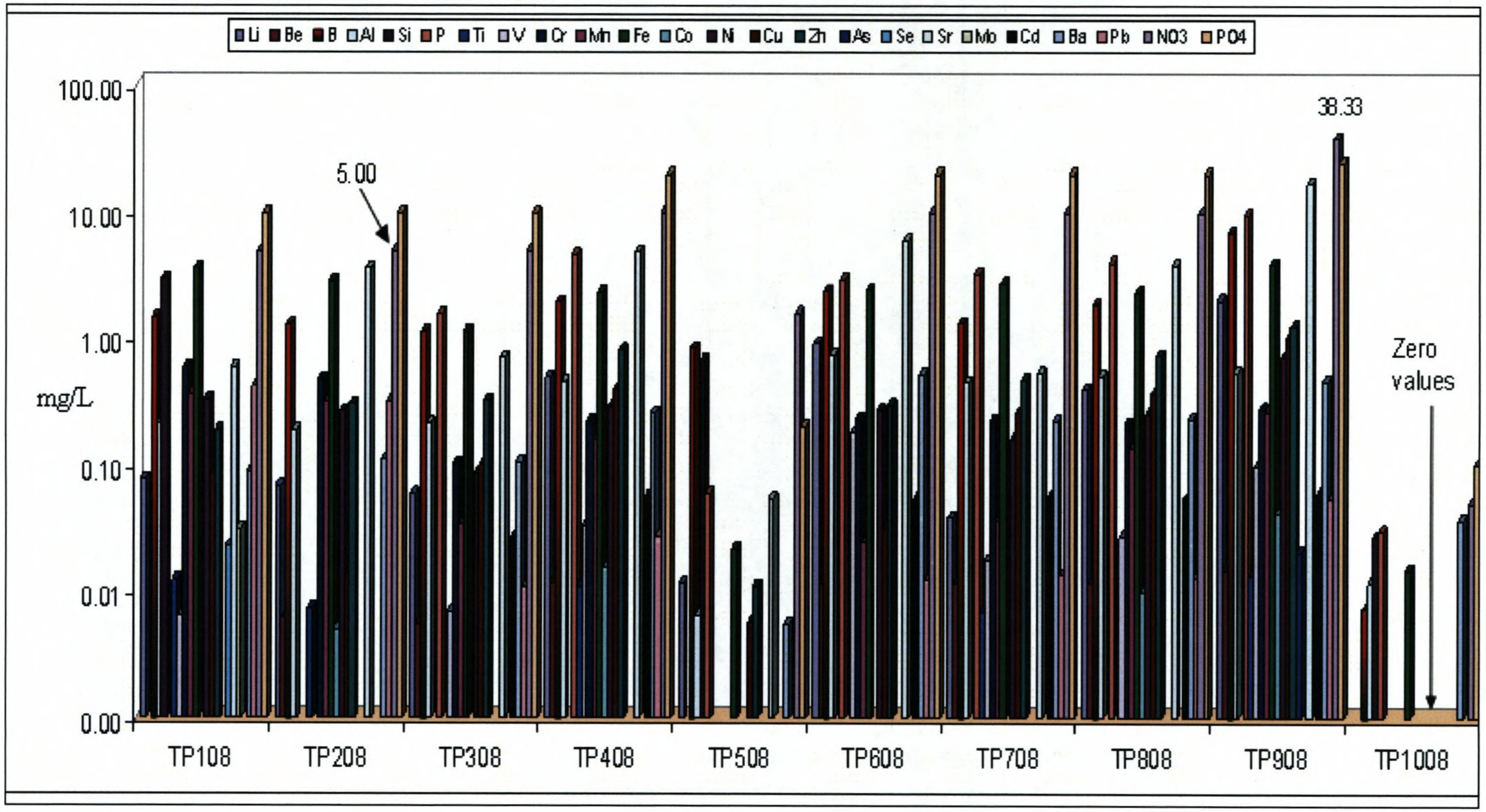


Figure 4.5: Trace elements in Tutuka Power Station 2008 samples.

treatment process while reverse osmosis, vapour compression and brine treatment are the main important treatment stages in this study.

4.2.3.1 Toxic Trace Elements

The toxic trace elements found in the specified waters (section 4.33) are shown in Fig 4.6.

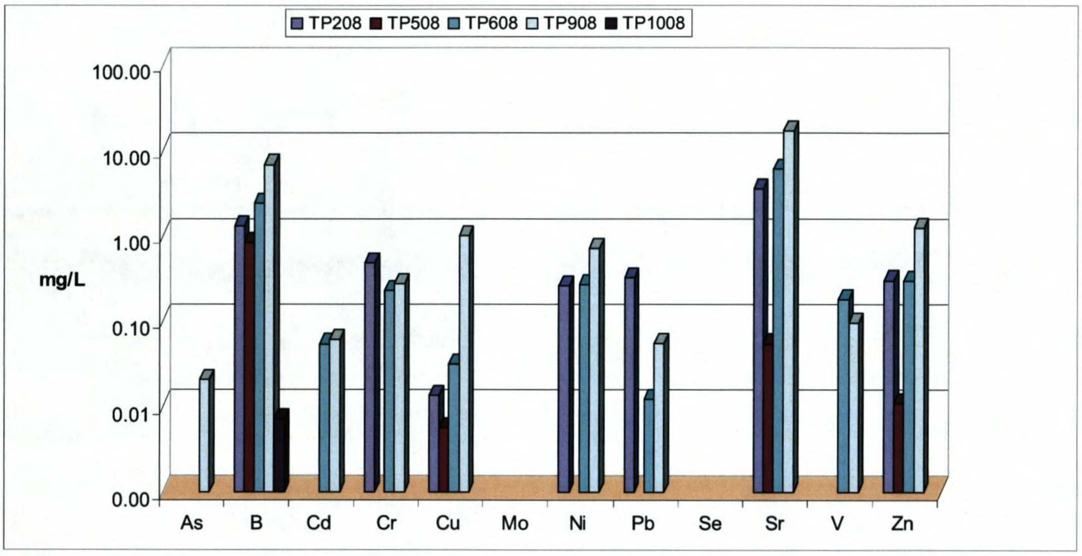


Figure 4.6: Toxic elements in mine water (TP208), RO permeate (TP508), VC product (TP1008) VC brine (TP908) and brine after contact with ash (TP608).

Fig 4.6 shows that arsenic was found only in the highly concentrated vapour compressor brine (TP908) at 0.02 mg/L. This water also contained the highest concentrations of boron, cadmium, copper, nickel, strontium and zinc as compared to the other samples. Brine after contact with ash (TP608) contained the highest amount of vanadium while molybdenum and selenium are not detected in this set of samples. The vapour compressor product (TP1008) only contained boron from the toxic subset of trace elements and RO permeate (TP508) contains boron, copper, strontium and zinc.

4.2.3.2 Non-Toxic Trace Elements

The non-toxic trace elements in the specified samples are shown in Fig 4.8. From Fig 4.8 reverse osmosis and vapour compression treatment stages showed a greatest ability to remove the non-toxic trace elements from the contaminated waters. However the results showed that silicon is only present in vapour compressor product and RO permeate. It was earlier reported to be present in ultra pure water as a major cation observed upon analysis of this water source in section 4.2 of this chapter. The concentration range of the non-toxics ranged from 0.0 mg/L to 38.33 mg/L in the samples presented in Fig 4.10, with the highest concentration coming from nitrates in the vapour compressor brine.

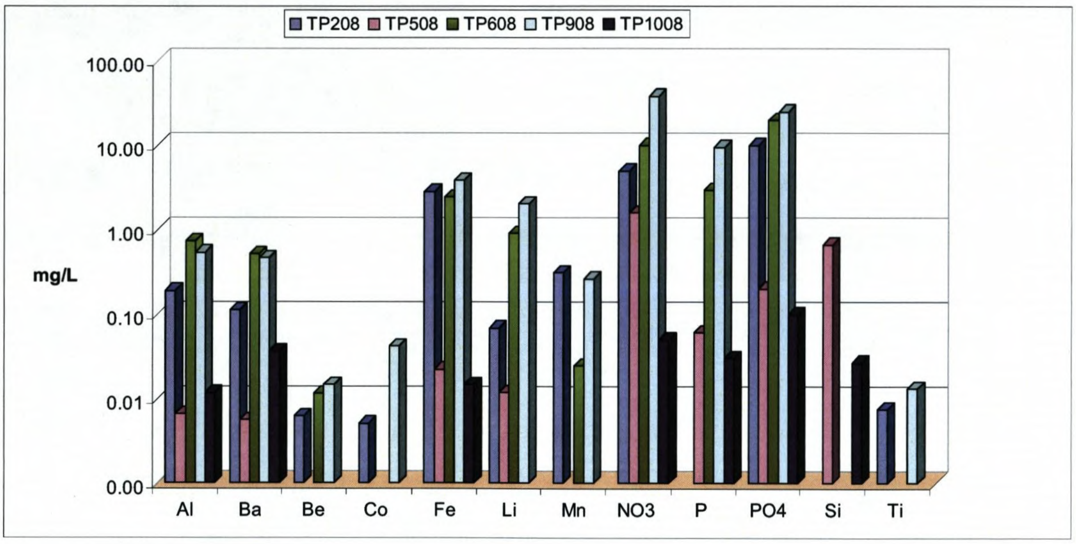


Figure 4.7: Non-toxic elements in mine water (TP208), RO permeate (TP508) VC product (TP1008), VC brine (TP908) and brine after contact with ash (TP608).

4.2.4 Total Alkalinity

Fig 4.9 shows total alkalinity results for samples taken in 2008 (see Appendix A3) at Tutuka Power Station as per the titrimetric method described in chapter 3. Alkalinity is of prime importance to any brine analysis because it is related to the pH and to the bicarbonate concentration, HCO_3^-, both used to predict scale tendency and corrosion potential of brine (Brine Chemistry Consortium, 2009). Alkalinity is generally the sum of two primary components, HCO_3^- and carboxylic acids (e.g. acetate), in the brine (Brine Chemistry Consortium, 2009). Acetate was not determined, which is one of the delimitations in this study. The main reason why carboxylic acids were not analysed, is that there was no simple titration method to use immediately after sampling in the field. Generally, it is necessary to do gas chromatography (Brine Chemistry Consortium, 2009). The drawback of not considering carboxylic acids in determining total alkalinity, as is generally done in industry, is that the calculated pH in the water will be too high and the scale tendency estimate will be too large. This can cause over treatment for scale, when, in fact, the water is corrosive, due to a low pH (Brine Consortium, 2009).

Alkalinity at Tutuka Power Station from the 2008 samples ranged from 6.80 to 1147.6 mg/L $CaCO_3$. The lowest alkalinity was from the vapour compressor product (TP1008) which has most of the salts removed. The highest alkalinity was from the vapour compressor brine (TP908), which was the most concentrated brine on the site. The alkalinity of the brine after contact with ash (TP608) was less than that of the brine before contact with ash. However, the Tutuka Power Station 2007 results showed the opposite (see Appendix A2). This could possibly be due to a laboratory analysis error or that the SRO brine was temporarily used to quench the bottom ash prior to sampling.

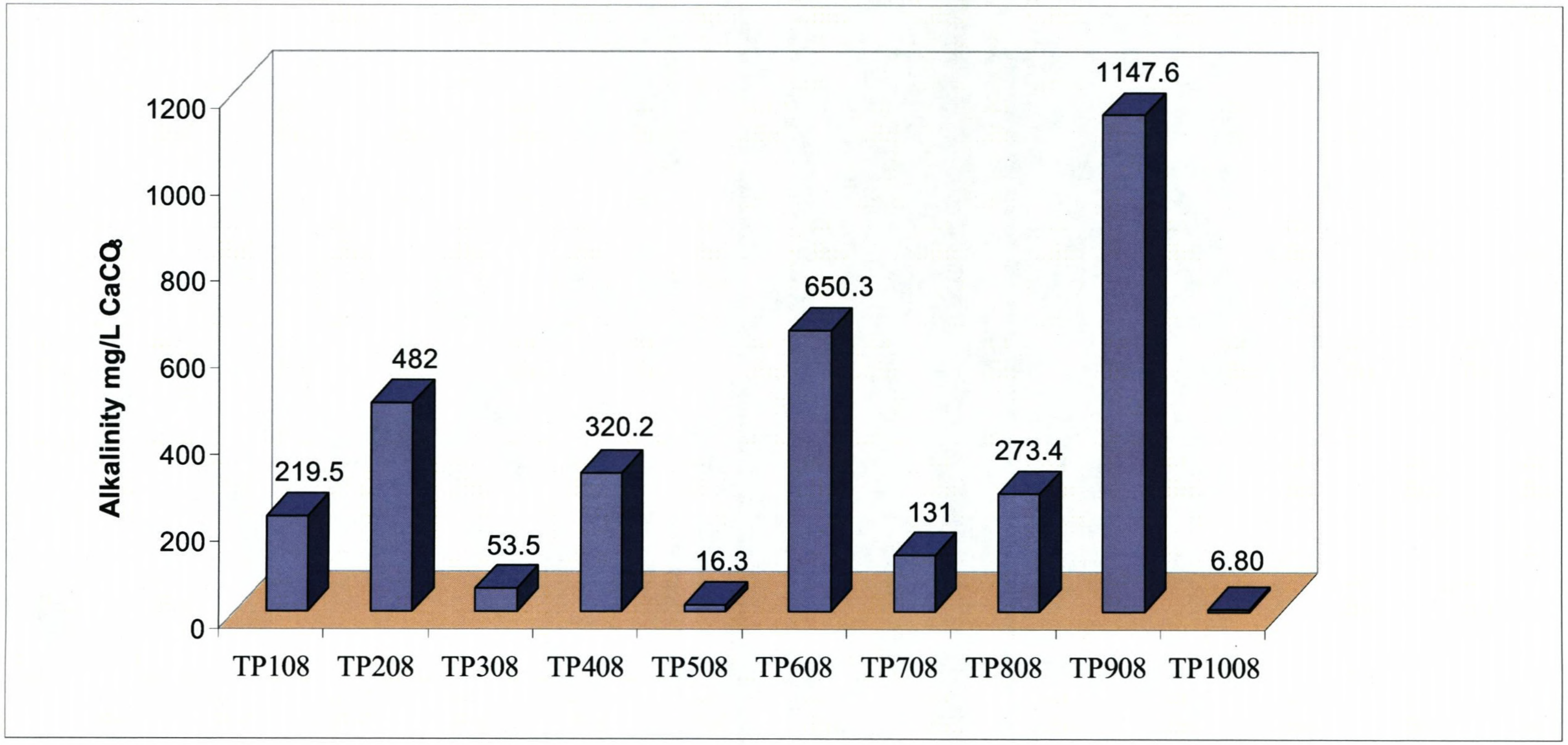


Figure 4.8: Alkalinity in Tutuka Power Station 2008 samples.

4.2.5 pH

The pH of water samples was determined by the method discussed in Chapter 3 section 3.2.1. The pH of water determines the solubility and biological availability of its chemical entities (USGS, 2009). In the case of heavy metals, the degree to which they are soluble determines their toxicity. Metals tend to be more toxic at lower pH because they are more soluble at that pH (USGS, 2009). The relationship between pH and saturation indices of some selected minerals will be discussed later in this chapter. Fig 4.10 shows the pH of Tutuka Power Station samples over a period of three years. It varied between 5.37 and 12.85. The pH was always lowest in RO permeate and highest in brine after contact with ash.

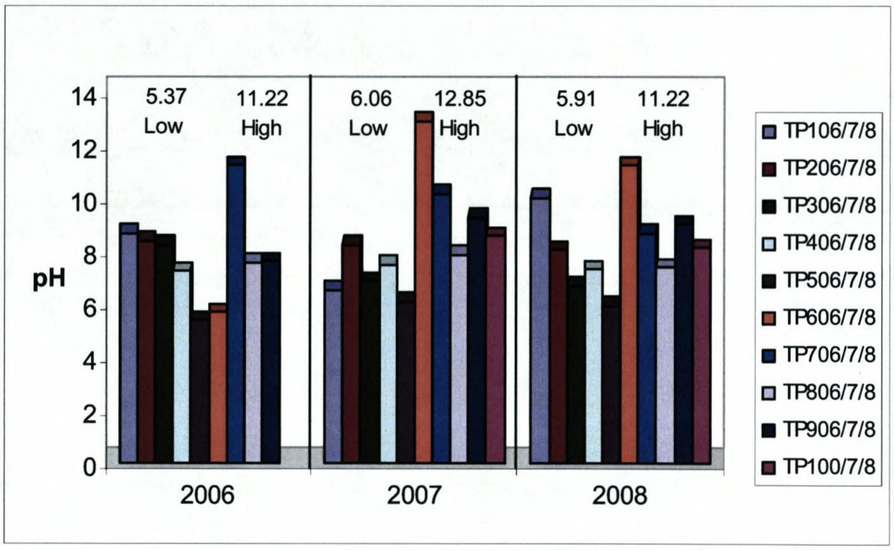


Figure 4.9: pH of water samples from Tutuka Power Station.

N.B: The first two letters and first two digits in sample numbers were common for each year. The last digit is unique and it signified the year the sample was taken.

4.2.6 Sodium Absorption Ratio

The sodium absorption ratio (SAR) is a parameter widely used to classify irrigation waters. The SAR of waters at Tutuka Power Station was calculated using the Aq.QA software. Fig 4.11 shows the SAR values of the different waters which will be used to evaluate their suitability for use in irrigation. According to the Texas University Agricultural Services (TUAS) water classes (see chapter 2 section 2.3.3.2), only water with SAR values below 10 is permitted to be used as irrigation water. Fig 4.11 shows that only the vapour compressor product will fall under water suitable for irrigation under the TUAS water class system.

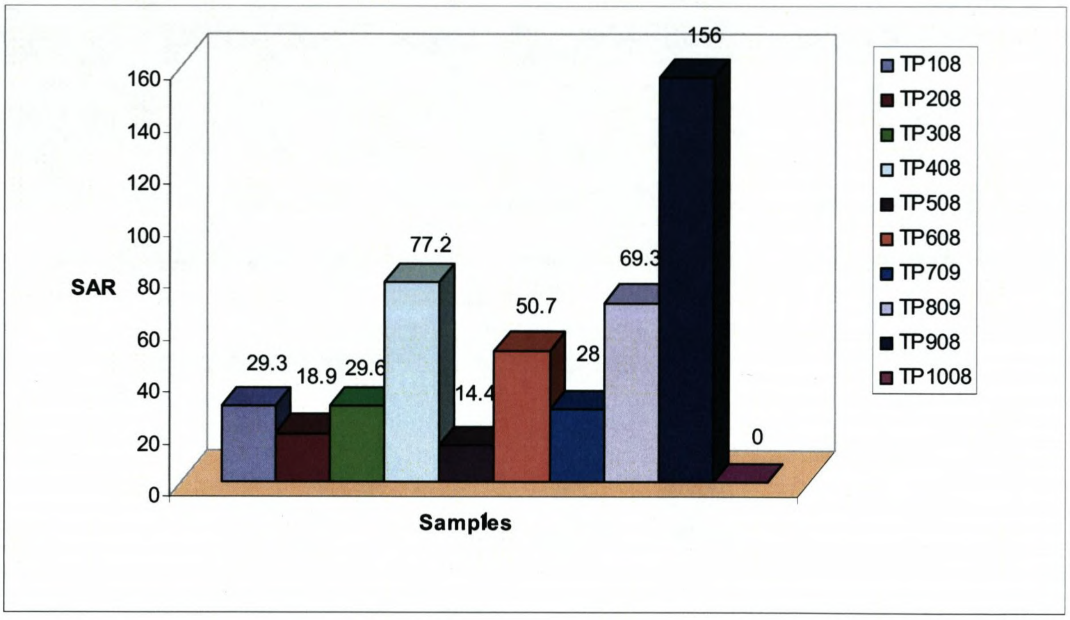


Figure 4.10: Sodium adsorption ratio (SAR) values of Tutuka Power Station samples taken in 2008.

4.2.7 Evolution of Water Streams at Tutuka Power Station

Cooling water from the evaporation towers and mine water are the starting point in the water treatment process at Tutuka Power Station as to date. Previously in 2006, raw water from the nearby Grootbaai Dam was also used as cooling water make up.

Only the current water treatment process in place is going to be discussed in this chapter using the 2008 results. The mine water-cooling water mixture evolves as it progresses through each stage of treatment. Fig 4.12 shows the samples taken for analysis and their positions in the water treatment process. To show the increase or decrease in the salt load in each stream, differences in ion content were calculated in relation to the starting water (TP108), using the following equations .

$D\ (mg/L) = I_w - I_{sw}$ ....Equation 4.1

$\%D = \frac{I_w - I_{sw}}{I_{sw}} \times 100$ ....Equation 4.2

Where, D is ion concentration difference in mg/L

I_w is ion concentration of a water stream in mg/L (except pH)

I_{sw} is ion concentration of the starting water in mg/L (except pH)

% D is the percentage difference in relation to the starting water

A negative percentage difference indicates that the parameter in question decreased with the given percentage while a positive one indicates that the parameter increased with that percentage. A zero value indicates no change in concentration from the starting water. For the purposes of this study, I have used this format to explain the variability in ion concentration in the water streams.

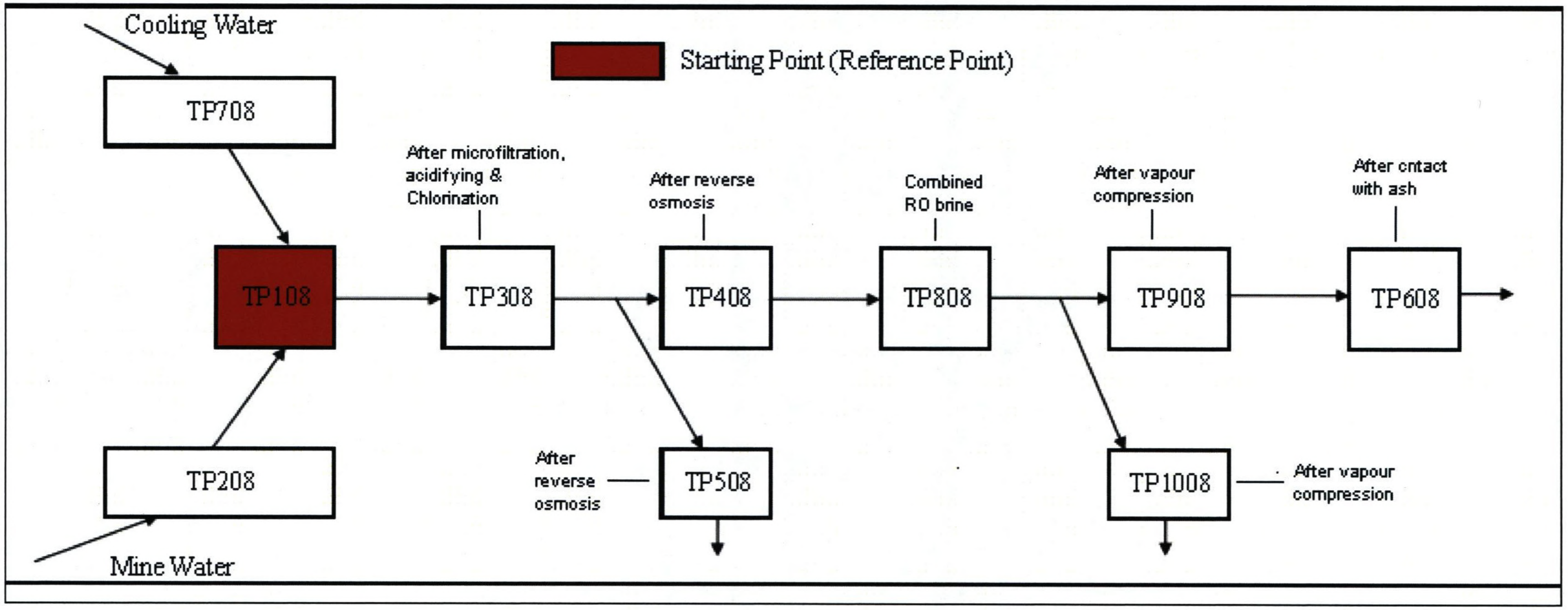


Figure 4.11: Sampling points in 2008 and their positions in the water treatment process at Tutuka Power Station.

Table 4.1: Percentage differences in ion concentration from TP108.

Parameter	TP108	TP208	TP308	TP408	TP508	TP608	TP708	TP808	TP908	TP1008
Ca	0.0	263.1	-1.3	517.4	-91.9	1937.0	135.7	417.9	1930.0	-99.0
Mg	0.0	71.0	-8.7	526.2	-92.3	-96.2	-22.0	388.2	1894.4	-99.9
Na	0.0	-2.3	-2.2	554.6	-86.2	331.2	7.4	425.5	2237.1	-99.8
Li	0.0	-11.0	-22.2	537.0	-84.6	1077.9	-50.1	409.1	2520.7	-99.8
Be	0.0	252.0	217.5	570.6	-97.8	550.1	551.9	553.1	736.8	-100.0
B	0.0	-11.3	-21.9	33.6	-43.2	63.9	-10.2	27.8	366.3	-99.5
Al	0.0	-11.3	1.4	112.4	-96.9	243.2	109.2	135.3	152.6	-94.6
Si	0.0	-100.0	-100.0	-100.0	-77.6	-100.0	-100.0	-100.0	-100.0	-99.1
P	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K	0.0	-69.3	-4.5	549.0	-86.9	370.2	64.8	441.3	2203.2	-99.8
Ti	0.0	-40.4	-82.7	-11.1	-97.9	-61.2	-44.1	-72.6	6.0	-99.2
V	0.0	-68.6	7.3	402.7	-91.7	2660.2	173.6	315.4	1383.6	-98.1
Cr	0.0	-21.1	-83.0	-62.9	-99.7	-61.9	-62.9	-65.3	-53.8	-99.9
Mn	0.0	-14.3	-90.8	-56.7	-98.9	-93.3	-90.1	-62.6	-28.1	-99.9
Fe	0.0	-21.2	-68.5	-34.5	-99.4	-31.8	-23.9	-35.1	6.7	-99.6
Co	0.0	224.8	73.6	914.1	-93.3	28.2	60.6	540.7	2564.1	-100.0
Ni	0.0	-20.4	-74.1	-11.8	-99.0	-18.9	-51.1	-24.4	113.9	-99.8
Cu	0.0	-83.9	15.7	358.3	-93.3	-62.7	204.5	326.6	1064.9	-99.6
Zn	0.0	60.7	72.6	332.6	-94.1	57.3	151.5	285.3	565.2	-97.8
As	0.0	-100.0	-81.5	295.6	-73.1	-133.2	-100.0	-60.1	2522.8	-89.3
Se	0.0	-100.0	-100.0	-99.6	-97.9	-100.0	-100.0	-100.0	-100.0	-98.6
Sr	0.0	498.3	18.0	707.0	-90.9	903.2	-10.9	539.9	2702.4	-99.6
Mo	0.0	-100.0	-100.0	-100.0	-97.6	-100.0	-100.0	-100.0	-100.0	-99.5
Cd	0.0	-132.3	2815.3	6013.1	-47.0	5812.8	6074.4	5681.7	6515.6	-71.5
Ba	0.0	27.1	19.9	194.2	-93.7	486.2	150.1	165.2	426.7	-58.5
Pb	0.0	-24.1	-97.5	-93.5	-99.9	-97.1	-96.8	-96.9	-87.0	-100.0
Cl	0.0	-8.7	-1.3	564.1	-75.5	339.5	15.0	450.0	2265.1	-99.9
NO_3	0.0	0.0	0.0	100.0	-67.7	100.0	100.0	100.0	666.6	-99.0
PO_4	0.0	0.0	0.0	100.0	-98.0	100.0	100.0	100.0	150.0	-99.0
SO_4	0.0	-7.0	5.2	624.4	-91.0	379.6	11.4	469.2	2377.7	-99.8
pH	0.0	-19.8	-33.4	-27.3	-41.0	12.1	-13.6	-26.5	-10.3	-19.1

Table 4.1 shows that TP208 (mine water) has 263.1 % more calcium than after it is mixed with cooling water to give TP108 (the starting water). TP308 (sampled after chlorination, pH adjustment and microfiltration), removes 1.3 % calcium from TP108 (the starting water). The evolution of silica requires further investigation as it disappears and reappears in the water treatment circuit. For instance, it is at a concentration of 0.00 mg/L in TP308 (RO feed) but reappears at 0.67 mg/L in RO permeate and is at 0.00 mg/L in RO brine. This could be as a result of detection problems in sample analysis or the water treatment methods being used at Tutuka Power Station could not significantly remove silica.

Table 4.2: Summary of major ions removed by major treatment stages (pH included).

Parameter	TP308	TP508	TP1008
Ca	-1.3	-91.9	-99.0
Mg	-8.7	-92.3	-99.9
Na	-2.2	-86.3	-99.8
Cl	-1.3	-75.5	-99.9
SO_4	-5.2	-91.0	-99.8
K	-4.5	-86.9	-99.8

To further illustrate the data given in Table 4.1, Table 4.2 summarises the removal of major ions after;

(i) Clarification, acidification by sulphuric acid, chlorination, sodium bisulphite addition and microfiltration (TP308)

(ii) Reverse osmosis (TP508)

(iii) Vapour compression (TP1008)

In TP308, the treatment processes identified in (i) above collectively remove 1.3 % calcium, 8.7 % magnesium, 2.2 % sodium, 1.3 % chloride and 4.5 %. However sulphate increases by 5.2 %. This comes from the sodium bisulphite that is added to remove any traces of chlorine in the reverse osmosis feed water. Chlorine damages the reverse osmosis membranes.

In TP508, reverse osmosis reduces the concentration of major ions by a percentage ranging from 75.5 % to 92.3 % in relation to TP108. The vapour compression product comes out 99 to 99.9 % cleaner than TP108 as far as major ions are concerned and its pH reduced by 19.1 % in relation to TP108.

Tutuka power station utilises brine to condition ash during ash transportation as well as at the ash dams. During this research, samples of brine before and after contact with ash were taken and analysed as per the methods of analysis described in chapter 3 section 3.2. Fig 4.13 shows the samples of brines before and after contact with ash and Table 4.3 sets out the major ion chemistry before and after contact with ash. TP408 is RO brine which is further treated by the vapour compressor to give VC brine TP908. TP908 is used to condition ash and TP608 is the brine obtained after TP908 has been in contact with ash.

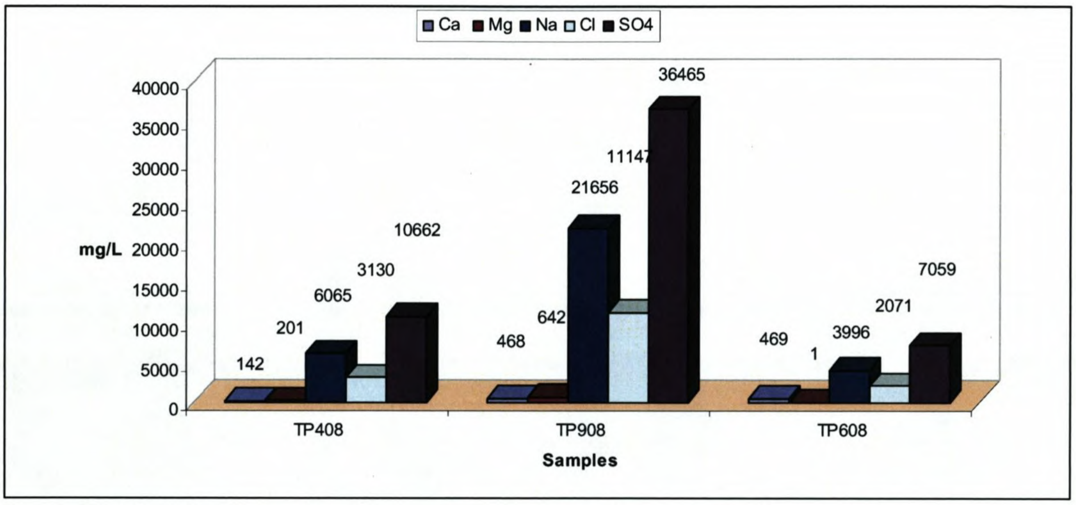


Figure 4.12: Diagram showing major ion chemistry evolution of brines before and after contact with ash at Tutuka Power Station.

Key: TP408=RO brine, TP908=VC brine, TP608=Brine after contact with ash.

Table 4.3: Major ion chemistry in Tutuka Power Station brines before and after contact with ash.

Parameter	TP408	TP908-TP408	Comment	TP908	TP908-TP608	Comment	TP608
Ca	142.25	325.46	228.8% increase	467.71	-1.62	0.35% increase	469.32
Mg	201.49	440.22	218.5% increas	641.70	640.49	99.8% decrease	1.21
Na	6065.39	15590.93	257.0% increase	21656.32	17660.26	81.6% decrease	3996.05
Cl	3130.03	8017.27	256.1% increase	11147.30	9075.93	81.4% decrease	2071.37
SO_4	10661.51	25803.49	242.0% increase	36465.00	29406.45	80.6% decrease	7058.55
pH	7.28	1.70	23.4% increase	8.98	-2.24	24.9% increase	11.22

Table 4.3 shows that RO brine major ions are concentrated in the vapour compressor by between 218 % and 257 % in relation to the RO brine. The pH is increased by 1.7 units signifying an increase in alkalinity (see Fig 4.9 section 4.3.4). Dissolution and hydrolysis of the basic oxides (CaO and MgO) contribute to the pH increase in brines after contact with ash (Gitari et al., 2009). The change in pH may also be influenced

by ingress of CO_2 from the atmosphere (Gitari et al., 2009). After TP908 has been in contact with ash, the major ions are reduced by between 80.6 % and 99.8 % with the exception of calcium which increases by 0.35 %. This is in relation to TP908 and it signifies an increase in alkalinity in contrast to the discussion in section 4.3.4 where alkalinity titration results show a decrease. It confirms the idea that alkalinity test results could have been misleading. However this should be treated with caution since carboxylic acids were not determined and their effect is discussed in section 4.3.4. Thus ash can be used to reduce the ion concentration in brines but it was found to increase some ions such as Ca as well as pH.

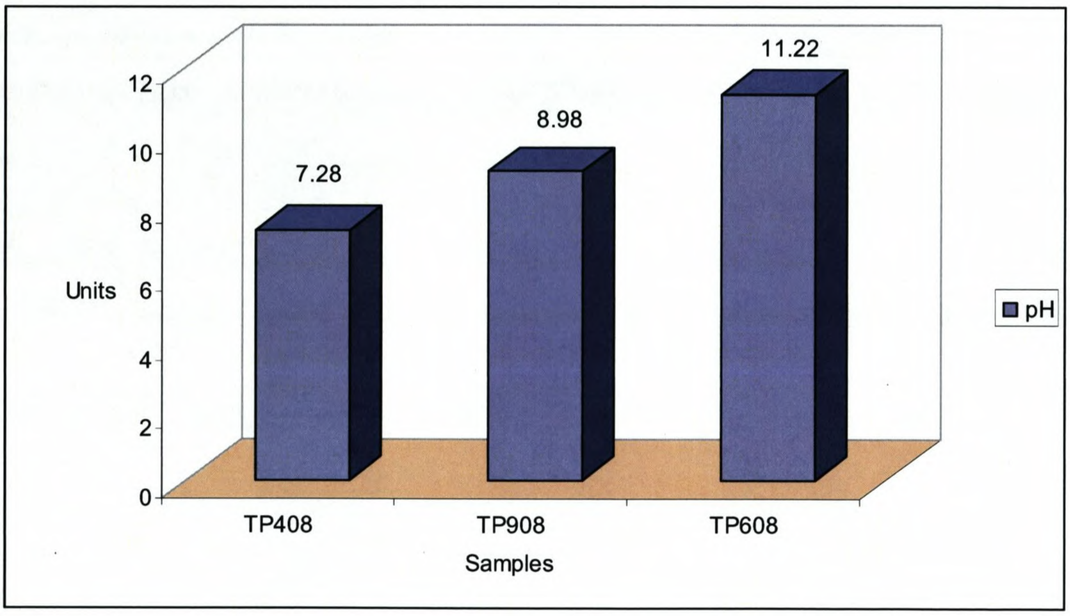


Figure 4.13: Increase in pH in Tutuka Power Station brines before and after contact with ash.

Table 5.4 illustrates the behaviour of trace elements in Tutuka Power Station brine samples before and after contact with ash. The vapour compressor concentrates the trace elements by between 8.2 % and 563 % from the RO brine. The increases and decreases in Be, Ti, Se and Mo are very small and almost insignificant (see detailed results in the Appendices A1-A3). They were found to be present in very minute concentrations to the order of 0.01 mg/L. TP608 shows that contact with ash reduces the trace ion concentration by percentages ranging from 10.6 % to 101.3 %. The results indicated that contact with ash also increased Al content by 35.9 %, V content by 86.0 % and Ba content by 11.3 %. Therefore ash was found to remove many trace elements as well as add some trace elements into brine.

Table 4.4: Trace element levels in Tutuka brines before and after contact with ash.

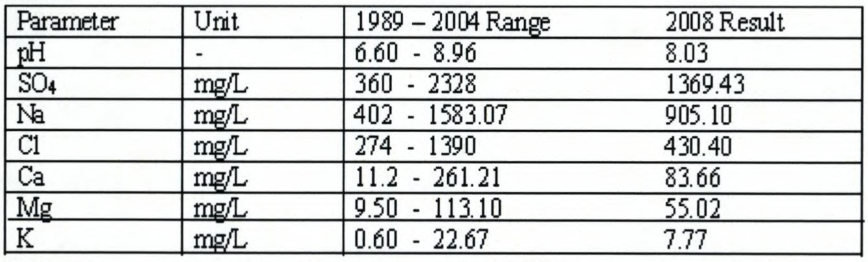
Parameter	TP408	TP908-TP408	Comment	TP908	TP908-TP608	Comment	TP608
Li	0.493	1.534	311.4% increase	2.027	1.116	55.1% decreae	0.911
Be	0.012	0.003	0.0	0.015	0.003	22.3% decrease	0.011
B	1.959	4.877	248.9% increase	6.836	4.433	64.8% decrease	2.403
Al	0.455	0.086	19.0% increase	0.541	-0.194	35.9% increase	0.735
Si	0.000	0.000	0% increase	0.000	0.000	0.0	0.000
P	4.665	4.808	103.1% inrease	9.473	6.534	69.0% decrease	2.939
K	164.300	418.783	254.9% increase	583.083	464.037	79.6% decrease	119.047
Ti	0.011	0.002	0.0	0.013	0.008	63.4% decrease	0.005
V	0.033	0.064	195.1% increase	0.097	-0.084	86.0% increase	0.181
Cr	0.225	0.056	24.7% increase	0.280	0.049	17.5% decrease	0.231
Mn	0.158	0.105	66.0% increase	0.263	0.238	90.7% decrease	0.025
Fe	2.372	1.487	62.7% increase	3.859	1.391	36.0% decrease	2.468
Co	0.016	0.026	162.7% increase	0.042	0.040	95.2% decrease	0.002
Ni	0.293	0.418	142.6% increase	0.711	0.441	62.1 decrease	0.270
Cu	0.394	0.607	154.2% increase	1.001	0.969	96.8% decrease	0.032
Zn	0.817	0.439	53.8% increase	1.256	0.959	76.4% decrease	0.297
As	0.003	0.018	563.0% increase	0.021	0.021	101.3% decrease	0.000
Se	0.000	0.000	0.0	0.000	0.000	0.0	0.000
Sr	4.852	11.998	247.3% increase	16.850	10.818	64.2% decrease	6.032
Mo	0.000	0.000	0.0	0.000	0.000	0.0	0.000
Cd	0.057	0.005	8.2% increase	0.061	0.007	10.6% decrease	0.055
Ba	0.259	0.205	79.0% increase	0.464	-0.052	11.3% increase	0.517
Pb	0.028	0.027	99.4% increase	0.055	0.043	77.4% decrease	0.012
NO_3	10.000	28.328	283.3% increase	38.328	28.328	73.9% decrease	10.000
PO_4	20.000	5.000	25.0% increase	25.000	5.000	20% decrease	20.000

4.2.8 Tutuka Power Station Mine Water Historical Data

Historical data on the mine water used at Tutuka Power Station spanning a period of 15 years was obtained. Mine water is of paramount importance in this research as it is the main feed to the water treatment process. Although the data obtained was not continuous as some months' or even years' data was not available, it provided a good enough insight in the ranges in ion concentration over a long period. The detailed results are presented in the Appendices F1 and F2. The reason for the use of historic data in this study was to compare the data to results obtained during the research. It would be of no use to speciate and predict precipitation in a water that is not within the range experienced over a considerable period of time. It would be synonymous to incorporating an outlier in data analysis. In the historical data, outliers were left out of the graphs shown in Fig 4.16 (a), Fig 4.16(b) and Fig 4.16(c) but they can still be viewed in the detailed result sheet in the Appendices F1 and F2.

The following table summarizes the ranges of pH and the major ions from 1989 to 2004 and the corresponding results obtained in 2008 on which speciation modelling was carried out.

Table 4.5: Summary of historical pH and major chemistry in mine water at Tutuka Power Station.



Parameter	Unit	1989 – 2004 Range	2008 Result
pH	-	6.60 - 8.96	8.03
SO_4	mg/L	360 - 2328	1369.43
Na	mg/L	402 - 1583.07	905.10
Cl	mg/L	274 - 1390	430.40
Ca	mg/L	11.2 - 261.21	83.66
Mg	mg/L	9.50 - 113.10	55.02
K	mg/L	0.60 - 22.67	7.77

From Table 4.5, the analysis done in 2008 fit well within the ranges obtained from the historical data and thus modelling on the 2008 results would yield a fairly representative model of the scenario at Tutuka Power station.

Rainfall is nature's recharge to groundwater. One of the reasons why historical data was used in this research was to investigate the effect of rainfall on the concentration of trace and major elements in mine water used in desalination. This provides an insight into when higher salt loads are expected and therefore seasonal scaling potentials of the water. Monthly rainfall figures for 2003 were obtained from the South African Weather Service and compared to mine water trace and major ion concentrations in the same period. The outcomes of this comparison are shown if Fig 4.17, Fig 4.18(a) and Fig 4.18(b).

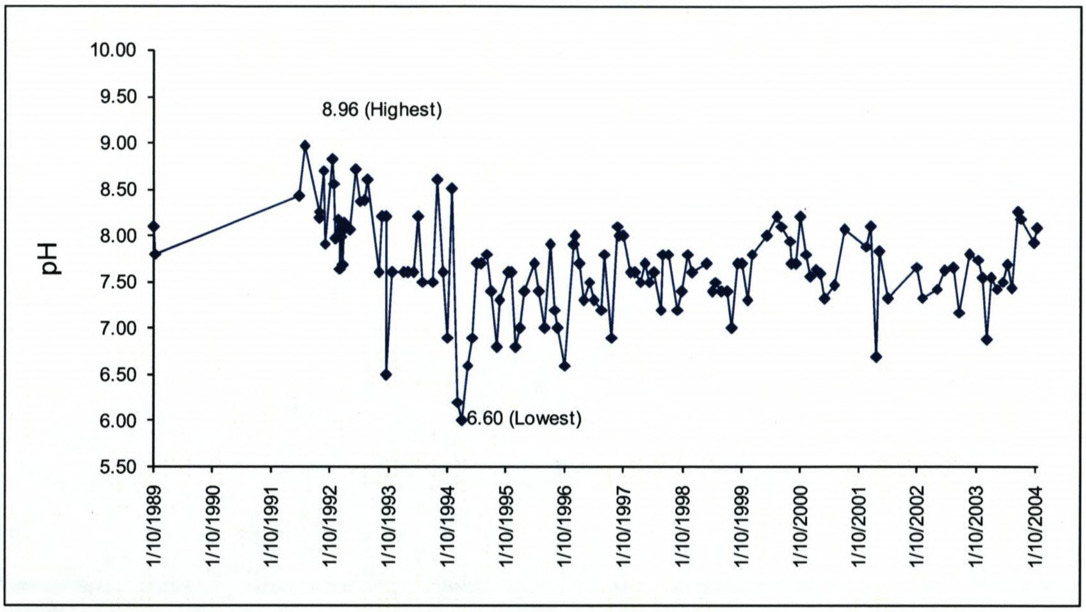


Figure 4.14: Historical data on pH of mine water at Tutuka Power Station.

From Fig 4.15, the lowest pH in the historical data was 6.60 and the highest was 8.96. Fig 4.16(a) shows Cl^- with 274.00 mg/L as the lowest and 1390 mg/L as the highest content experienced from 1989 to 2004. Ca ranged from a low of 11.20 mg/L to a high of 261.21 mg/L. Fig 4.16(b) shows Mg ranging from 9.50 to 113.10 mg/L and K from 0.60 to 22.67 mg/L. Fig 4.16(c) shows Na had a low of 402.00 mg/L and a high of 1583.07 mg/L. The lowest SO_4^{2-} content was 360.00 mg/L and the highest 2328.00 mg/L from 1989 to 2004. The lowest and highest values are shown in each graph.

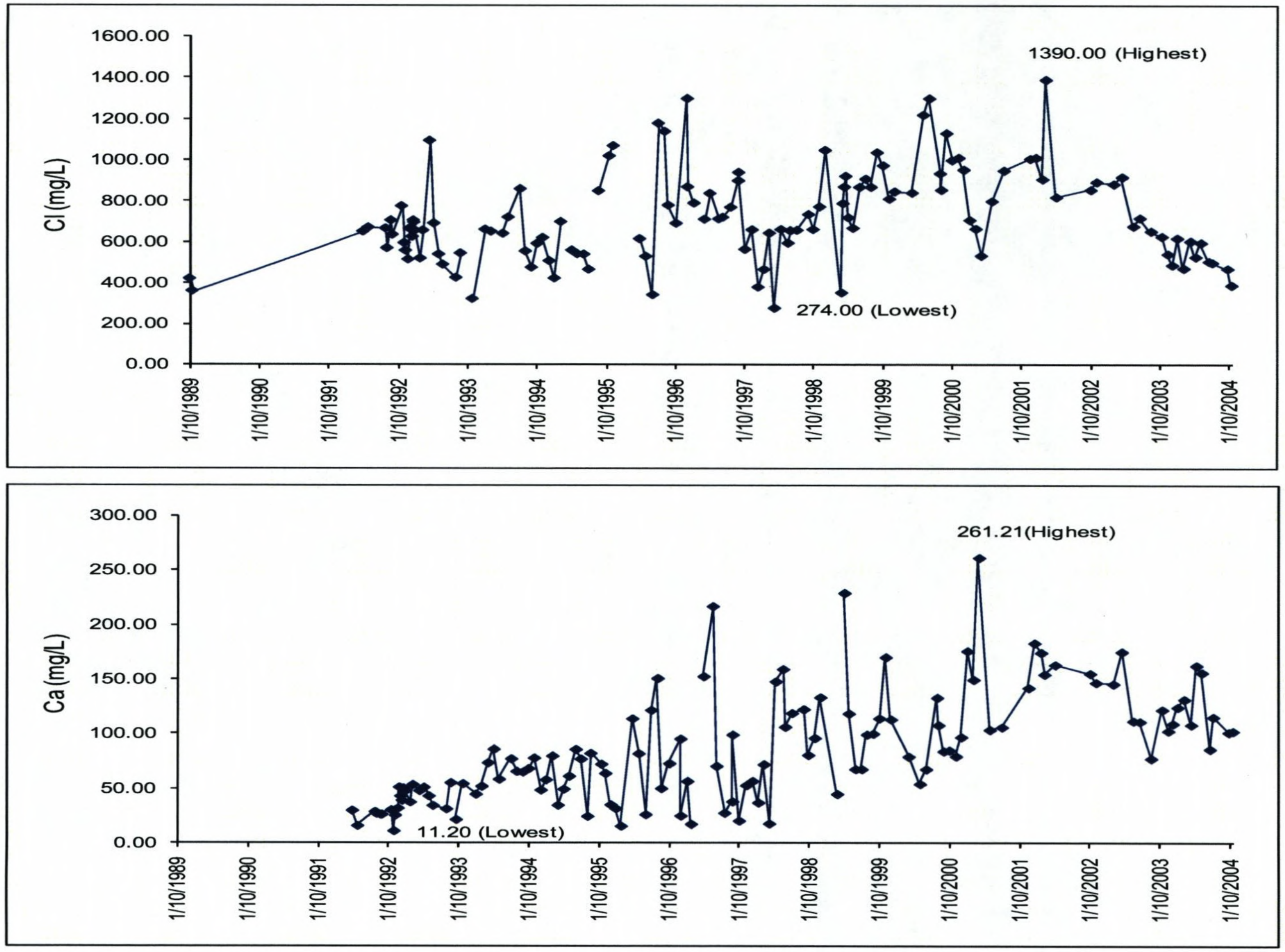


Figure 4.15(a): Historical data on major ion chemistry (Ca and Cl) of mine water at Tutuka Power Station.

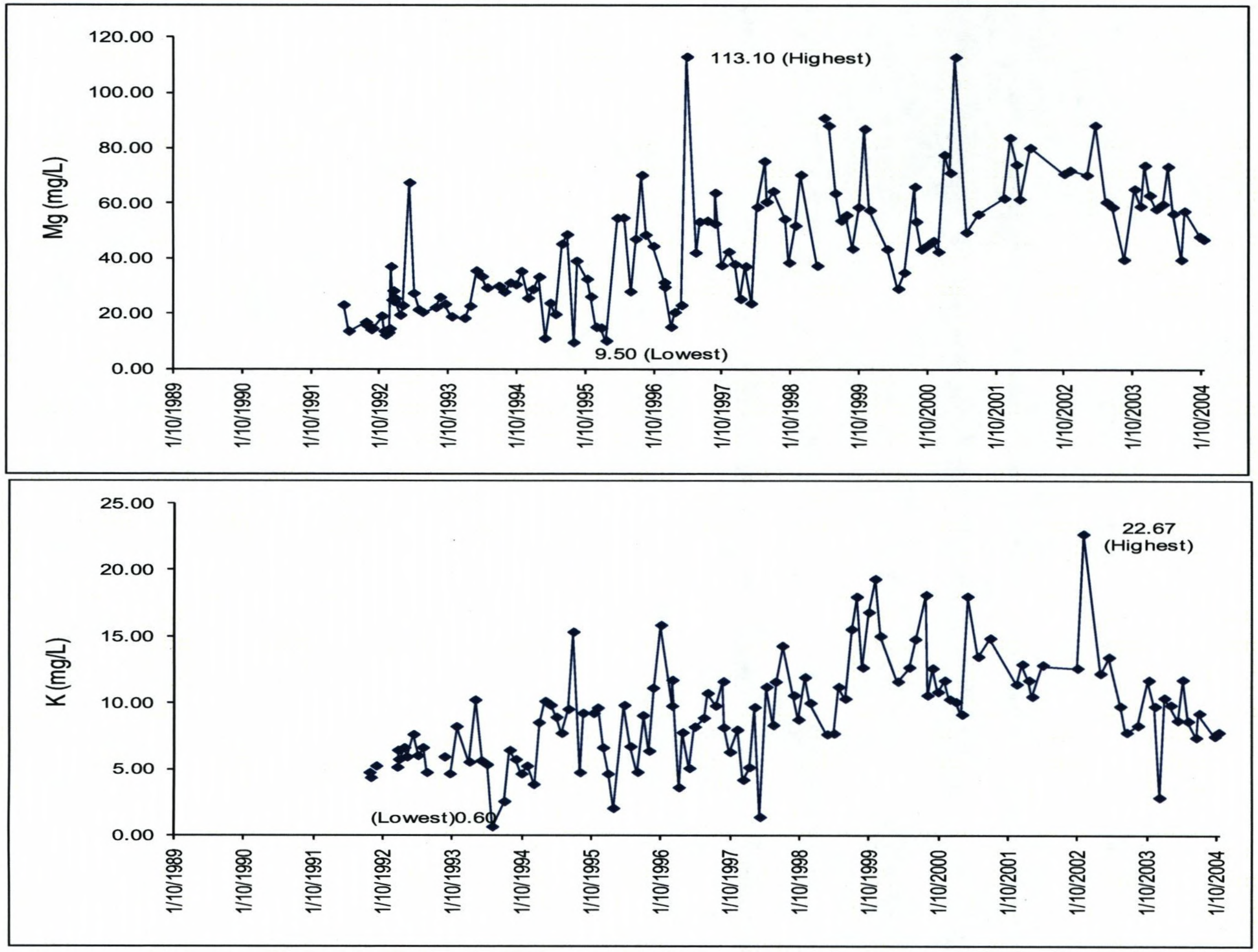


Figure 4.15(b): Historical data on major ion chemistry (Mg and K) of mine water at Tutuka Power Station.

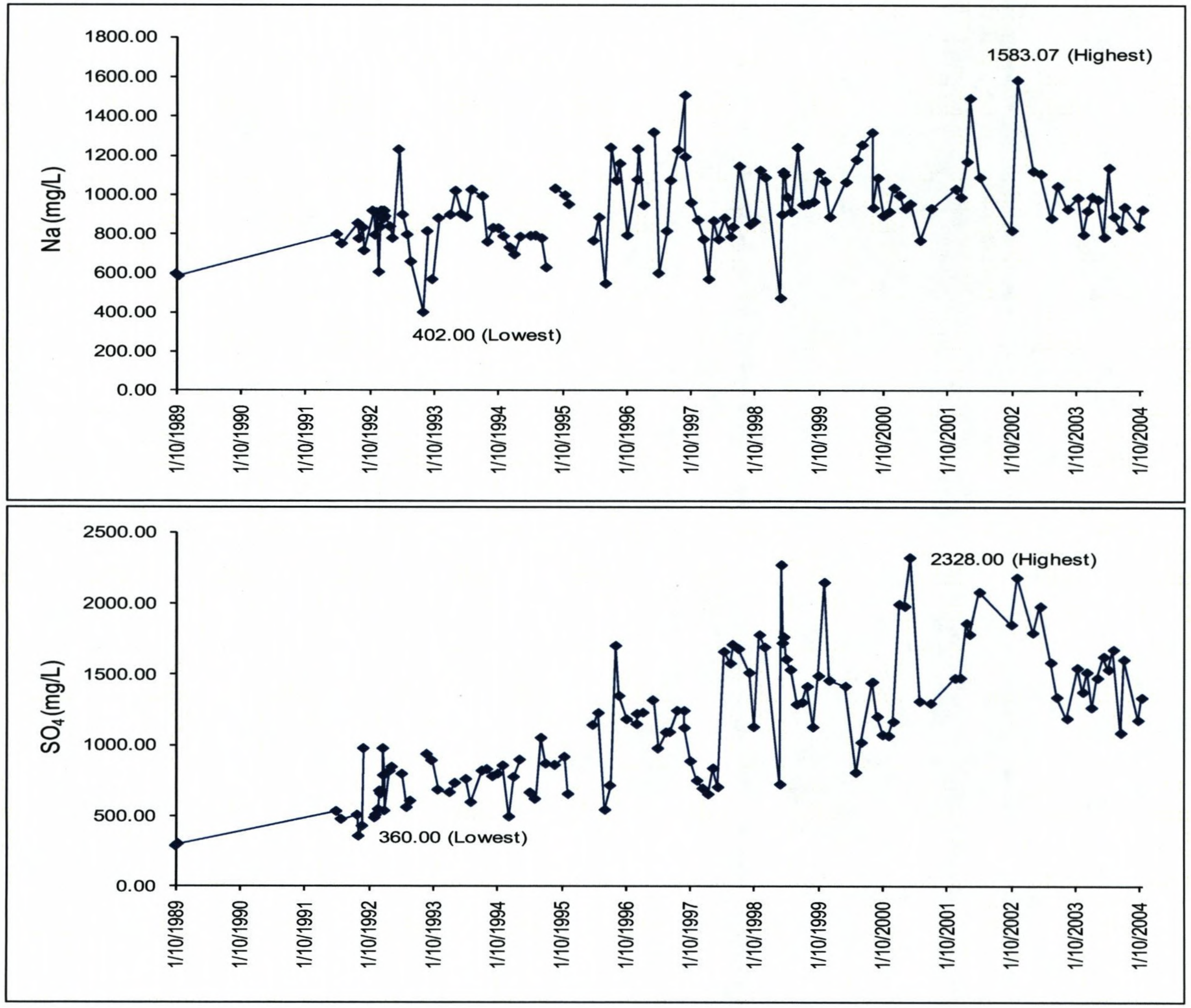


Figure 4.15(c): Historical data on major ion chemistry (Na and SO_4) of mine water at Tutuka Power Station.

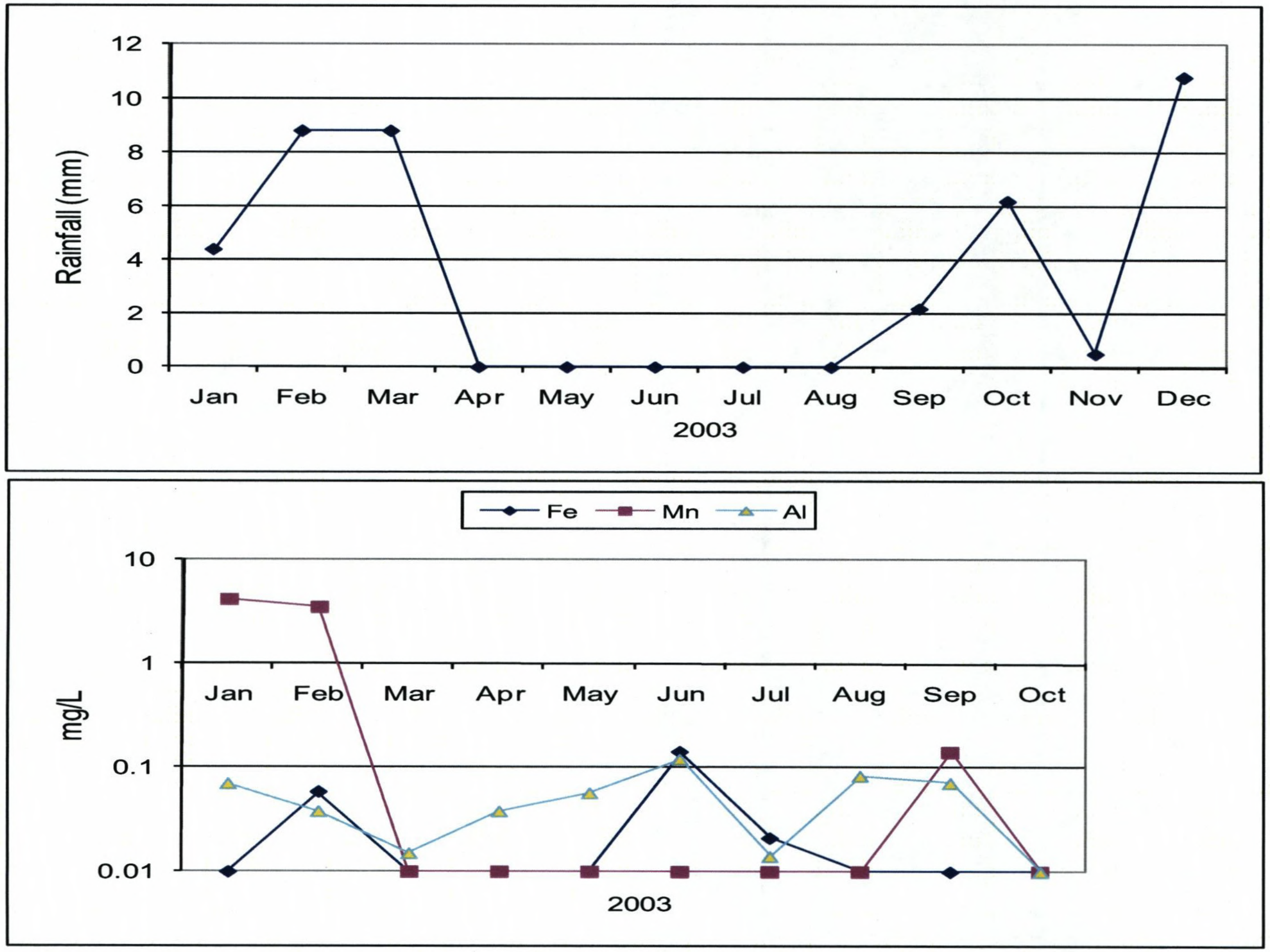


Figure 4.16: Graphs showing the effect of rainfall on Fe, Mn and Al concentration in mine water in 2003 at Tutuka Power Station.

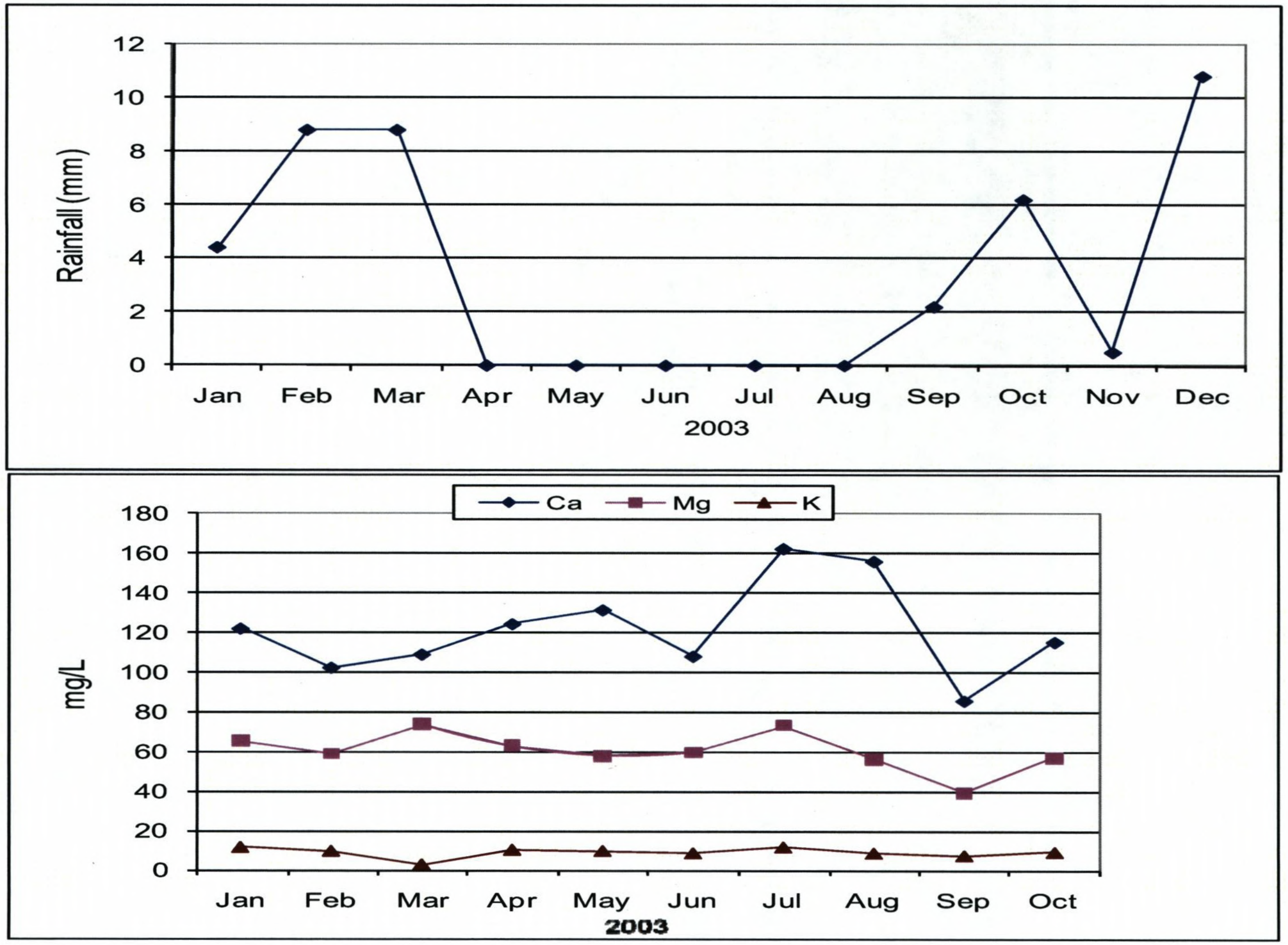


Figure 4.17 (a): Graphs showing the effect of rainfall on Ca, Mg and K concentration in mine water in 2003 at Tutuka Power Station.

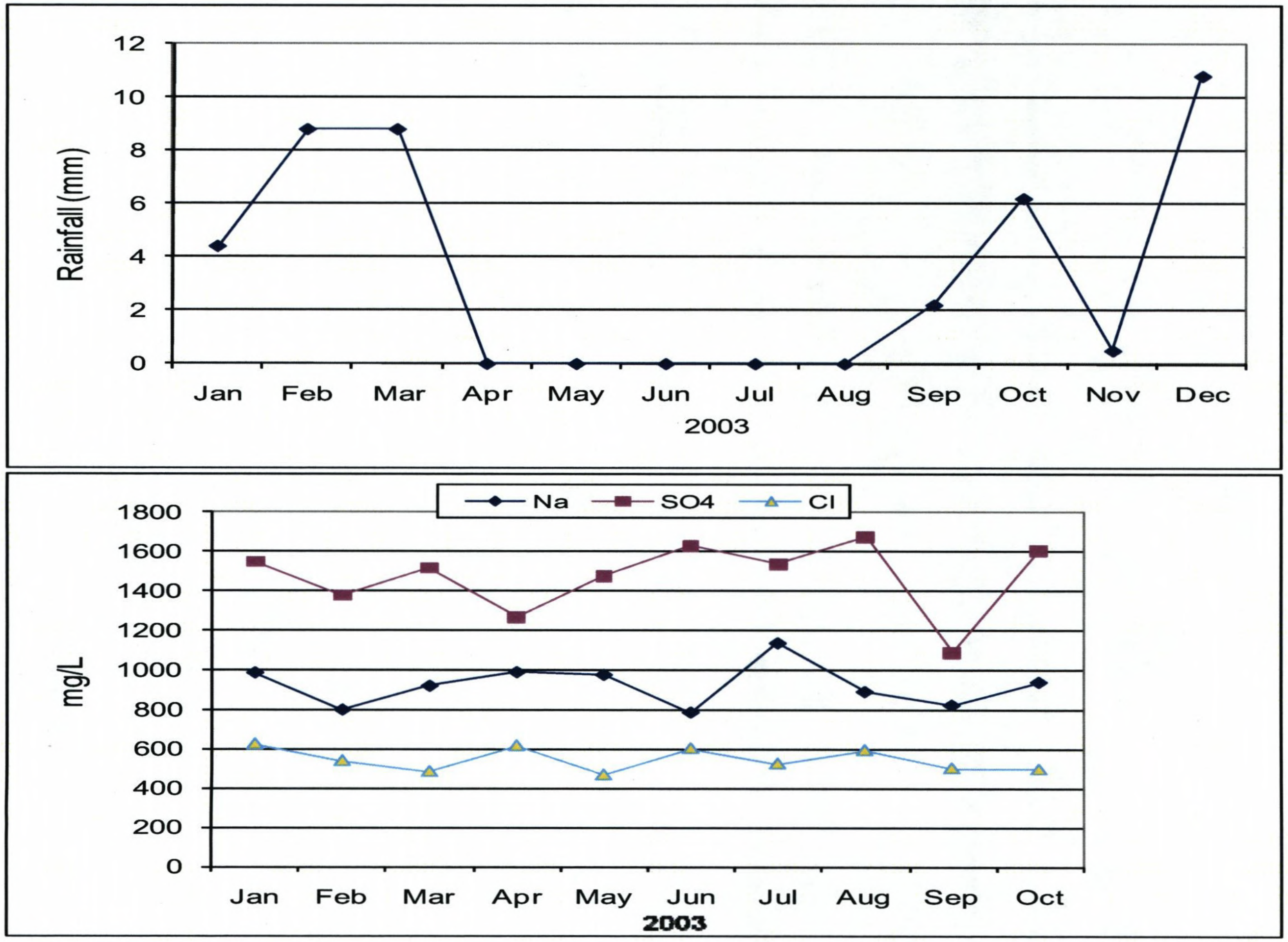


Figure 4.17(b): Graphs showing the effect of rainfall on Na, SO_4 and Cl concentration in mine water in 2003 at Tutuka Power Station.

Fig 4.17 shows the relationship between the concentration of trace elements in mine water and the amount of rainfall received in the area. Mn was the only element that showed a trend which was similar to that of the rainfall pattern. This result showed that the rainfall can affect the amount of Mn in groundwater. Fe shows the same trend but the shape formed by the trend is lagging behind the rainfall trend. Al does not show any trend similar to that of the rainfall.

Ca, Mg, Na, Cl, K and SO_4 show a general trend of low concentration when the rainfall is high and high concentration when the rainfall is low. This signifies that dilution of water input streams at Tutuka Power Station by rain may thus have a significant effect on water quality as can be expected but the correlation is not direct or inverse in all cases, with lag times observed as well as inconsistencies that point to other factors such as possible inputs of water treatment chemicals. At Tutuka Power Station, they add on average 100 kg/day of sodium bisulphite, 400 L/day of 98 % H_2SO_4.

4.3 Chemical Composition of Water Streams at Sasol Synfuels Complex at Secunda

Sasol Synthetic Fuels Complex in Secunda has a more complex water treatment process than Tutuka Power Station. It is a closed loop system that is in accordance with their endeavours to attain zero liquid discharge. Due to the amount of samples involved with Sasol Synfuels Complex, only the essentially important samples to a discussion will be considered. Process cooling water blowdown was sampled but was not fully analyzed because of its very oily state. Filtration was impossible and some important field measurements could not be taken. However historical data on process cooling water and process cooling water blowdown was obtained and a discussion on its character will be done in this chapter. Speciation modeling was only done on the most concentrated brine and mine water for comparison purposes with Tutuka Power Station. Trace elements will be dealt with solely when discussing the evolution of water streams at this study site.

4.3.1 Major Ion Chemistry

The water types found at the Sasol Synfuels Complex in Secunda are characterised in Fig 4.19 by use of the Piper diagrams (see Appendix B3 for sample identification and Fig 4.25 for sampling points). Using the diagram showing the classification of hydrochemical facies in section 4.3.2, the cation triangles of the Piper diagrams belonging to samples taken in 2006, 2007 and 2008, all show the data points clustered in the Na + K corner. This means the dominant cation is sodium in all the samples taken at Sasol Synfuels Complex. All the anion triangles belonging to all the three years in which samples were taken, samples are lined up on the sulphate edge. Those below the 50 % mark have the chloride as the dominant anion and those above the 50 % mark have the sulphate as the dominant anion. In the polygon where the data points have been projected, the points formed a single line along the Ca + Mg edge. This shows that the waters are from the same source and are intermediates of

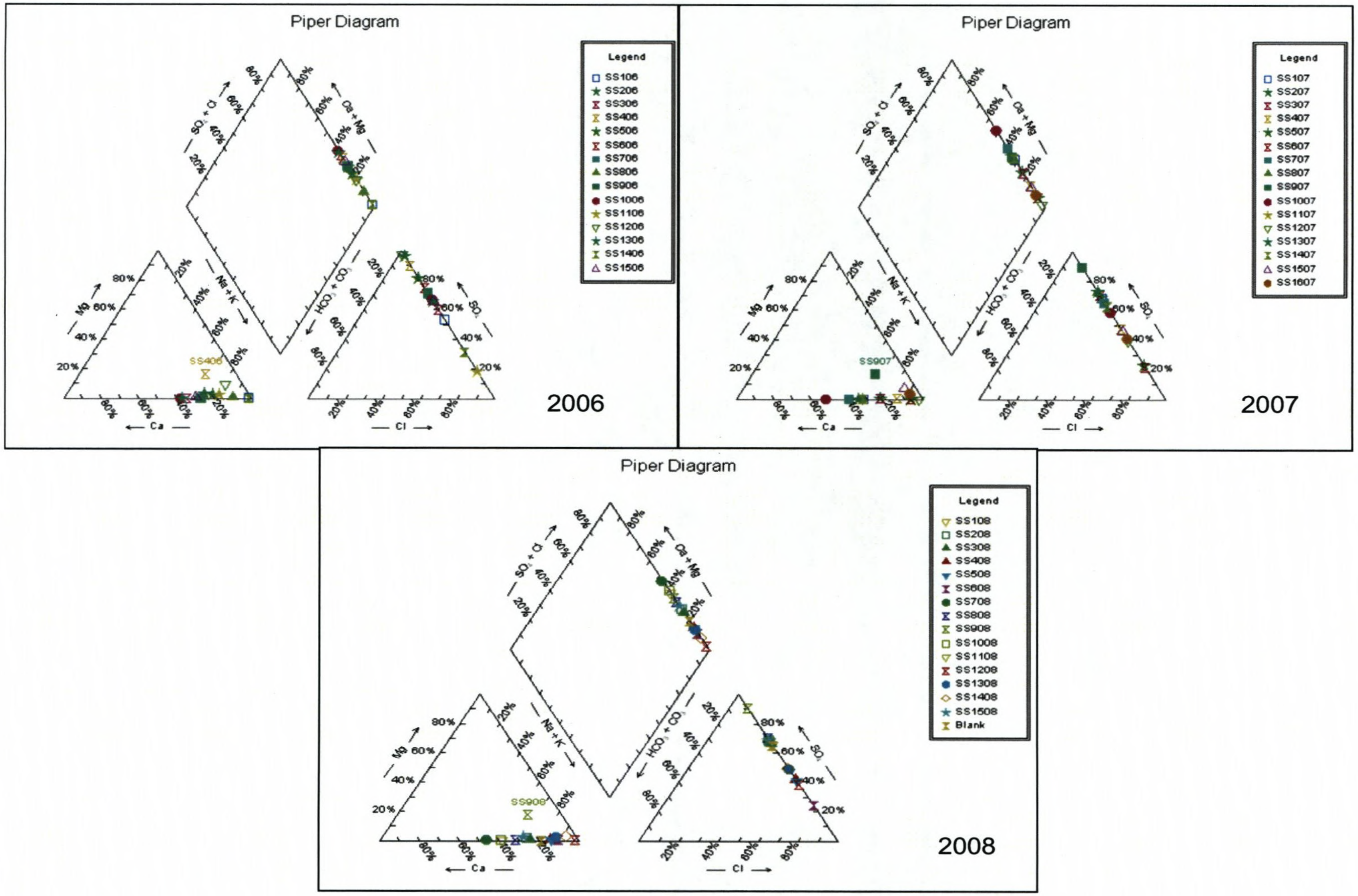


Figure 4.18: Piper diagram showing major ion chemistry of Sasol Synfuels Complex samples taken in 2006.

each other. It is a sign of waters that have mixed and this is because the water treatment process at Sasol Synthetic Fuels Complex is a closed loop system.

Fig 4.20 shows the line graph illustrating the trend of the major ion concentration along the treatment process. Major ion data was obtained from experimental techniques described in sections 3.2.6 and 3.2.7. Sampling points in the water treatment circuit are shown in Fig 4.25 and sample identification is detailed in Appendix B3 and Fig 4.25.

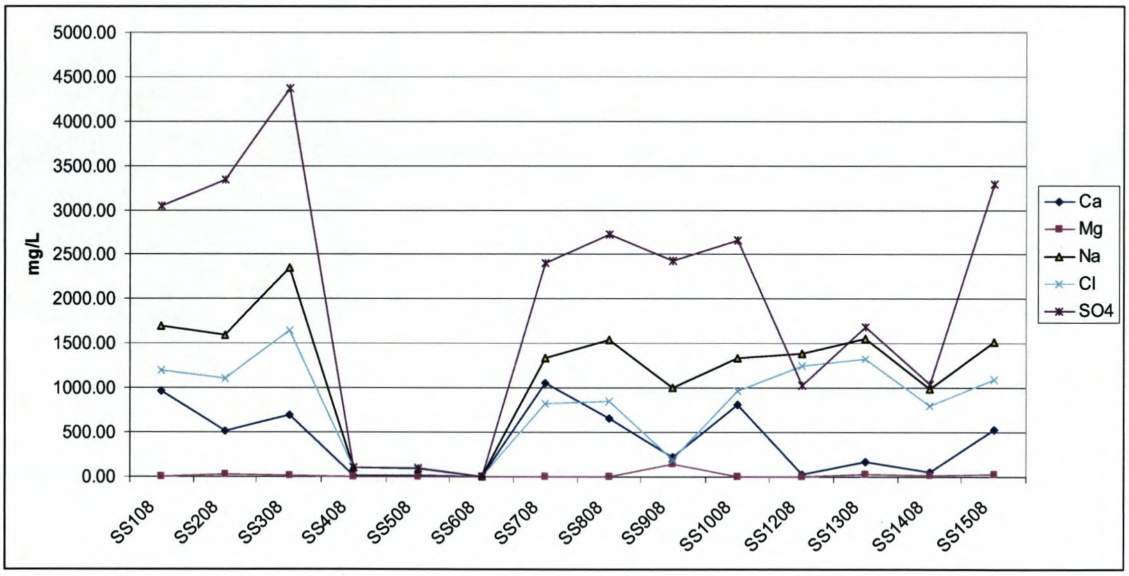


Figure 4.19: Major ion concentration trend at Sasol Synfuels Complex.

The following table best summarizes the variation of the major ions in the different water streams sampled in 2008 as illustrated by Fig 4.20. The ranges shown in Table 4.6 show the minimum and maximum values obtained for each ion from the pool of 14 samples shown in Fig 4.20. The source water of the highest values is also shown in Table 4.6. For example, Mg varied from 0.01 to 142.01 mg/L in the 14 samples collected in 2008 and mine water (SS908) has the highest Mg concentration among all the samples taken in 2008.

Table 4.6: Variation of major ions in water at Sasol Synfuels Complex in 2008.

Parameter	Unit	Range	Source of highest concentration
Mg	mg/L	0.01 - 142.01	Mine water (SS908)
Ca	mg/L	0.27 - 1052.69	FA and FAM (SS708)
Na	mg/L	1.92 - 2355.53	TRO brine (SS308)
SO_4	mg/L	0.50 - 4364.88	TRO brine (SS308)
Cl	mg/L	1.20 - 1320.05	Dam penstock overflow (SS1308)

Key: FA = Fly ash
FAM = Fly ash make-up
TRO = Tubular reverse osmosis
SRO = Spiral reverse osmosis

The lowest concentrations in major ions were found in TRO and SRO permeates with the highest concentrations being found in sources described in Table 4.6. Trends will be discussed further when the evolution of the waters at Sasol Synfuels Complex is looked at in section 4.45.

The water streams at Sasol Synfuels Complex were also characterized by the use of Stiff diagrams. As explained earlier, these are a tool which can be used to quickly see what has been added or removed from a water stream as it progresses along its flow path. By looking at the dominant ions from the Stiff diagrams, the water was characterised and the results compared to characterisation done by Aq.QA software. Table 4.7 shows the types of the waters as characterized by the Stiff diagram and by Aq.QA.

Table 4.7: Sasol water characterization by Stiff diagrams and Aq.QA software.

	Water Type by Stiff diagram			
Sample	Dominant Cation	Dominant Anion	Water Type	Water Type by Aq.QA
SS108	Na	SO_4	Na-SO_4	Na-OH
SS208	Na	SO_4	Na-SO_4	Na-SO_4
SS308	Na	SO_4	Na-SO_4	Na-SO_4
SS408	Na	Cl	Na-Cl	Na-Cl
SS508	Na	Cl	Na-Cl	Na-Cl
SS608	Na	HCO_3	Na-HCO_3	B-HCO_3
SS708	Na	HCO_3	Na-HCO_3	Na-OH
SS808	Na	SO_4	Na-SO_4	Na-OH
SS908	Na	SO_4	Na-SO_4	Na-SO_4
SS1008	Na	SO_4	Na-SO_4	Na-SO_4
SS1108	n/a	n/a	n/a	n/a
SS1208	Na	Cl	Na-Cl	Na-Cl
SS1308	Na	Cl	Na-Cl	Na-Cl
SS1408	Na	Cl	Na-Cl	Na-Cl
SS1508	Na	SO_4	Na-SO_4	Na-SO_4
Blank	Na	SO_4	Na-SO_4	Na-SO_4

Key: Blank = Ultrapure water used to dilute samples prior to analysis

Sample SS1108 is process cooling water blowdown and it was not analysed for ion content because of the significant hydrocarbon content. Only alkalinity and pH was analysed in the field therefore it could not be characterised here using Aq.QA or the Stiff diagram.

Fig 4.21(a)-(d) show the Stiff diagrams of Sasol Secunda samples taken in 2008. The water types they characterise are tabulated in Table 4.7. SS1508 (clear ash effluent) is feed into TRO desalination membranes to give TRO brine (SS304) and TRO permeate (SS408). SS1508 is a Na-SO_4 water type which gives a Na-SO_4 (SS308) and a Na-Cl (SS408) type of water. This illustrates how Stiff diagrams can be used to identify ion additions and/or subtractions from water streams.

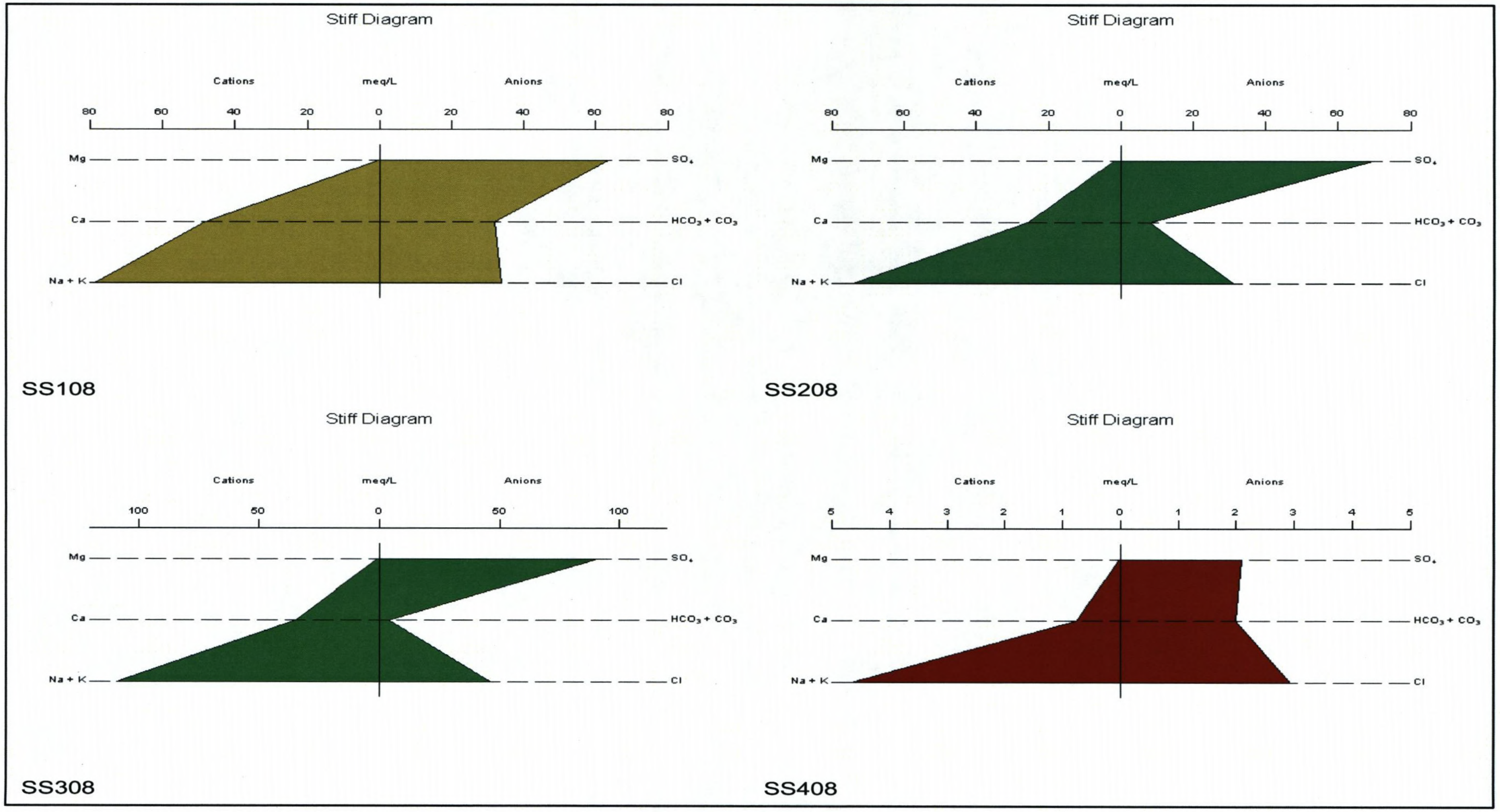


Figure 4.20(a): Stiff diagrams for Sasol Synfuels Complex 2008 water samples.

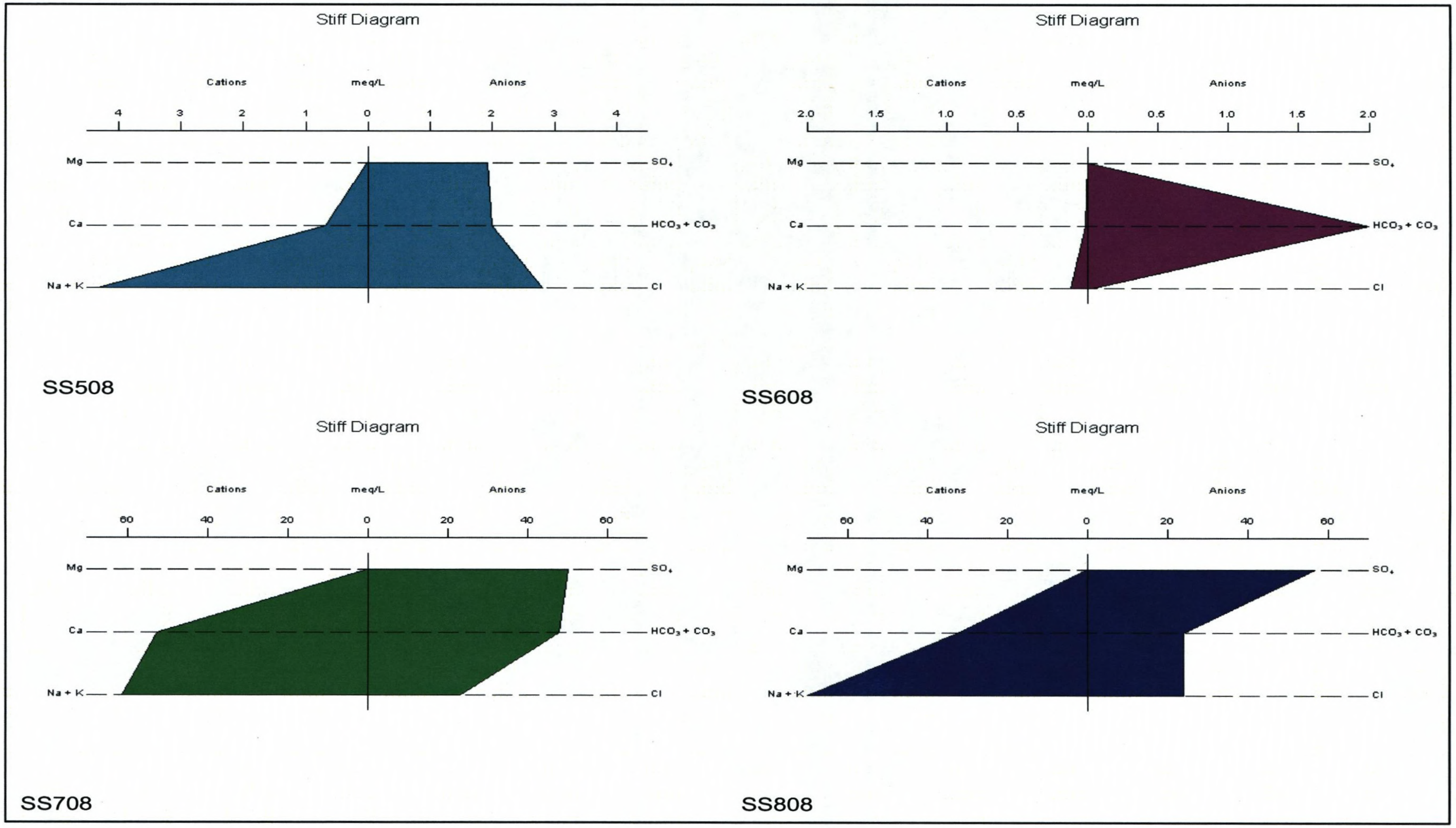


Figure 4.20(b): Stiff diagrams for Sasol Synfuels Complex 2008 water samples.

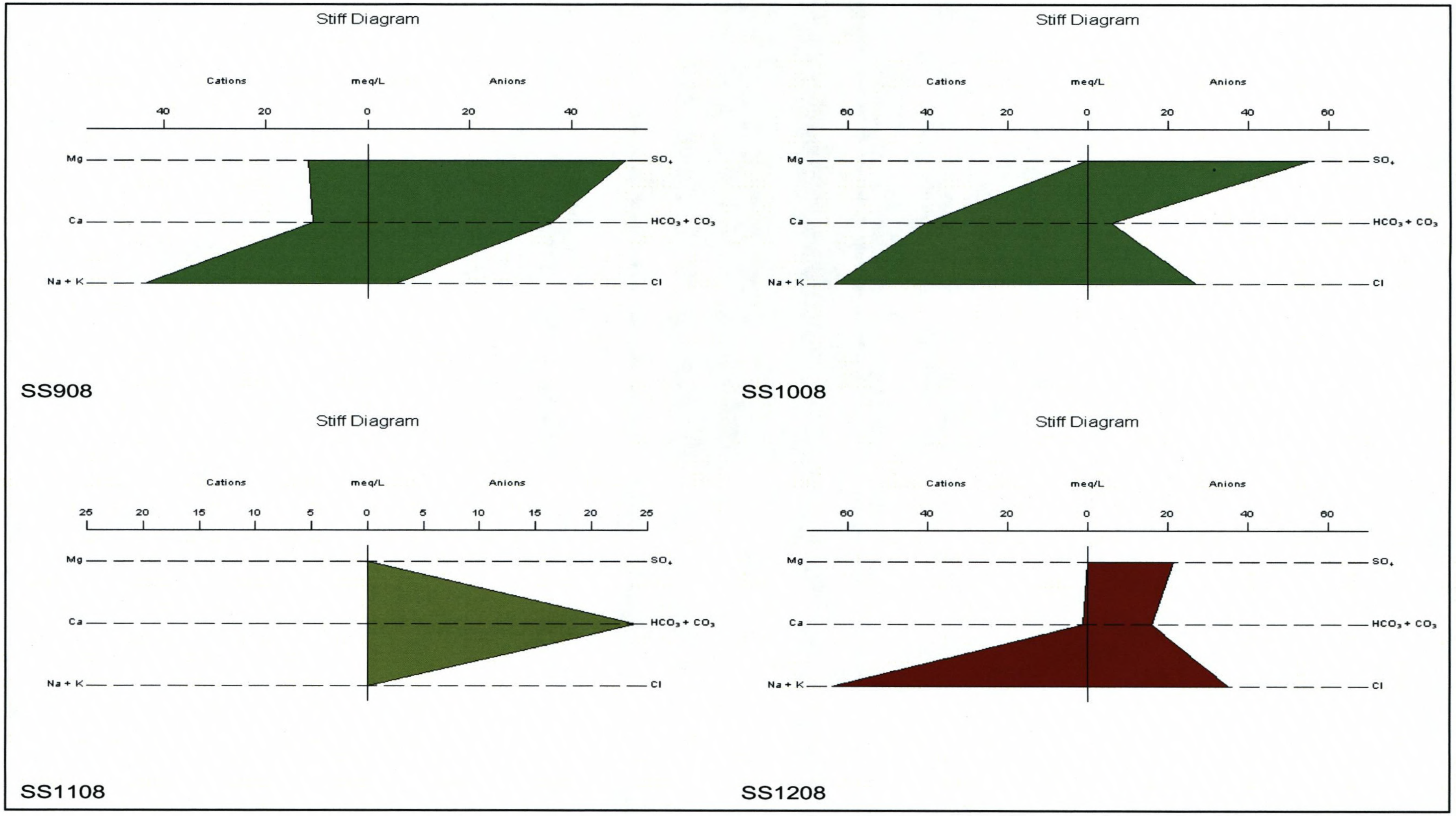


Figure 4.210(c): Stiff diagrams for Sasol Synfuels Complex 2008 water samples.

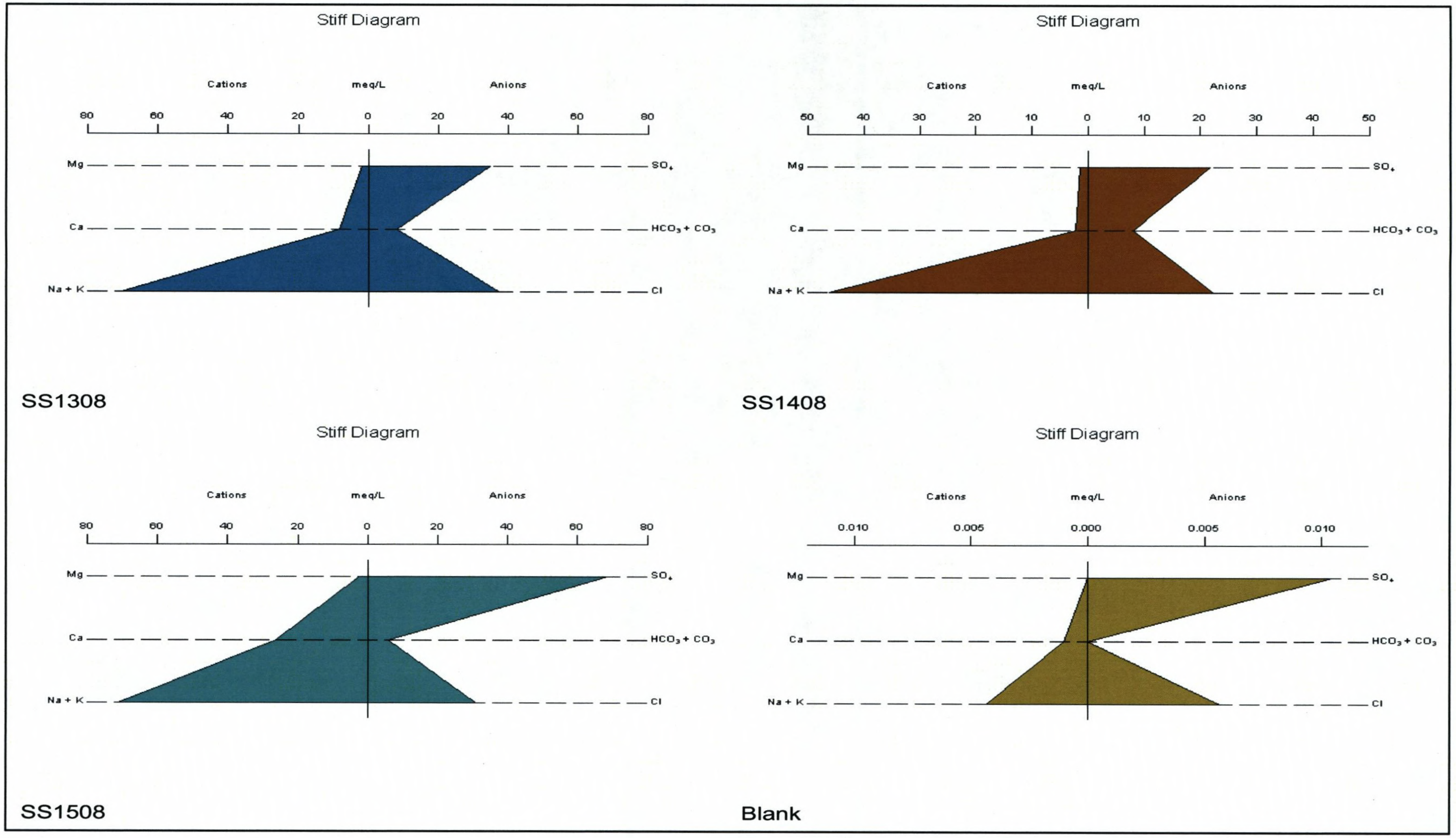


Figure 4.20(d): Stiff diagrams for Sasol Synfuels Complex 2008 water samples.

One disadvantage of characterising waters using Stiff diagrams is that they can not identify scenarios where ions other than Ca, K, Mg, Na, CO_3, HCO_3, SO_4, and Cl are more significant. The differences in water types given by Aq.QA software to those given by Stiff diagrams, is virtually due to this disadvantage that Stiff diagrams possess.

4.3.2 Total Alkalinity

Fig 4.23 shows total alkalinity results obtained at Sasol Synfuels Complex in 2008 by titration as described in chapter 3 section 3.2.5. Acetate was not determined, as previously mentioned in this chapter. The alkalinity of a water sample is related to the pH and HCO_3 concentration and therefore the scaling potential.

Alkalinity in 2008 at Sasol Synfuels Complex (Fig 4.22) ranged from 100 to 1200 mg/L $CaCO_3$. The lowest alkalinity was from TRO brine (SS508), TRO permeate (SS408) and SRO permeate (SS608). The highest alkalinity of 2400 mg/L $CaCO_3$ was from the FA plus FAM from the eastern plant (SS708). The FA plus FAM from the western plant (SS1008) had a much lower alkalinity of 300 mg/L $CaCO_3$ compared to the FA plus FAM from the eastern plant. The alkalinity of the other brines after contact with ash (at the dams) ranged from 300 to 800 mg/L of $CaCO_3$.

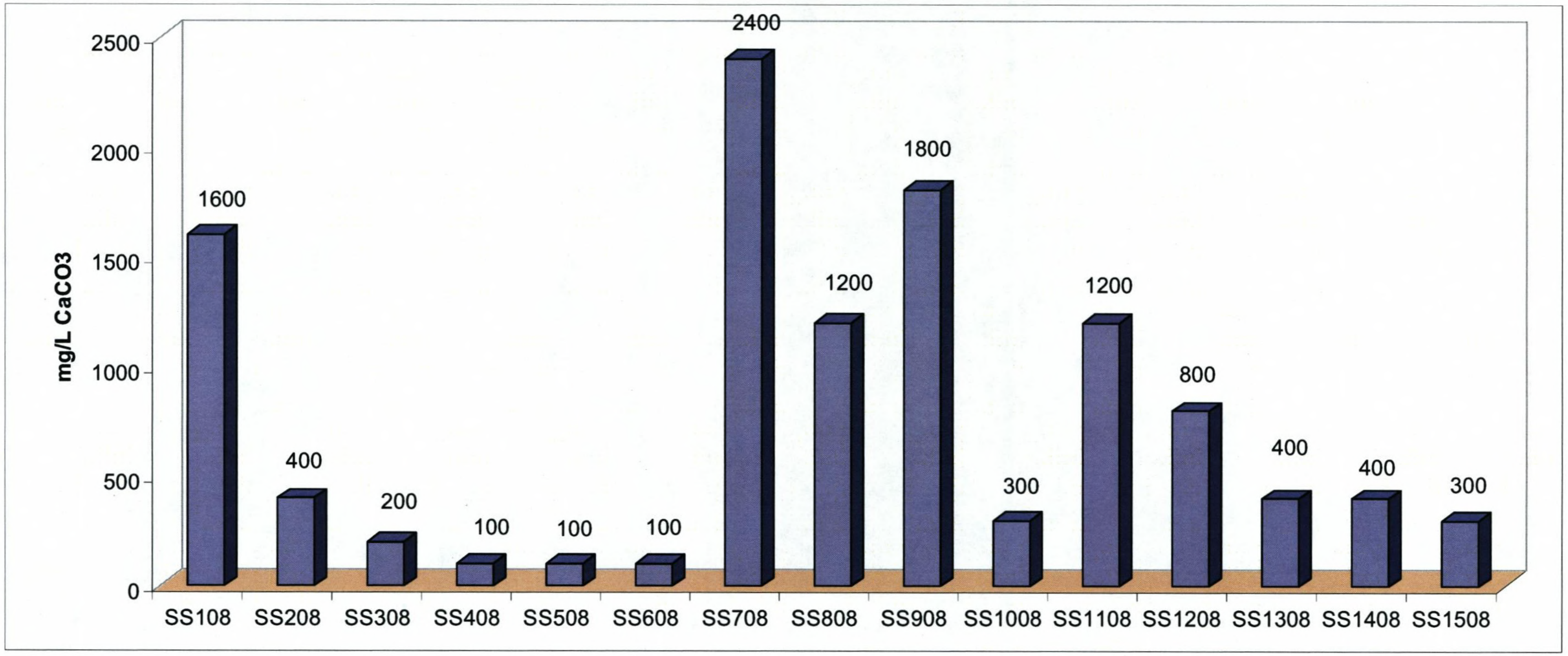


Figure 4.21: Alkalinity in Sasol Synfuels Complex samples in 2008.

4.3.3 pH

The pH of water samples at Sasol Synfuels Complex was determined by the method discussed in chapter 3 section 3.2.1. Fig 4.24 shows the pH of Sasol Synfuels Complex samples taken in 2006, 2007 and 2008. Values varied between pH 2.3 and 12.63. The pH was always lowest in RO permeate and highest in brine after contact with ash. Samples 2 and 12 of the year 2006 were very low as they were cation/anion regeneration effluent and water from the neutralizing tank on the west plant respectively. The low pH can therefore be due to the fact that acids are used to regenerate resins. The pH of brines before and after contact with ash will be discussed later in this chapter. Fig 4.24 shows the ranges in pH in each year of sampling. Thus, for example, in 2006 the pH ranged from 2.3 to 11.74 for the different points sampled.

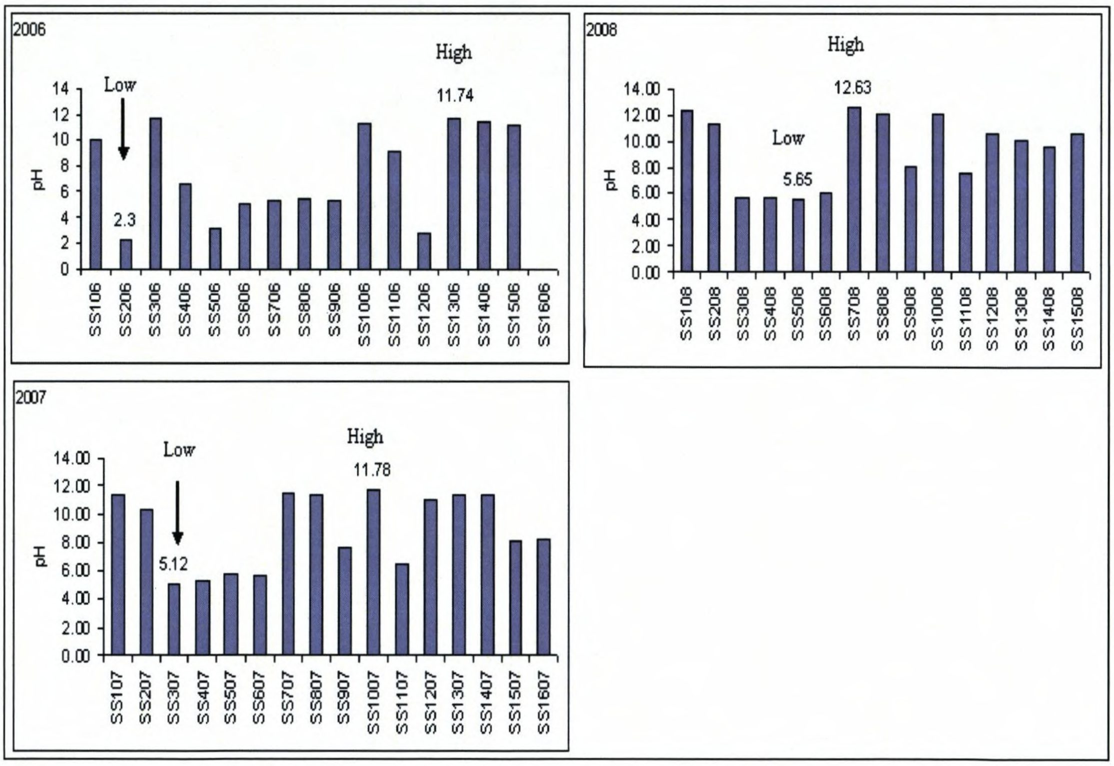


Figure 4.22: The pH of water samples from Sasol Synfuels Complex in 2006, 2007 and 2008.

Sample number identification for Fig 4.23 is detailed in Appendix B3.

4.3.4 Sodium Absorption Ratio

The sodium absorption ratio (SAR) is a parameter widely used to classify irrigation waters. The SARs of waters at Sasol Synfuels Complex were calculated using the Aq.QA software. Fig 4.25 shows the SAR values of the different waters. According the Texas University Agricultural Services (TUAS) water classes (see chapter 2), only water with SAR values below 10 is permitted to be used as irrigation water. Fig 4.25 shows that only TRO permeate, SRO brine and SRO permeate fall under water suited for irrigation under the TUAS water class system. It is important to note that the SRO brine is not as saline as other brine because at Sasol Synfuels Complex, the SRO is used to polish the EDR and TRO permeates.

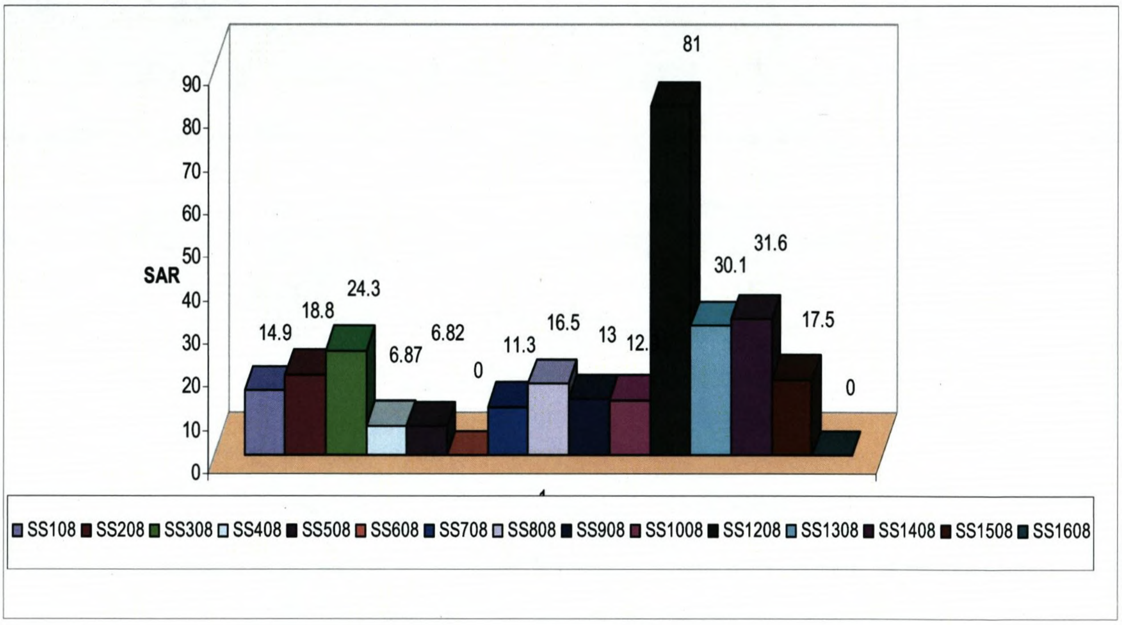


Figure 4.23: SAR values of water samples from Sasol Synfuels Complex.

4.3.5 Changes in Composition of water streams at Sasol Secunda

The same method used to show how the water streams lose or gain ions at Tutuka Power Station was also used at Sasol Synfuels Complex (see section 4.3.7). Percentage differences in ion content were calculated in relation to the starting water, SS908, using the equations 1 and 2 in section 4.3.7. A negative percentage difference indicates that the parameter in question decreased with the given percentage while a positive one indicates that the parameter increased with that percentage in relation to the starting water. A zero value indicates no change in concentration from the starting water.

Fig 4.25 shows the water treatment cycle at Sasol Secunda. The lines in Fig 4.26 are dotted to show that the samples may or may not be directly connected. There may be other processes in between the samples. For the purposes of this study, the whole water treatment circuit process was divided into four distinct sections, namely;

(i) desalination
(ii) wet ash handling
(iii) ash dams
(iv) clear ash effluent dams

Firstly, all samples were considered in evaluating the changes in concentration along the flow paths in the treatment process. For evaluating changes in character of brine before and after contact with ash, mean values of similar samples taken during 2008 from each section were used. Only data collected in 2008 was analysed. For example, the mean values of FA and FAM samples from the eastern and western plants were used instead of the individual values. Sasol Synthetic Fuels Complex uses mine water (SS908) as their input to the water treatment process. It was therefore used as the starting point for all calculations.

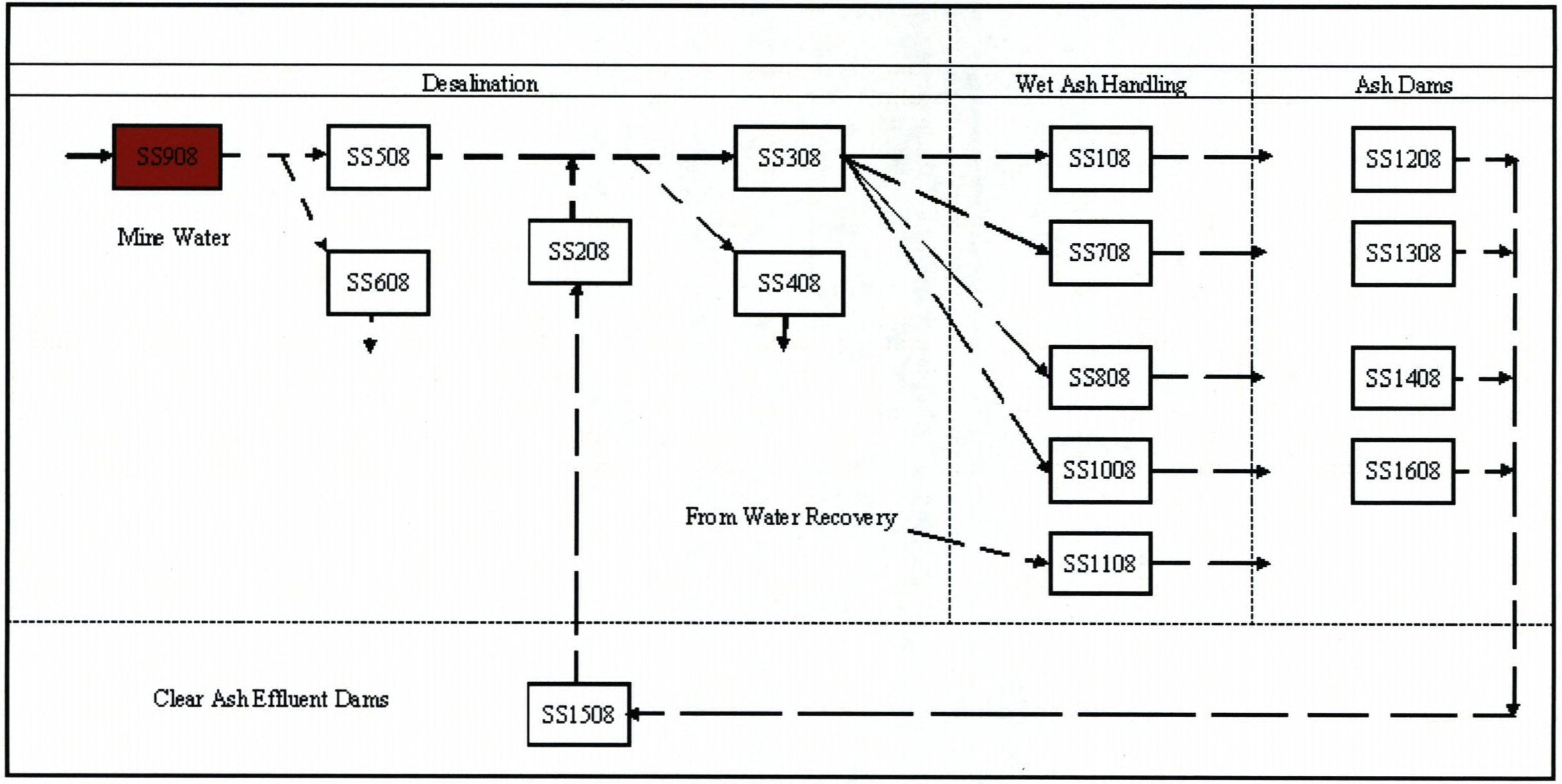


Figure 4.24: Water treatment circuit at Sasol Synfuels Complex showing where samples were taken in 2008.

From the water evolution analysis presented in Table 4.8, the aim is only to provide a guide to the extent to which individual process stages can remove and concentrate the water as it passes along. As previously reiterated, the water treatment process at Sasol is very complex. Mine water as an input, is many treatment stages away from the desalination stages shown in Fig 4.25. To quickly recap on the process (see section 1.4.2.2), mine water goes through the clarification process and is fed to the EDR. The EDR clean water is fed to the SRO. SRO brine is fed to the evaporators with the EDR and evaporator brine going to ash handling and ultimately taken to the clear ash effluent (CAE) dams. On the other hand, raw water from the Vaal River is flocculated and is used to cool systems after which it goes through ion exchange. Ion exchange regeneration effluent is sent to ash handling and ultimately to the clear ash effluent dams. Oily process water blowdown is also sent to ash handling. Lastly, clear ash effluent is then sent back into the cycle to a separate TRO/SRO treatment section.

Four samples will be used to illustrate the evolution of the water. This will be TRO brine (SS308), TRO permeate (SS408), FA + FAM (SS1008), Dam 5 penstock overflow (SS1308) and clear ash effluent (SS1508). Table 4.8 shows that the TRO process (desalination section) removes 92.89 % Ca, 99.88 % Mg, 90.11 % Na, 95.88 % SO_4 and 46.42 % Cl in SS408. The pH is reduced by 29.44 %. In the reject brine (SS308), TRO concentrates mine water by 223.87 % Ca, 136.15 % Na, 79.68 % SO_4 and 747.78 % Cl. Mg in the brine is reduced by 94.04 %. This is because mine water is the source of the highest concentration of Mg and is therefore distributed into the different streams (see Table 4.6). These figures come from sample SS408 and SS308 in Table 4.8. They necessarily mean that this is what was achieved by all the processes preceding the TRO treatment.

Taking SS1008 in the ash handling section, Table 4.8 also shows that mixing brine with ash increases Ca by 275.26 %, Na by 34.32 %, SO_4 by 9.31 % and Cl by 396.06 %. pH increases by 50.31 % while Mg is reduced by 98.01 % in relation to the mine water (mine water is the highest source of Mg at Sasol Secunda). Similarly in the ash dam section (SS1308), Ca decreased by 23.91 %, Mg by 82.69 % and SO_4 by 30.92 % in relation to mine water. The elements that increase in this section were Na, by 56.43 % and Cl by 580.73 % in relation to mine water, which signify that ash has a role in removal of cations and anions. Lastly in the clear ash effluent dams (SS1508), Ca increased by 143.45 %, Na by 52.34 %, SO_4 by 35.66 %, Cl by 466.15 % and pH by 31.68 %. Mg decreased by 78.68 %.

The changes in concentration across the designated sections can be illustrated further by Fig 4.26, which shows the trends. It is important to note that a negative percentage value means an ion has been removed from the water by that percentage in relation to mine water and the reverse is true for a positive percentage value.

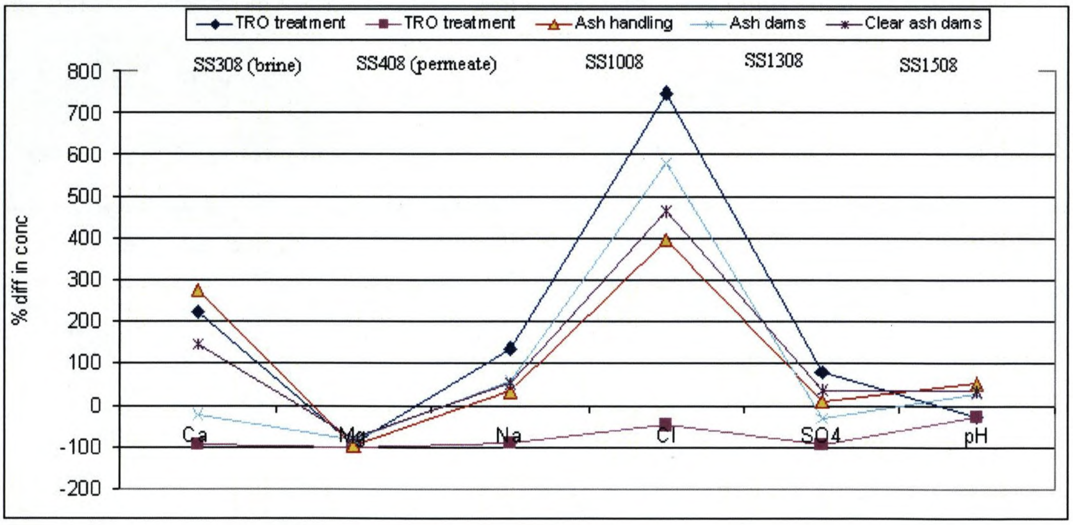


Figure 4.25: Water stream major ion and pH evolution trends at Sasol Synfuels Complex in Secunda.

In Fig 4.25, the percentage differences are calculated in relation to mine water. Therefore, mine water is represented by the x axis with a value of 0 % difference in concentration.

Table 4.8: Percentage differences in ion concentration from SS908 (the starting water) at Sasol Secunda.

Parameter	SS108	SS208	SS308	SS408	SS508	SS608	SS708	SS808	SS908	SS1008	SS1208	SS1308	SS1408	SS1508
Ca	348.48	137.99	223.87	-92.89	-93.71	-99.87	387.69	200.93	0.00	275.26	-90.56	-23.91	-79.03	143.45
Mg	-98.16	-84.49	-94.04	-99.88	-99.88	-99.99	-98.35	-98.43	0.00	-98.01	-99.25	-82.69	-87.53	-78.68
Na	69.65	59.83	136.15	-90.11	-90.75	-99.81	33.95	54.38	0.00	34.32	38.61	56.43	-0.90	52.34
Li	8543.50	8652.93	10507.03	290.36	262.41	-95.28	4585.84	3918.24	0.00	6043.50	6145.34	5166.24	4672.10	8920.23
Be	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
B	635.19	583.25	659.72	354.96	350.33	13.12	1156.04	1002.66	0.00	1301.12	366.47	540.94	231.92	684.98
Al	620.20	208.82	183.46	-21.86	-26.72	-97.92	664.22	512.77	0.00	637.25	1126.55	1750.18	594.78	366.90
Si	-9.15	-42.68	-17.75	-100.00	-92.23	-100.00	80.25	169.22	0.00	-16.06	-2.71	-100.00	-100.00	-42.73
P	328.87	196.79	69.94	-98.02	-97.72	-99.10	482.98	384.75	0.00	383.18	54.46	312.77	113.19	110.49
K	1383.60	1293.34	1762.55	7.03	-13.38	-88.97	837.30	719.87	0.00	1336.58	941.72	637.64	783.48	1252.69
Ti	374.15	227.97	67.83	-96.87	-94.78	-98.12	797.91	457.65	0.00	1891.45	2985.56	1223.85	38.81	315.76
V	2253.74	825.01	691.51	-83.01	-82.09	-98.03	833.08	5361.09	0.00	6543.36	545.01	6034.98	553.43	590.45
Cr	854.08	456.07	342.09	-88.81	-89.85	-98.66	553.64	850.62	0.00	1074.95	211.85	746.97	298.25	263.52
Mn	755.06	160.37	-20.17	-95.83	-94.59	-98.28	1148.28	1145.59	0.00	254.24	460.20	695.20	210.24	378.21
Fe	541.36	384.68	129.22	-96.65	-97.75	-98.95	429.53	417.47	0.00	741.17	237.35	830.49	200.38	202.33
Co	394.13	1241.16	151.23	-89.04	-97.02	-99.87	-100.00	173.59	0.00	2030.25	-10.39	1713.64	437.03	142.82
Ni	542.53	353.73	279.77	-93.84	-94.90	-98.94	413.94	442.93	0.00	523.17	742.38	830.68	521.00	235.23
Cu	137.37	62.98	137.01	-92.51	-92.80	-98.37	143.04	190.93	0.00	218.46	-12.59	233.70	-52.37	55.03
Zn	839.70	153.60	187.07	-86.80	-89.33	-95.56	289.44	297.78	0.00	301.05	306.68	1326.21	133.83	279.64
As	1844.42	1083.59	735.87	-80.93	-77.12	-98.99	1329.96	975.17	0.00	825.94	740.00	573.55	618.43	280.63
Se	308.92	214.74	336.97	-83.31	-82.51	-98.26	919.95	429.33	0.00	615.38	354.46	16.09	167.10	165.44
Sr	371.23	270.69	403.10	-89.60	-90.51	-99.93	301.30	166.47	0.00	253.48	-62.07	32.08	-20.62	265.86
Mo	1961.71	2739.19	3567.66	-22.12	-7.37	-98.55	3605.92	1671.46	0.00	893.01	3829.22	-100.00	3359.75	1338.99
Cd	447.08	233.01	100.15	-98.01	-97.96	-99.05	349.88	365.45	0.00	425.21	126.13	455.98	155.01	127.76
Ba	1327.60	394.59	392.28	-89.73	-88.69	-63.32	956.30	1139.16	0.00	909.66	141.87	437.46	125.39	237.57
Pb	3090.45	1293.84	798.05	-97.12	-96.97	-99.49	281.25	173.85	0.00	193.54	126.91	287.79	70.44	237.37
Cl	516.83	472.96	747.78	-46.42	-48.59	-99.38	324.31	339.38	0.00	396.06	542.43	580.73	308.46	466.15
NO_3	400.00	100.00	100.00	-59.09	-59.66	-99.00	400.00	400.00	0.00	402.67	150.00	400.00	100.00	100.00
PO_4	400.00	100.00	100.00	-98.00	-98.00	-99.00	400.00	400.00	0.00	400.00	150.00	400.00	100.00	100.00
SO_4	25.27	37.50	79.68	-95.88	-96.20	-99.98	-0.89	12.05	0.00	9.31	-57.48	-30.92	-57.15	35.66
pH	53.91	40.37	-28.45	-29.44	-29.81	-25.09	56.89	49.69	0.00	50.31	32.05	25.47	19.75	31.68

From Fig 4.26, the trend for a water stored in the ash dam revealed that by holding the water in the ash dam, it;

(i) lost Ca,
(ii) lost Mg,
(iii) gained Na,
(iv) gained Cl,
(v) lost SO_4,
(vi) gained pH units.

The length of the period the water was held in the dam before sampling could not be ascertained. Slurry is pumped irregularly into ash dams.

To show how toxic trace elements evolve along the water treatment path, a graph (Fig 4.27) was constructed. It shows which trace element concentration increases and which does not in each section of the water treatment sections designated in Fig 4.25.

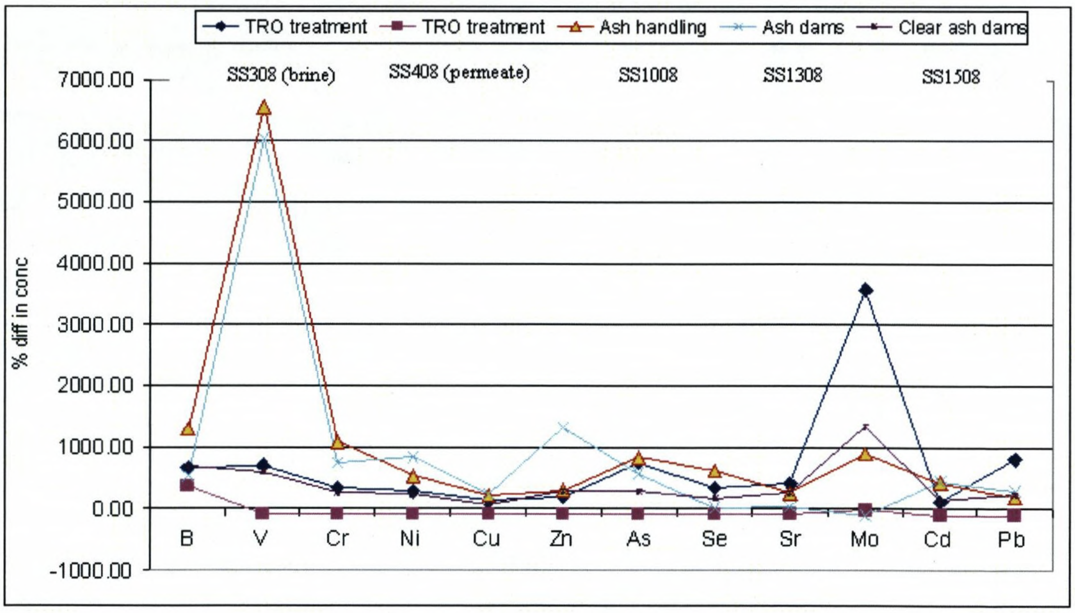


Figure 4.26: Water stream toxic trace elements evolution trends at Sasol Synfuels Complex in Secunda.

In Fig 4.27, mine water is represented by the x-axis. Fig 4.27 shows that the TRO treatment process removes all toxic trace elements except B. Ash dam holding periods removed Mo by 100 % in relation to mine water. The results were presented in percentages. A small increase in the minute quantities characteristic of trace elements corresponds to a large percentage increase. Percentage increases/decreases were preferred to mg/L in order to easily compare changes in concentration values between different ions.

4.3.6 Major ion chemistry of Sasol brines (before and after contact with ash)

The way brine is mixed with ash at Sasol Secunda is different from how it is done at Tutuka Power Station. At Sasol, it is not only brine that gets mixed with ash. Regeneration effluents and oily process cooling water blowdown end up in the fly ash make-up as well. The comparison between brine and brine after contact with ash does not reflect the amount of ions contributed by the other added streams; it however shows roughly how ash can reduce the salt load in brines.

To illustrate the effect of mixing ash with brine at Sasol, TRO brine, the mean of fly ash make up samples, the mean of fly ash plus fly ash make up samples, ash dam samples and clear ash effluent samples were considered. Samples numbers are shown in Table 4.9. Sample identification is detailed in Appendix B3.

Table 4.9: Major ion chemistry mean concentrations (mg/L) in brine samples taken from the different sections before and after contact with ash.

	Before contact with ash				After contact with ash							
	TRO Brine	Fly Ash Make Up		Mean	Fly Ash + Fly Ash Make-Up		Mean	Ash Dams			Mean	Clear Ash Effluent
	SS308	SS108	SS808		SS708	SS1008		SS1208	SS1308	SS1408		SS1508
Ca	**699.09**	968.06	649.56	**808.81**	1052.69	810.01	**931.35**	20.37	164.23	45.27	**76.62**	**525.48**
Mg	**8.46**	2.62	2.22	**2.42**	2.34	2.82	**2.58**	1.07	24.59	17.71	**14.45**	**30.28**
Na	**2355.53**	1692.22	1539.93	**1616.08**	1336.11	1339.87	**1337.99**	1382.65	1560.33	988.53	**1310.50**	**1519.61**
Cl	**1643.98**	1196.13	852.03	**1024.08**	822.82	961.93	**892.38**	1245.79	1320.05	792.07	**1119.30**	**1097.85**
SO_4	**4364.88**	3043.00	2721.92	**2882.46**	2407.63	2655.32	**2531.48**	1032.78	1678.13	1040.97	**1250.63**	**3295.42**
pH	**5.76**	12.39	12.05	**12.22**	12.63	12.10	**12.37**	10.63	10.10	9.64	**10.12**	**10.60**

Fig 4.27 further illustrates table 4.9. Only the means of fly ash make up, fly ash + fly ash make up, ash dam water streams, TRO brine and clear ash effluent shown in Table 4.9 were plotted. The results are from samples obtained in 2008. Fig 4.28 (a) shows that Ca increases from 699 mg/L in TRO brine to 809 mg/L in fly ash makeup (FAM). This is due to the fact that other brines from the EDR and evaporators are also added to FAM as well as the regeneration effluents and process cooling water blowdown. When mixed with ash, Ca concentration increases to 931 mg/L and then is reduced to 77 mg/L in the ash dams. An increase in Ca concentration to 525 mg/L was observed in the clear ash dams. This could be due to dissolution of some Ca minerals in the dam.

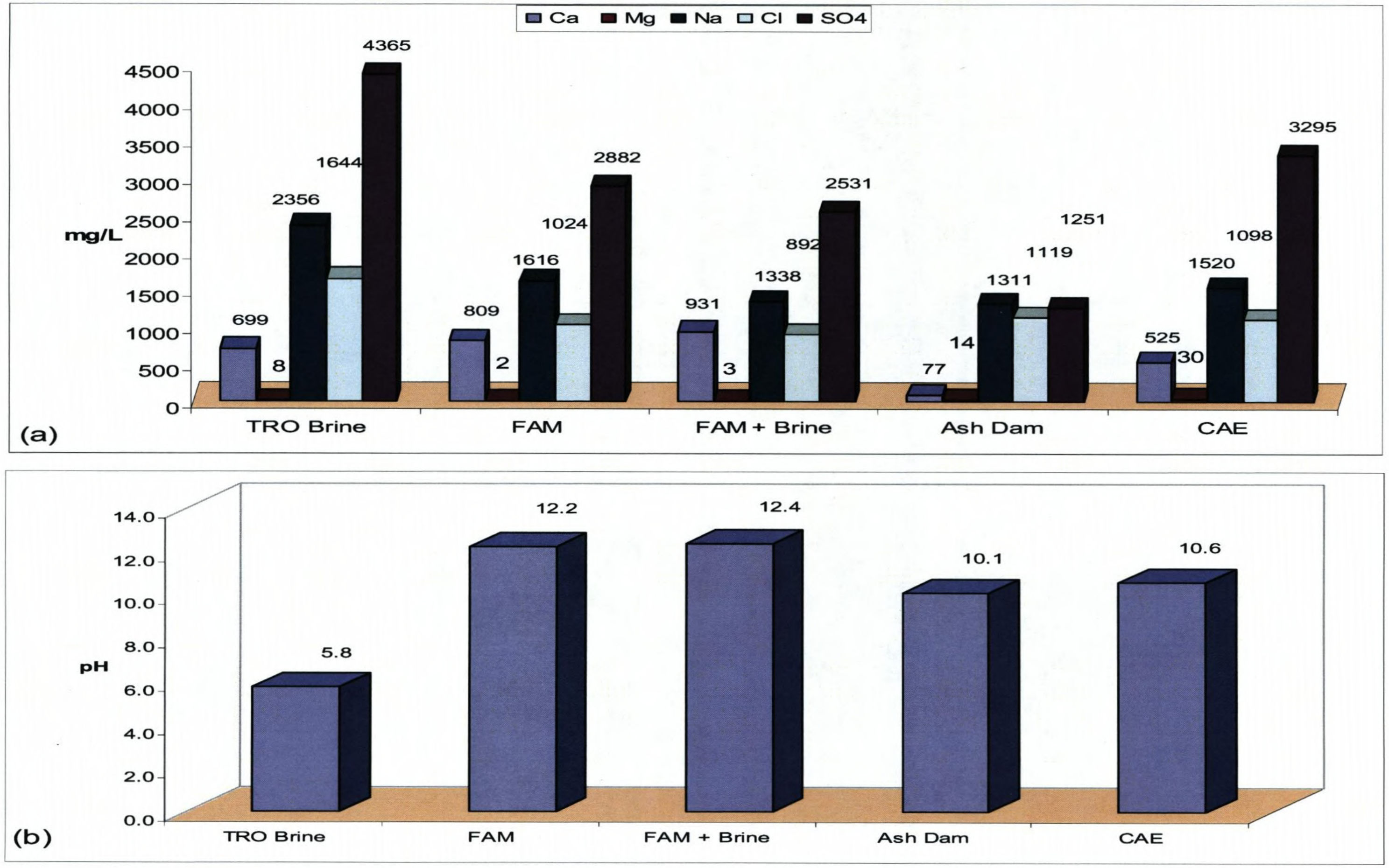


Figure 4.27: Major ion chemistry of (a) brine before and after contact with ash and (b) pH at Sasol Secunda in 2008.

Key: FAM = Fly ash make-up
FA = Fly ash
CAE = Clear ash effluent

As Fig 4.28 (a) shows, Mg, Na, Cl and SO_4 concentrations were much higher in TRO brine than in FAM confirming the dilution factor due to other streams that are added to bring about FAM.

The major trend that can be seen in Fig 4.28 is that the major ions generally decrease when brine comes into contact with ash. The extent with which they decrease at Sasol is less significant than at Tutuka Power Station. Comparing concentrations in FAM and concentration in the ash dams (Table 4.9), the results showed that Ca decreased by 90.5 %, Na by 18.9 %, SO_4 by 56.6% and pH by 17.2 %. Mg on the contrary increased by 496.9 %.

Fig 4.29 (a) and Fig 4.29 (b) show the effect of mixing ash with brine on (a) minor cations and anions and (b) trace elements at Sasol. Elements below a concentration of 2.7 mg/L were plotted on a separate graph (Fig 4.29 (c)) for ease of reference. NO_3 increased by 43.4 % after FAM came into contact with ash but decreased by 42.9 % in the clear ash effluent dam. Generally the changes in concentration of the minor cations and anions after contact with ash follow the same trends as the major ion trends. FAM concentrations before contact with ash are generally less than TRO brine concentrations due to the dilution effect. The results also show that the concentrations of the TRO brine trace elements are close to the concentration of the clear ash effluent. This was also true in the case major ion concentrations. It is also noteworthy that Sr and B were present in most waters in relatively high concentration and that contact with ash increased levels of B in process waters. The effluent waters have high concentration in elements such as Al, Cr, Zn, Mo and Ba as show in Fig 4.29 (c). Appendix H shows the DWAF elemental limits in waters and the limits show that this water can not be released into the environment. Fig 4.29 (a) also shows high K concentrations in the effluents while the input water (mine water) has only 13.82 mg/L K. The high concentrations might be due to the cycles of concentration involved at Sasol. The water treatment process has a closed loop circuit.

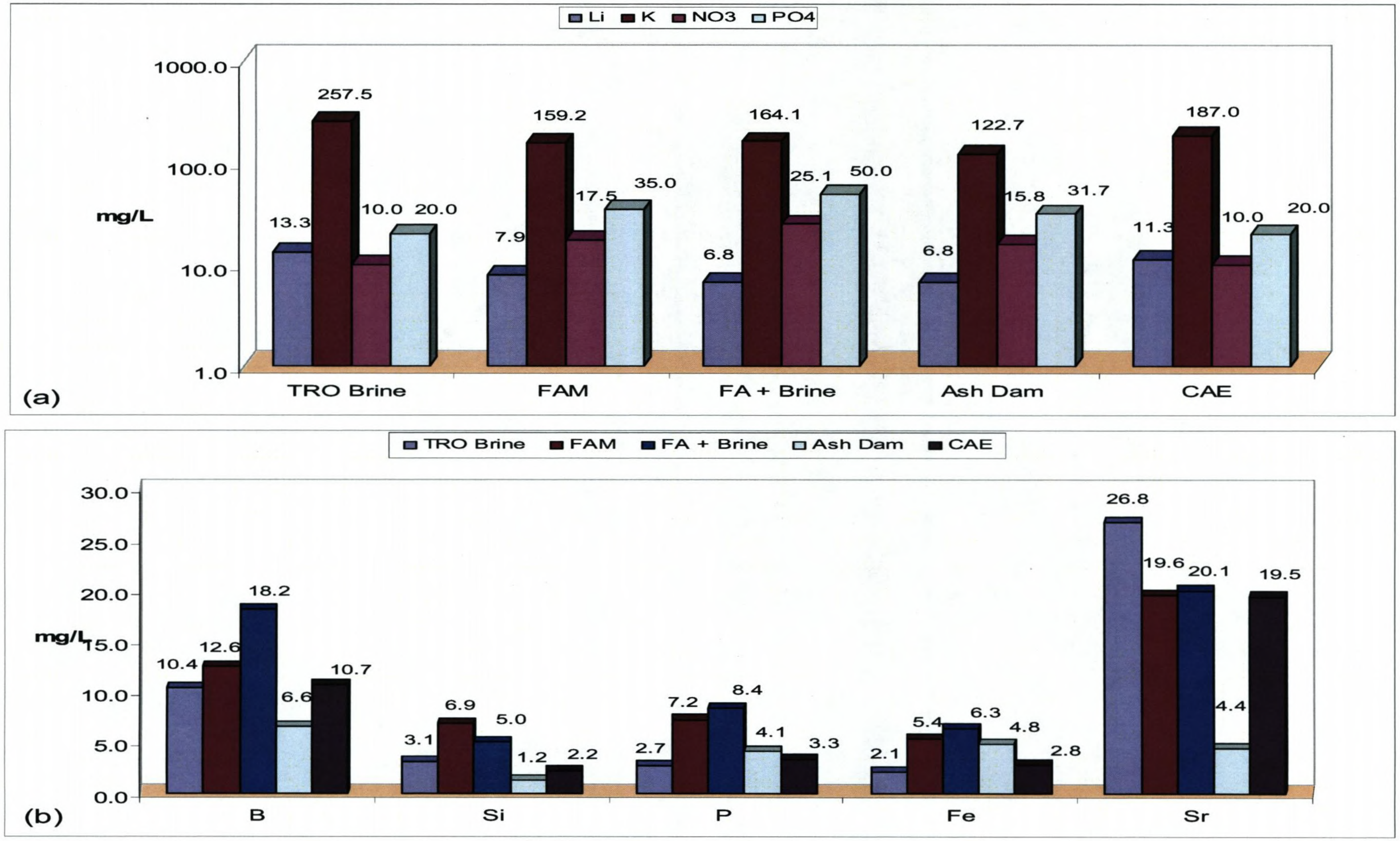


Figure 4.29: (a) Minor anions and cations and (b) Trace elements in brine before and after contact with ash at Sasol Secunda.

Key: FAM = Fly ash make up FA = Fly ash CAE = Clear ash effluent TRO = Tubular reverse osmosis

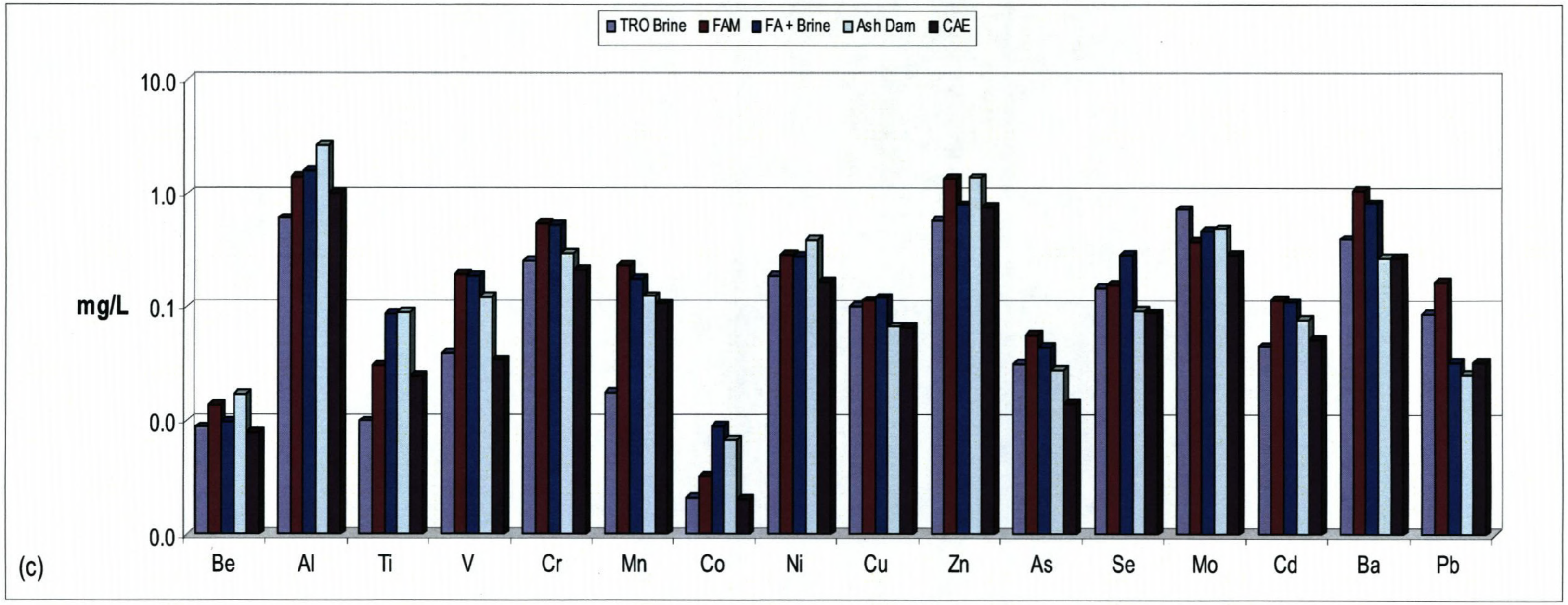


Figure 4.29: Trace elements of brine before and after contact with ash at Sasol Secunda.

4.3.7 Process Cooling Water and Process cooling water Blowdown

Process cooling water and process cooling water blowdown samples were not analyzed fully because of the oily nature of the sample, coupled with unsuitable filtration equipment for field analysis. However historical data (2004 to 2007) was obtained from Sasol Water Research Laboratory. The monthly data is presented in the Appendices D1 and D2. In this section data for process cooling water (PCW) and process cooling water blowdown (PCWB) is presented in stiff diagrams (Fig 4.30). Saturation indices are calculated (Table 4.10) and yearly averages for 2004 – 2007 are given in Figs 4.31, 4.32 and 4.33.

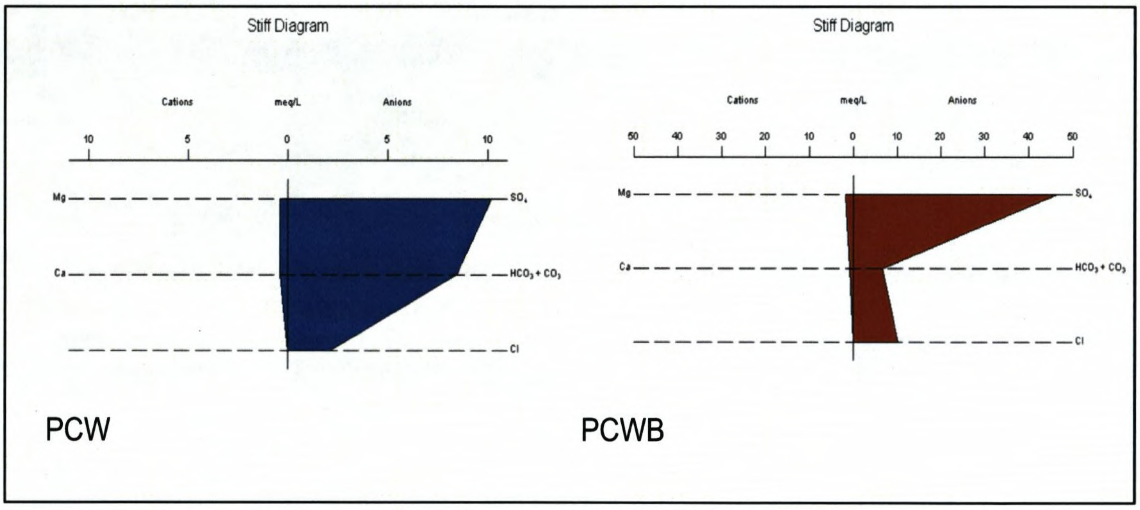


Figure 4.30: Characterisation of 2007 data for process cooling water and cooling process water blowdown by Stiff diagrams.

Fig 4.30 shows that the process cooling water (PCW) and process cooling blowdown (PCWB) are Ca-SO_4 and Mg-SO_4 water types respectively. Due to the Stiff diagram shortcomings, the two waters are actually Si-SO_4 water types as classified by Aq.QA. The Stiff diagram cannot identify other dominant cations ions other than Na, Mg, K, and Ca.

The yearly average 2007 results of process cooling water and process cooling water blowdown were input into Aq.QA. Aq.QA predicted undersaturation of calcite and aragonite with saturation indices of -0.2305 and -0.3948 respectively. The process cooling water blowdown 2007 yearly average analysis data was also input into PHREEQC and as found by Aq.QA, it also reported undersaturation of $CaSO_4$ (anhydrite) and $CaSO_4.2H_2O$ (gypsum) with saturation indices of -1.65 and -1.43 respectively. Table 4.10 shows what mineral phases are likely to precipitate out of process cooling water blowdown as calculated by PHREEQC.

Table 4.10: Minerals likely to precipitate out of process cooling water blowdown.

Name	SI	Formula
Chalcedony	1.11	SiO_2
$Fe(OH)_3$(a)	2.07	$Fe(OH)_3$
Fluorite	3.06	CaF_2
Goethite	7.97	FeOOH
Hematite	17.94	Fe_2O_3
Quartz	1.51	SiO_2
SiO2(a)	0.27	SiO_2

Key: SI = saturation index.

From the SI calculated by PHREEQC, it can be seen that process cooling water shows high scaling potential from Si and Fe minerals. Scale-forming compounds that may be present in water generally include compounds such as calcium sulphate, alkaline-earth bicarbonates of calcium and magnesium, compounds of silica, iron, and other minor elements, such as strontium (Roller 1981). These could pose a serious risk in equipment scale build up. Amorphous silica scales cause significant fouling problems when industrial waters contain high quantities of silica. Generally, high quantities of silica mean that the industrial waters contain at least 5.0 mg/L and up to about 1000 mg/L dissolved silica (Dubin 1986). The 2007 yearly average Si content of process cooling water blowdown at Sasol was 213.4 mg/L, well above the 5.0 mg/L minimum level sufficient to form scale (Dubin 1986).

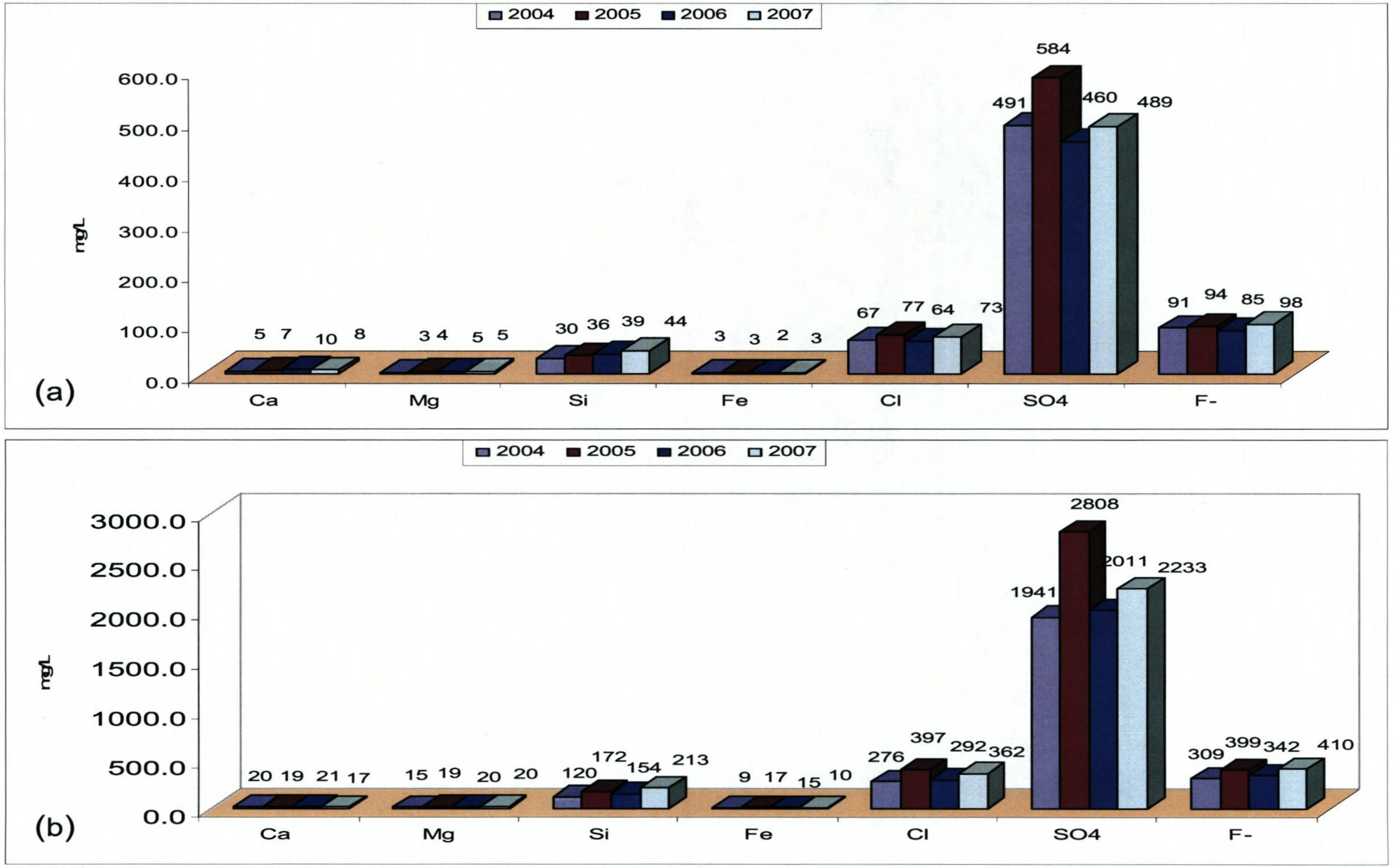


Figure 4.31: Yearly average concentration (a) process cooling water (b) process cooling water blowdown for the period 2004 – 2007.

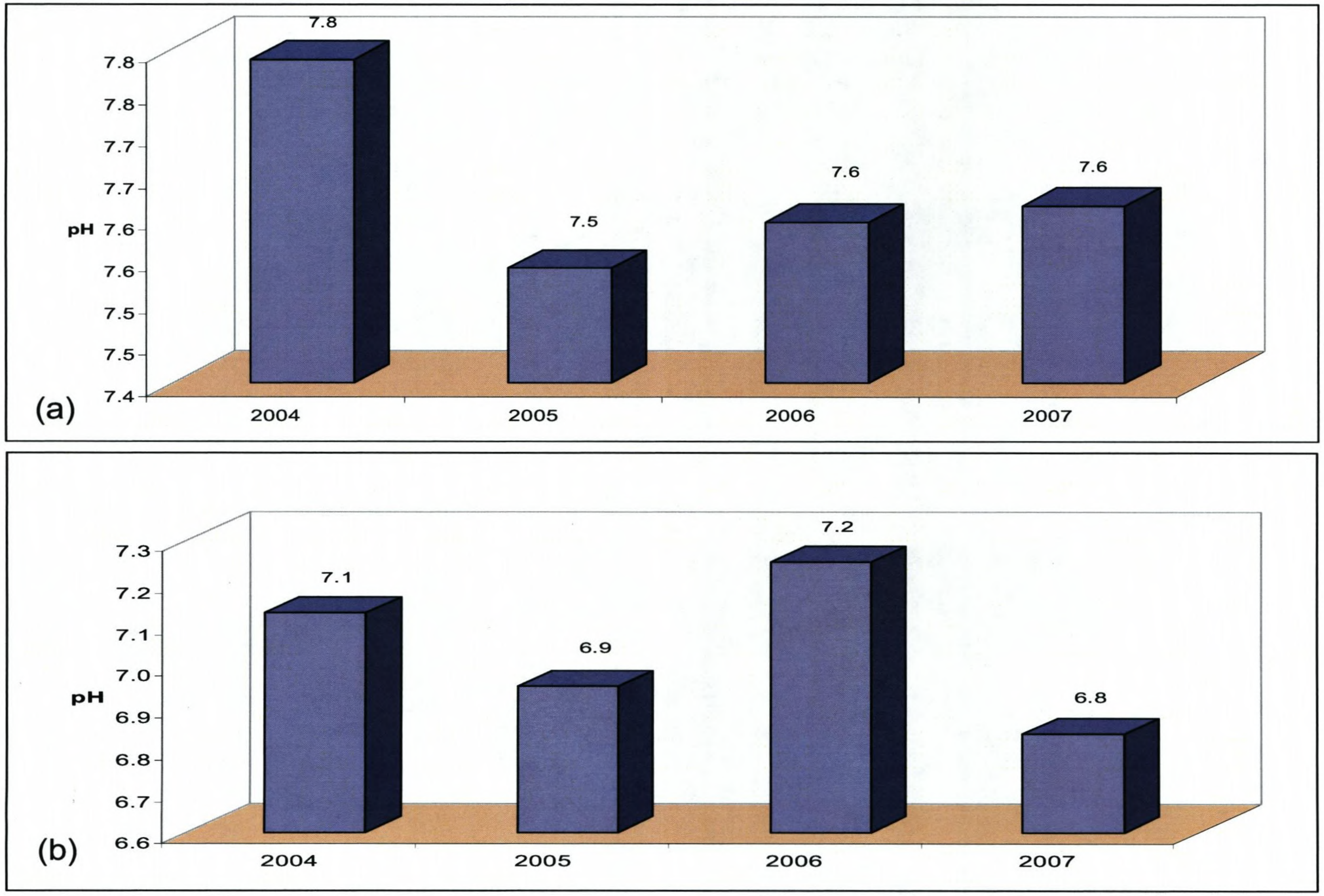


Figure 4.32: Yearly average pH of (a) process cooling water and (b) process cooling water blowdown for the period 2004 – 2007.

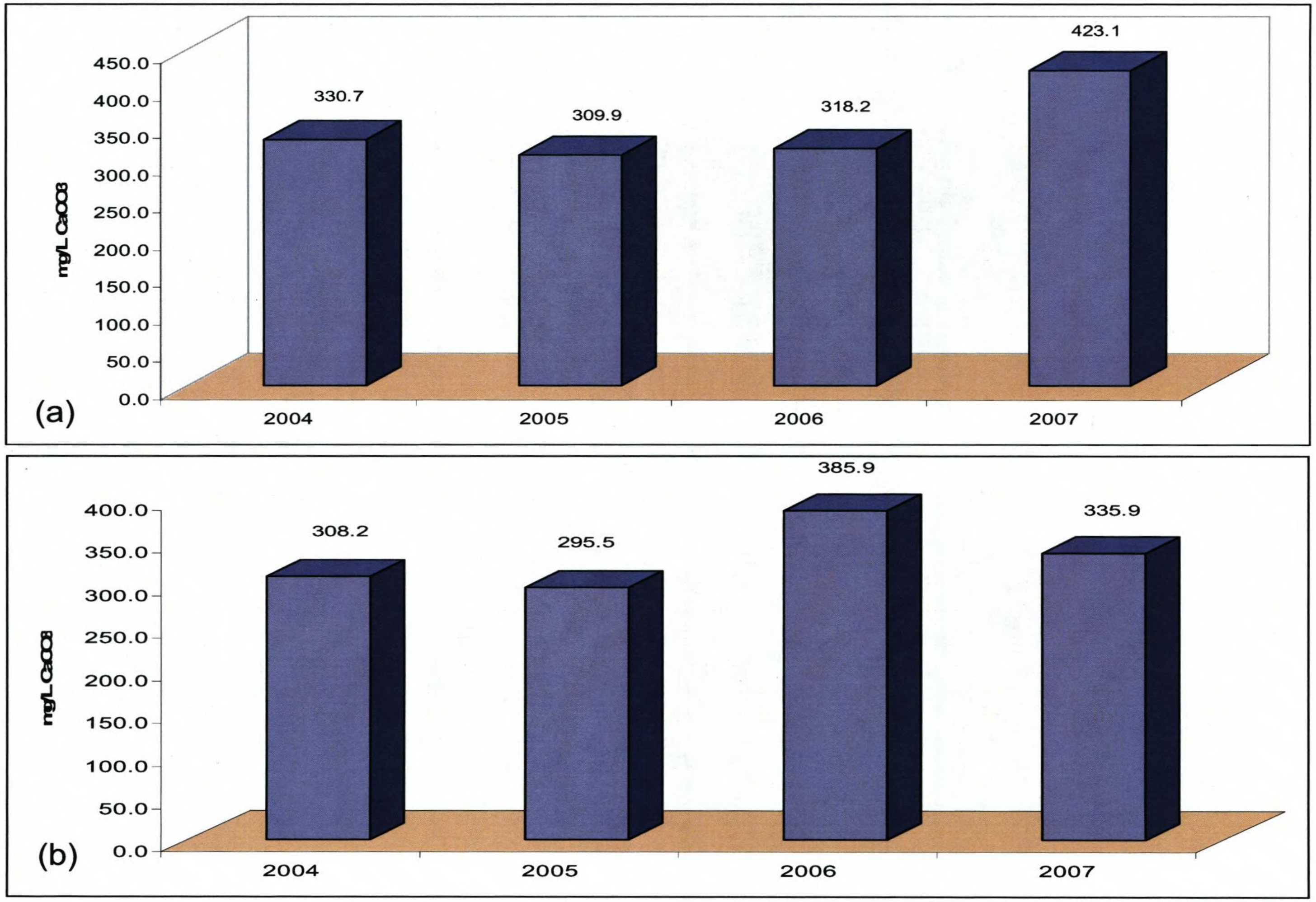


Figure 4.33: Yearly average total alkalinity of (a) process cooling water and (b) process cooling water blowdown for the period 2004 – 2007.

Fig 4.31 (a) shows process cooling water yearly average concentration of Ca, Mg, Si, Fe, Cl^-, SO_4^{2-} and F^- from 2004 to 2007. The results show that process cooling water blowdown was more concentrated than the process cooling water. Compared to the process cooling water, the process cooling water blowdown has generally a lower pH and less total alkalinity except in 2006 when the alkalinity was 385.9 mg/L $CaCO_3$ as compared to 318.2 mg/L $CaCO_3$ in the process cooling water. Fig 4.31 shows that the HCO_3 and CO_3 concentration is less in the process cooling water. The parameter differences between process cooling water and process cooling water blowdown are shown in Table 4.11. The values were obtained from equation 3

$$\text{Difference} = \frac{(\text{PCWB value} - \text{PCW value})}{\text{PCW value}} \times 100\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 4.3}$$

Where: PCWB = process cooling water blowdown

PCW = process cooling water

The % differences show how the cooling water has been contaminated while in circulation. A negative % difference value means that the PCWB parameter in question was less than the corresponding parameter in PCW with the give percentage and the reverse is true for a positive % difference. For example, Table 4.11 shows that the pH of PCWB in 2004 was 0.1 % less than the pH of PCW in 2004 and the calcium content was 3.3 % more in PCWB than in PCW.

Table 4.11: Yearly average percentage differences between process cooling water and process cooling water blowdown.

Parameter	Unit	Differences			
		2004	2005	2006	2007
Ca	mg/L	3.3	1.8	1.1	1.2
Mg	mg/L	3.8	3.3	3.1	3.1
Si	mg/L	3.0	3.8	2.9	3.8
Fe	mg/L	1.9	4.9	5.6	2.7
Cl	mg/L	3.1	4.1	3.6	3.9
SO_4	mg/L	3.0	3.8	3.4	3.6
Fluoride (as F^-)	mg/L	2.4	3.3	3.0	3.2
Conductivity (µS/cm)	µS/cm	1.8	2.7	2.4	2.8
pH(before filtration)		-0.1	-0.1	0.0	-0.1
COD	mg/L	2.5	3.0	2.7	2.9
Total Alkalinity	mg/L (as $CaCO_3$)	-0.1	-0.05	0.2	-0.2

4.4 Chemical Speciation Modelling

4.4.1 Introduction

The transport, mobility, bioavailability and toxicity of metals in waters can depend largely upon their chemical speciation. It is therefore desirable to have a model which can predict element and compound speciation chemistry in waste waters. In this study PHREEQC software was used to calculate the distribution of chemical species in the water samples and to calculate the saturation state of the solution with respect to minerals and gases. The other software used in this study was Aq.QA, which is a spreadsheet program capable of graphing water analyses data and check for analyses' internal consistency. It is also capable of calculating the carbonate equilibria of a water solution and mineral saturation in respect of calcite and aragonite only.

Table 4.12: Interpretation of SI values (Corrosionsource, 2009).

SI < 0	No potential to scale. Water will dissolve $CaCO_3$
SI > 0	Scale can form and $CaCO_3$ precipitation can occur
~ 0	Borderline scale potential. Water quality or changes in temperature or evaporation could change the index

The main purpose of speciation in this study was to investigate which minerals would precipitate out of a given water composition. This is achieved by calculating the mineral saturation indices, which are indicators of the mineral saturation states. SI values can be interpreted as the pH change required to bring water to equilibrium with respect to a given mineral. Hence it is an indicator of a water's corrosivity (Corrosionsource, 2009). Only minerals with a positive (>0) saturation indice in each water stream will be reported and some comparisons made on the indices calculated by the two software programs. All samples obtained from Tutuka Power Station had speciation calculations done on them in this study and are reported in this section. Only mine water and the most highly concentrated brine from Sasol Synfuels Complex were modelled in this study.

The water quality data was input without modification. In PHREEQC, the software's default *pe* of 4.0 was input in all calculations since different redox couples have different *pe*. Input concentrations of the members of the couples must be supplied to have any effect in the modelling process (USGS, 2009). Results for redox couples used in this study were given as the total element. For example iron was reported as total Fe, and not as individual members of the redox couple. In modelling, it is also essential to remember that "*there is no such thing as an "Eh" or "pe" of natural water*" (Thorstenson 1984) and that "*redox disequilibrium is the general rule*" (Lindberg and Runnels 1984).

4.4.2 Aq.QA vs PHREEQC

Aq.QA and PHREEQC software packages were used in this study. Aq.QA is an easy to use programme that is very useful in graphing data. It is capable of graphing time series plots, series plots, cross plots, ternary diagrams, Piper diagrams, Stiff diagrams, Durov diagrams, Schoeller diagrams, radial plots, ion balance diagrams and pie charts. Aq.QA is a spreadsheet that can convert units, check analyses for internal consistency and one can copy and paste data directly from an Excel spreadsheet. In data analysis, Aq.QA is useful in classifying irrigation waters, reporting fluid properties of water such as density, carbonate equilibria, geothermometry and reporting mineral saturation. Geothermometry is a technique of estimating the temperature at which the water last equilibrated with its environment. This is only applied to geothermal or hydrothermal waters. In reporting mineral saturation, Aq.QA only calculates indices for the $CaCO_3$ minerals aragonite and calcite, which is a major drawback since there are many minerals in waste waters, which are capable of forming scale. Aq.QA reported saturation indices which compared favourably with those reported by PHREEQC for the same samples (see Table 4.1.3 and Fig 4.34). Aq.QA is a very useful software package for water chemists.

PHREEQC simulates a variety of reactions and processes in natural waters and waste waters and it makes use of KEYWORDS to specify the problem in the input file. It is useful for investigations in unspoiled and contaminated environments (Parkhurst 2002). The simplest use of PHREEQC is to calculate the distribution of chemical species and to calculate the saturation state of water with respect to minerals and gases. This is the only application used in this study. The other capabilities of PHREEQC include mass-transfer reactions, surface complexes, inverse modelling and kinetic chemical and biological reactions (Parkhurst 2002). This is a program that requires sound knowledge of geochemistry and reaction equilibria and is very useful in predicting the saturation state of water with respect to numerous minerals.

To compare the two software packages, Table 4.13 and Fig 4.34 show the saturation indices calculated by PHREEQC and Aq.QA of Tutuka Power Station samples. Table 4.13 includes the pH of the samples identified in Appendix A3 and this will be discussed in the next section. The results show that the two softwares reported indices that are not significantly different. The only difference between the SI calculated by the different software programs was on sample TP808 where Aq.QA reported undersaturation of Calcite with an SI of -0.29 while PHREEQC estimated supersaturation of calcite with a SI of 0.14 (Fig 4.34).

Table 4.13: Saturation indices with respect to aragonite and calcite of Tutuka Power Station samples as determined by Aq.QA and PHREEQC.

Sample	Aragonite		Calcite		pH
	PHREEQC	Aq.QA	PHREEQC	Aq.QA	
TP108	1.07	1.63	1.21	1.8	10.01
TP208	0.55	0.86	0.7	1.02	8.03
TP308	-2.22	-1.89	-2.07	-1.72	6.67
TP408	-0.49	-0.07	-0.35	0.09	7.28
TP508	-4.19	-4.03	-4.05	-3.86	5.91
TP608	1.82	3.33	1.95	3.49	11.22
TP708	0.5	0.9	0.64	1.07	8.65
TP808	-0.44	-0.02	-0.29	0.14	7.36
TP908	1.81	2.77	1.94	2.93	8.98
TP1008	-2.74	-2.59	-2.61	-2.43	8.1

Sample identifications can be found in Appendix A3.

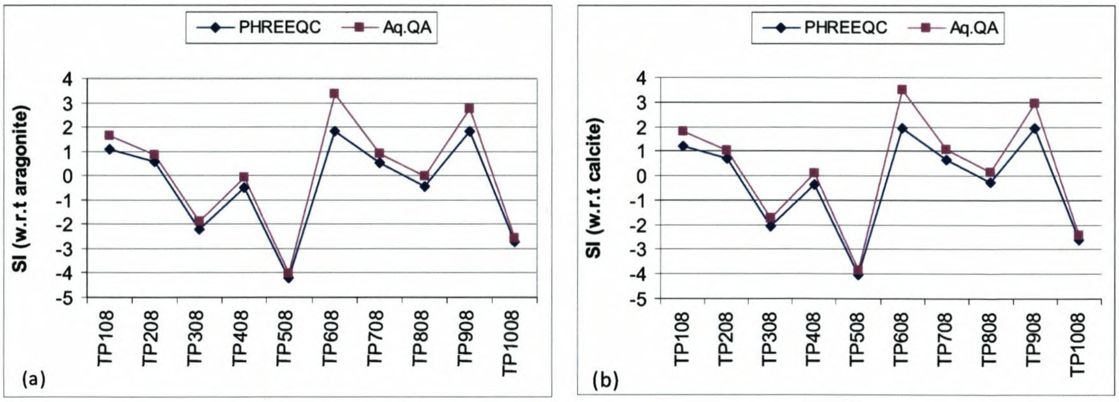


Figure 4.34: Comparison of saturation indices calculated using Aq.QA and PHREEQC with respect to (a) aragonite and (b) calcite.

4.4.3 Tutuka Power Station Speciation by Aq.QA

Table 4.13 in section 4.5.2 show saturation indices of calcite and aragonite alongside pH of Tutuka Power Station samples taken in 2008 calculated by Aq.QA. Fig 4.34 shows graphically the same samples given in Table 4.13 against saturation indices calculated by Aq.QA and PHREEQC. Fig 4.34 shows that samples TP108, TP208, TP608, TP708, and TP908 are supersaturated with respect to calcite and aragonite and these minerals are likely to form scale at and/or after the treatment stages where these samples were taken (refer to Fig 4.12). Sample TP808 is supersaturated and a change in conditions such as pH, can induce precipitation of calcite and aragonite. Samples TP308, TP408, TP508 and TP1008 have negative saturation indices, indicating that these waters are corrosive and corrosion of plant and equipment can occur at and/or after the treatment stages where these samples were obtained (refer to Fig 4.12).

4.4.4 Sasol Secunda Speciation by Aq.QA

Table 4.14 shows the saturation indices of Sasol Synfuels Complex at Secunda samples taken in 2008 calculated using Aq.QA software alongside the pH measured according to the procedure described in section 3.2.1. Sample identification is detailed in Appendix B3 and the water treatment stages sampled can be found in Fig 4.25.

Table 4.14: Saturation indices with respect to aragonite and calcite at Sasol calculated using Aq.QA.

	Aq.QA		pH
Sample	Aragonite	Calcite	
SS108	4.07	4.23	12.03
SS208	3.15	3.32	11.30
SS308	-0.90	-0.73	5.76
SS408	-2.59	-2.42	5.68
SS508	-2.65	-2.49	5.65
SS608	-3.82	-3.65	6.03
SS708	4.23	4.40	12.63
SS808	3.90	4.07	12.05
SS908	1.77	1.94	8.05
SS1008	3.33	3.50	12.10
SS1208	2.21	2.37	10.63
SS1308	2.64	2.81	10.10
SS1408	1.94	2.10	9.64
SS1508	3.00	3.18	10.60

The results in Table 4.14 show that aragonite and calcite are likely to precipitate in all water streams reported except in SS308, SS408, SS508 and SS608. Samples SS308, SS408, SS508 and SS608 had pH values of 5.76, 5.68, 5.65 and 6.03 respectively. The SI values hence show that the water is corrosive in and around the stages where these samples were obtained (see Fig 4.25).

4.4.5 Tutuka Power Station Speciation by PHREEQC

Speciation modelling using PHREEQC was carried out on all the samples from Tutuka Power Station. The indices of the most common scaling minerals were plotted against pH to determine the effect of increasing or decreasing pH to the SI of each of the common scaling minerals (see Table 4.15 and Fig 4.35). Sample identification is detailed in Appendix A3.

Table 4.15: Saturation indices with respect to common scaling minerals and pH of Tutuka Power Station samples taken in 2008 as calculated by PHREEQC.

Sample	pH	Aragonite	Calcite	Hematite	Gypsum	Anhydrite
TP108	10.01	1.07	1.21	18.8	-1.44	-1.67
TP208	8.03	0.55	0.7	20.81	-0.88	-1.13
TP308	6.67	-2.22	-2.07	15.29	-1.4	-1.63
TP408	7.28	-0.49	-0.35	18.22	-0.42	-0.65
TP508	5.91	-4.19	-4.05	7.75	-2.99	-3.22
TP608	11.22	1.82	1.95	14.43	-0.01	-0.13
TP708	8.65	0.5	0.64	19.88	-1.05	-1.25
TP808	7.36	-0.44	-0.29	19.21	-0.54	-0.75
TP908	8.98	1.81	1.94	18.73	0.17	0.13
TP1008	8.1	-2.74	-2.61	14.38	-5.12	-5.2

Before plotting the values shown in Table 4.15 into Fig 4.35, the data was rearranged into ascending order according to pH for the purposes of ease of reference. While interpreting this data, the reader should always bear in mind that the samples were of different physical and chemical composition.

Aragonite and calcite show SI values greater than zero at a pH of about 8.5 or more. These water samples also show supersaturation at a pH of about 8 with respect to calcite and aragonite. Gypsum achieves supersaturation at a pH of about 9 but at pH 10 became undersaturated and then increased to saturation at pH 11.22. It must be remembered that some other factors such as evaporation or dilution do affect the SI of minerals other than pH. The water at pH 10.01 is a mixture of mine water and cooling water, which is much more dilute than the other water streams. Hematite had a high positive SI value throughout the tested pH range of 5.91 to 11.22. All minerals showed a characteristic significant decrease in SI value at a pH of about 8.1. These results showed that controlling the pH of water streams may control scale deposition.

All samples taken in 2008 at Tutuka Power Station were modelled using PHREEQC. Only mine water (TP208), which is the main input to the treatment process and VC brine (TP908), which is the most contaminated waste water at the site will be discussed. Speciation provides information on what species will be (for example) available for uptake by biota and in what form. It is important information for toxicity studies as well as improving water treatment technologies. The minerals likely to precipitate in the other water streams sampled in 2008 are found in Appendices G1 and G2.

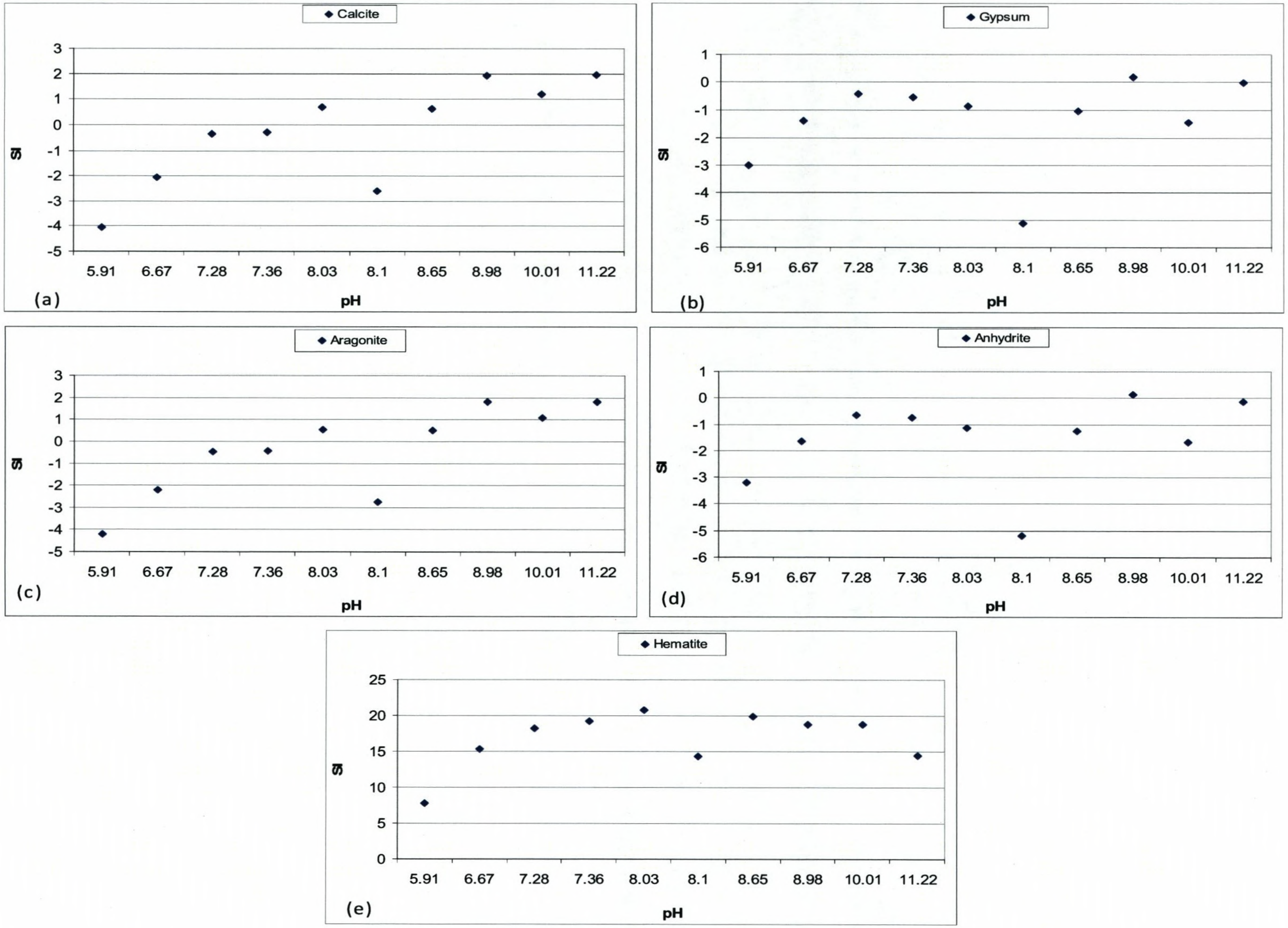


Figure 4.35: Variation of SI values with pH of (a) calcite (b) gypsum (c) aragonite (d) anhydrite (e) hematite from 2008 Tutuka samples.

(i) Mine Water (TP208)

Table 4.16 shows the minerals that were likely to precipitate out of mine water (TP208) at Tutuka Power Station as calculated by PHREEQC. Table 4.16 show that according to PHREEQC calculations, mine water at Tutuka, has a scaling potential.

Table 4.16: Minerals with SI>0 in Tutuka mine water as calculated by PHREEQC.

Mineral	**SI**	**Formula**
Aragonite	0.55	$CaCO_3$
Barite	1.09	$BaSO_4$
Calcite	0.7	$CaCO_3$
Dolomite	1.42	$CaMg(CO_3)_2$
$Fe(OH)_3(a)$	3.93	$Fe(OH)_3$
Gibbsite	1.81	$Al(OH)_3$
Goethite	9.43	FeO_2H
Hematite	20.81	Fe_2O_3
Jarosite-K	2.37	$KFe_3(SO4)_2(OH)_6$
Rhodochrosite	0.53	$MnCO_3$
Siderite	0.3	$FeCO_3$

Mine water as intake water is the main input to the water treatment circuit at Tutuka Power Station. From Fig 4.36 (a), chemical speciation of mine water estimated that Ca species existed as 66.97 % free Ca, 28.87 % as $CaSO_4$ and 1.25 % as $CaCO_3$. The sulphate species (Fig 4.36 (b)) mainly existed as the free SO_4^{2-} at 84.34 %, 4.62 % as $MgSO_4$ and 4.23 % as $CaSO_4$. The Cl^- species (Fig 4.36 (c)) are estimated at 100 % as the free Cl^-, supporting the fact that the Cl^- ion is very conservative chemically. Mg was estimated in Fig 4.36 (d) at 66.93 % as the free Mg ion and 29.09 % as $MgSO_4$. Carbonate and sodium speciation is shown in Fig 4.36 (a) and (b). The carbonates speciation (Fig 4.37 (a)) shows that the main carbonate species in Tutuka input mine waters would be HCO_3^- at 94.03 %. The predominant sodium species in Tutuka mine water (Fig 4.37 (b)) was found to be the free Na^+ ions. The findings based on PHREEQC calculations as shown by the percent species distribution diagrams in Fig 4.36 and 4.37, show that the Cl^- , HCO_3^- and the Na^+ are highly soluble in mine water and are unlikely to precipitate. Ca^{2+}, SO_4^{2-} and Mg^{2+} are also fairly soluble depending on pH and should also be available for uptake by plants, animals and humans in mine water.

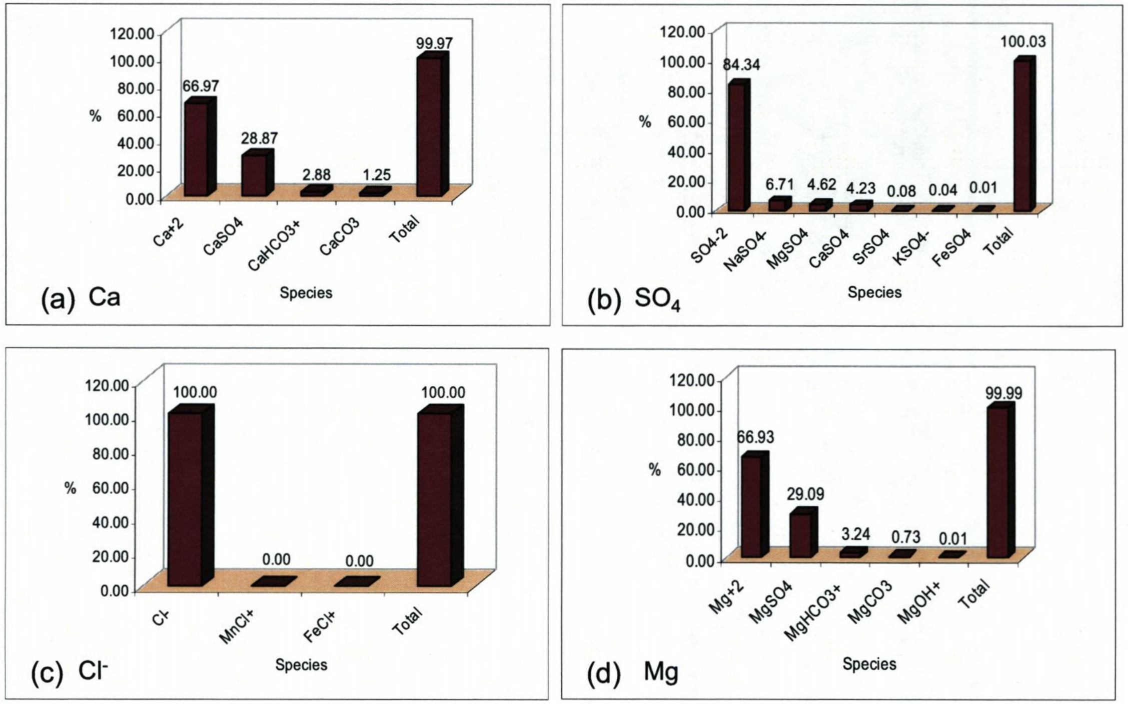
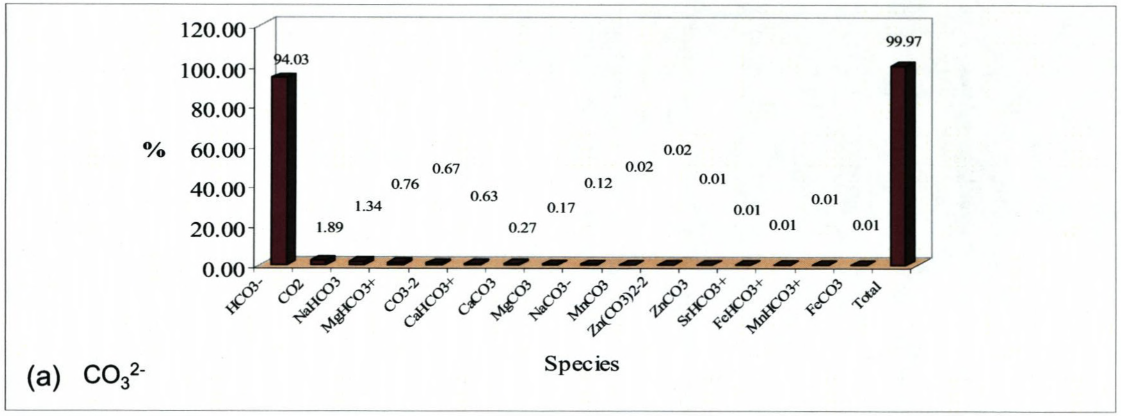
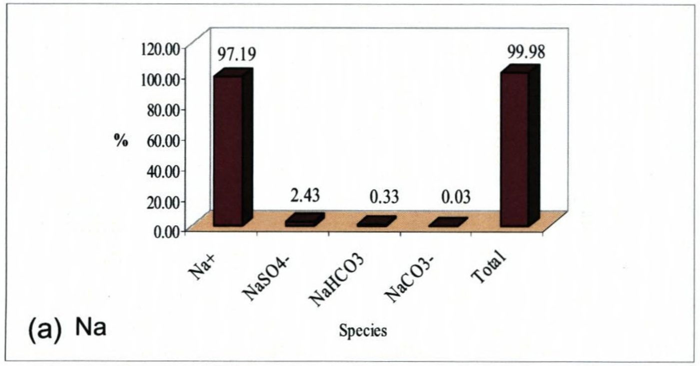


Figure 4.36: Percent major ion species (Ca, SO_4, Cl, Mg) distribution in mine water (TP208), intake at Tutuka Power Station.



(a) CO_3^{2-}



(a) Na

Figure 4.37: Percent major ion species (CO_3, Na) distribution in mine water at Tutuka Power Station.

(ii) Vapour Compressor Brine (TP908)

Vapour compressor brine is the most concentrated brine at Tutuka Power Station. Table 4.17 shows that vapour compressor brine has high scaling potential according to calculation of SI as determined by PHREEQC, with minerals such as anhydrite, aragonite, calcite, hematite, hydroxyapatite and gypsum among others, likely to precipitate. Speciation of highly concentrated brines similar to VC brine allows decisions to be made on pre-treatment methods that can be used before such brines are disposed of.

Table 4.17: Minerals with SI>0 in vapour compressor brine.

Mineral	**SI**	**Formula**
Anhydrite	0.13	$CaSO_4$
Aragonite	1.81	$CaCO_3$
Barite	1.45	$BaSO_4$
Calcite	1.94	$CaCO_3$
Celestite	0.52	$SrSO_4$
Dolomite	4.42	$CaMg(CO_3)_2$
$Fe(OH)_3(a)$	1.54	$Fe(OH)_3$
Goethite	8.3	FeO_2H
Gypsum	0.17	$CaSO_4:2H_2O$
Hausmannite	4.7	Mn_3O_4
Hematite	18.73	Fe_2O_3
Hydroxyapatite	12.02	$Ca_5(PO_4)_3OH$
Otavite	0.28	$CdCO_3$
Rhodochrosite	0.76	$MnCO_3$
Strontianite	0.85	$SrCO_3$

Vapour compressor brine was modelled using PHREEQC and the analytical results obtained from the experimental procedures described in section 3.2. Percent distributions of species in VC brine (TP908) are given in Fig 4.38 and 4.39. Distribution of species in water determines the behaviour of that water as well as its effects to the environment and biota. Chemical speciation [see Fig 4.38 (a)] estimated that 55.45 % of Ca species are in the $CaSO_4$ form and 3.77 % existed as $CaCO_3$. Among the sulphate species, Fig 4.38 (b), 58.36 % is in the free ionic form (SO_4^{2-}). The predominant chloride species Fig 4.38 (d) is the free Cl^- ion at 100 % and the predominant sodium species Fig 4.38(c) is the free Na^+ ion which existed at 85.44 %. Magnesium species, Fig 4.39 (b), have the predominant form as $MgSO_4$ at 73.30 % and the carbonates Fig 4.39 (a), have $NaCO_3^-$ at 53.33 %, HCO_3^- at 27.76 % and CO_3^{2-} at 6.99 %. The vapour compressor brine has the highest total alkalinity among all the water streams at Tutuka Power Station because of the high carbonate content.

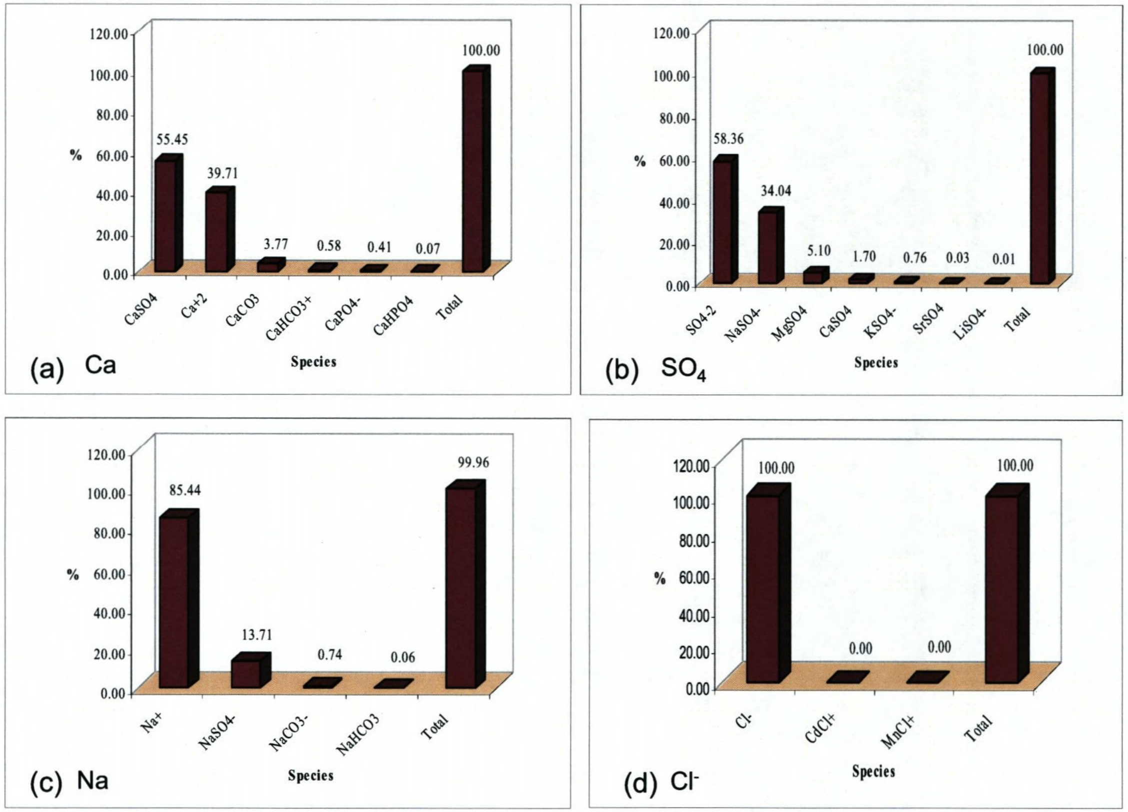


Figure 4.38: Percent major ion species (Ca, SO_4, Na, Cl) distribution in vapour compressor brine (2008) at Tutuka Power Station.

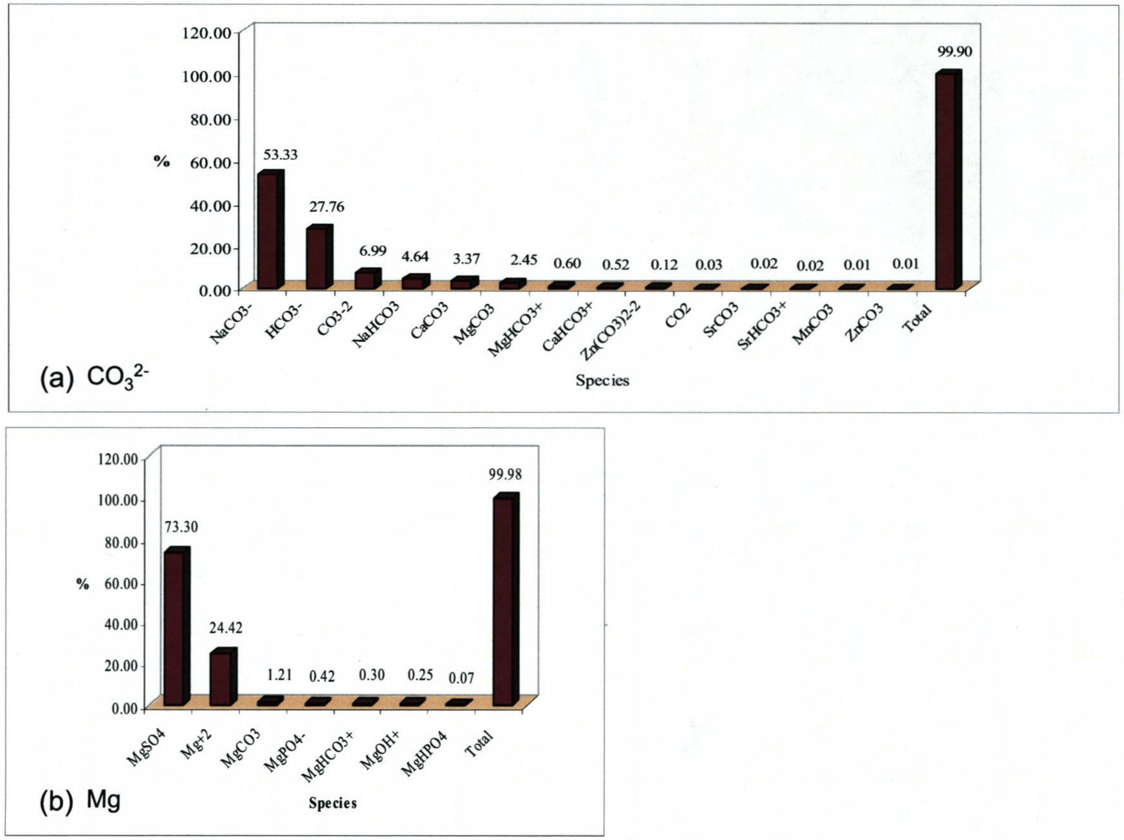


Figure 4.39: Percent major ion species (CO_3^{2-}, Mg) distribution in vapour compressor brine (2008) at Tutuka Power Station.

4.4.6 Sasol Synfuels Complex -Secunda Speciation by PHREEQC

Sasol Secunda has many different water streams in their water treatment process. Two streams sampled in 2008 and modelled using PHREEQC are going to be discussed in this section. Mine water (SS908) and TRO brine (SS308) will be discussed. Mine water is the main input to the water treatment process (see Fig 4.25) and TRO brine is the reject stream from the tubular reverse osmosis desalination of clear ash effluent and it was the most highly concentrated brine from the 2008 samples. Analytical results were obtained as per the experimental procedures described in section 3.2. Data obtained from the experimental procedures was input into PHREEQC without modification.

(i) Mine Water (SS908)

Mine water (SS908) from Sasol Secunda Synfuels Complex analytical results for 2008 (presented in Appendix B3) were modelled using PHREEQC. Table 4.18 presents the saturation indices calculated from the field, ICP and IC results presented in Appendix B3 for mine water and shows that mine water at Sasol has a high scaling potential. The most common scaling minerals such as aragonite, calcite and hematite have saturation indices greater than zero. Treatment is necessary before use in the plant to prevent scaling and corrosion problems.

Table 4.18: Minerals with SI > 0 in mine water at Sasol.

Mineral	**SI**	**Formula**
Aragonite	1.4	$CaCO_3$
Barite	1	$BaSO_4$
Ca-Montmorillonite	2.62	$Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$
Calcite	1.55	$CaCO_3$
Chlorite(14A)	2.26	$Mg_5Al_2Si_3O_{10}(OH)_8$
Dolomite	3.13	$CaMg(CO_3)_2$
$Fe(OH)_3(a)$	3.43	$Fe(OH)_3$
Gibbsite	1.87	$Al(OH)_3$
Goethite	8.91	FeOOH
Hematite	19.78	Fe_2O_3
Hydroxyapatite	5.17	$Ca_5(PO_4)_3OH$
Illite	2.68	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$
Jarosite-K	1.34	$KFe_3(SO_4)_2(OH)_6$
K-feldspar	0.1	$KAlSi_3O_8$
K-mica	9.38	$KAl_3Si_3O_{10}(OH)_2$
Kaolinite	4.43	$Al_2Si_2O_5(OH)_4$
Otavite	0.55	$CdCO_3$
Siderite	0.31	$FeCO_3$
Strontianite	0.48	$SrCO_3$
Talc	0.28	$Mg_3Si_4O_{10}(OH)_2$

Geochemical modelling of mine water (SS908) composition from Sasol Secunda was conducted with PHREEQC. PHREEQC contains a thermodynamic database which contains equilibrium constants for aqueous simple and complex species as well solubility products and redox potential. The software's default pe of 4.0 was input during modelling since redox couples were not measured independently during analysis. For example, Fe was reported as total Fe and not as Fe^{3+} and Fe^{2+}. The following parameters were used to formulate the input files for PHREEQC;

(i) Equilibrium solution pH values

(ii) Total concentration of cations and anions

(iii) Equilibrium solution temperature

The analytical data is provided in Appendix B3. Fig 4.40 (a) shows that chemical speciation using PHREEQC estimated that the predominant calcium species in mine water existed as Ca^{2+} at 57.11 % followed by $CaSO_4$ at 31.43 %. The sulphate species, Fig 4.40 (b), have the free ion SO_4^{2-} as the most abundant at 79.84 %. About 95.33 % of the sodium species, Fig 4.40 (c), exist as the free Na^+. The chloride ion, Fig 4.40 (d), constitutes 100 % of the chloride species and Mg^{2+} free ionic species Fig 4.41 (a) are the most dominant as magnesium species at 56.99 %. The carbonates Fig 4.40 (b) are mainly in the form of HCO_3^- at 92.55 %.

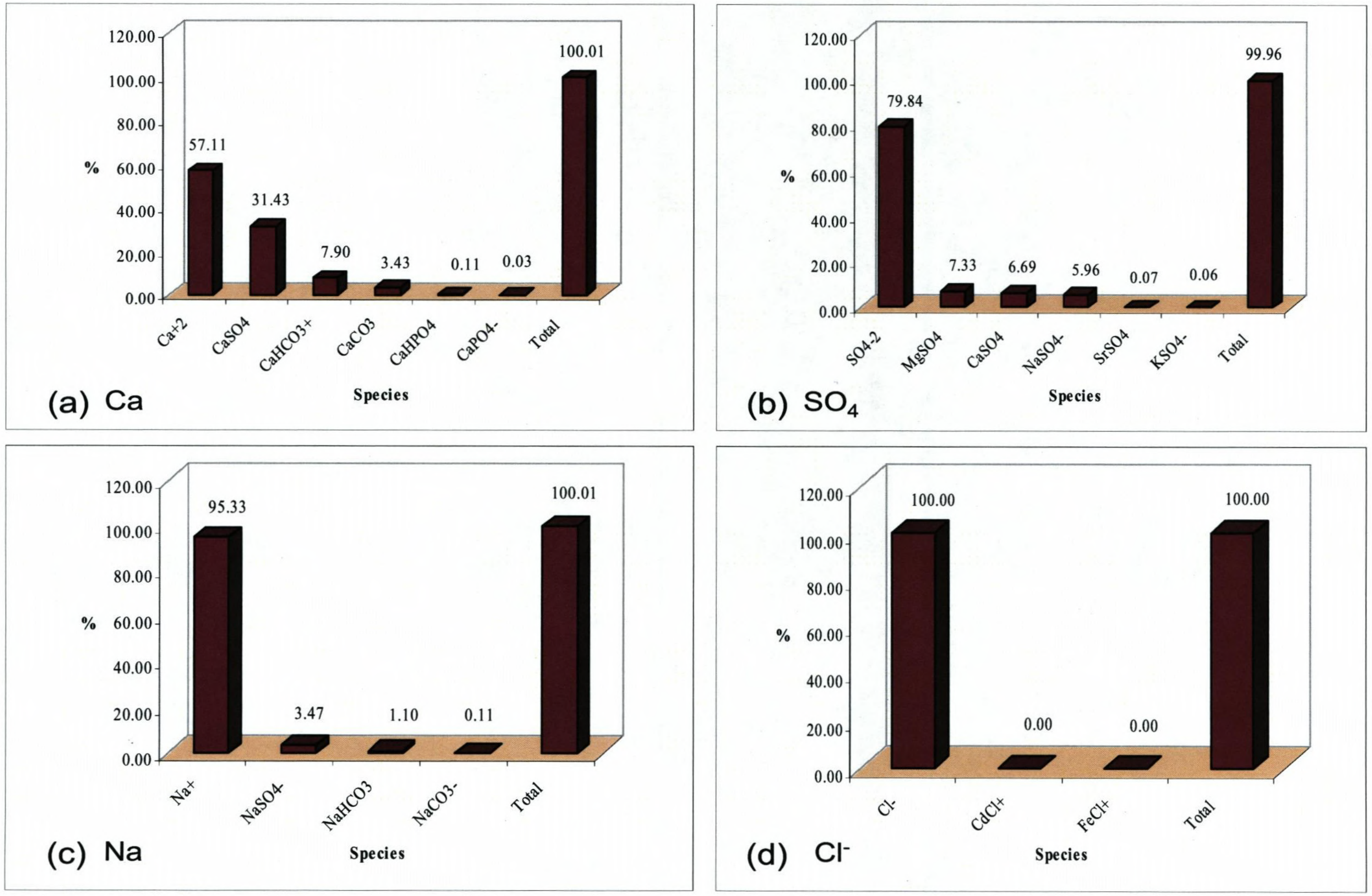
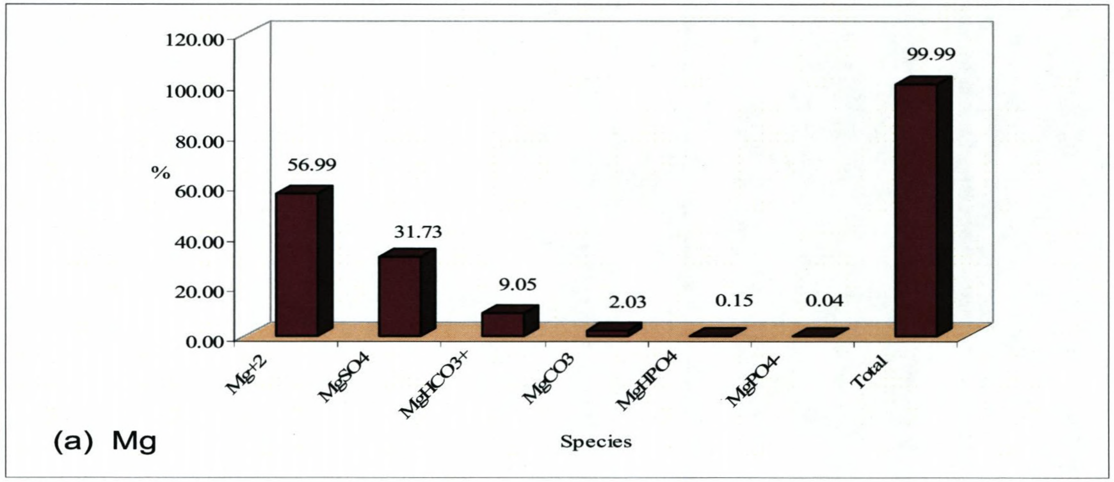


Figure 4.40: Percent major ion species distribution in mine water at Sasol.



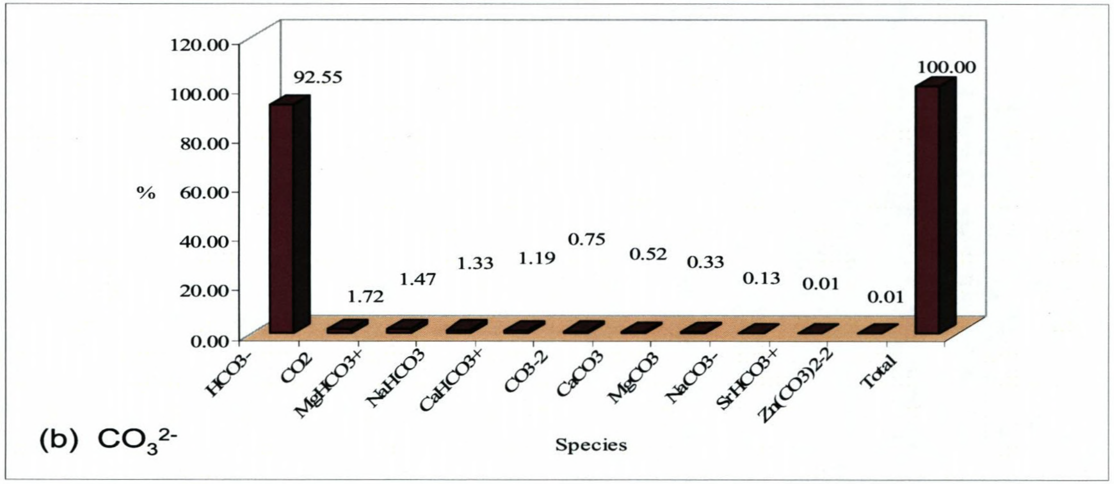


Figure 4.41: Percent major ion species distribution in mine water at Sasol.

(ii) TRO Brine

TRO brine (SS308) was the most highly concentrated water stream sampled in 2008 at Sasol Secunda. It is the reject brine after RO treatment of the clear ash effluent (see Fig 4.25). Analytical data used to formulate the input file in PHREEQC is detailed in Appendix B3. TRO brine, as shown in Table 4.19, has a high scaling potential from precipitation of minerals such as gypsum and hematite.

Table 4.19: Minerals with SI>0 in TRO brine at Sasol.

Mineral	SI	Formula
Alunite	9.46	$KAl_3(SO_4)_2(OH)_6$
Barite	1.54	$BaSO_4$
Ca-Montmorillonite	2.68	$Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$
Celestite	0.44	$SrSO_4$
Gibbsite	2.44	$Al(OH)_3$
Goethite	4.13	FeOOH
Gypsum	0.14	$CaSO_4{:}2H_2O$
Hematite	10.27	Fe_2O_3
Illite	1.39	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$
K-mica	9.6	$KAl_3Si_3O_{10}(OH)_2$
Kaolinite	5.15	$Al_2Si_2O_5(OH)_4$

What is interesting is that PHREEQC did not predict precipitation of $CaCO_3$ from such a highly concentrated brine. Fig 4.42 (a) shows that the most abundant calcium species are Ca^{2+} ions and $CaSO_4$ and the carbonate species are dominated by CO_2. The brine is at a pH of 5.76 as can be seen from Table 4.14 or Appendix B3 and this might be the reason that calcium is not reacting fast enough with CO_3 to reach equilibrium and precipitate. The carbonate species in TRO brine are shown in Fig 4.43 (b). As with all the other samples, the Cl^- free ionic species constitutes 100 % of the chloride species [Fig 4.42 (d). However, the carbonates, Fig 4.43(b) are dominated by CO_2 at 72.59 % as estimated by PHREEQC.

The corrosion of carbon steel is accelerated when an anion of a weak acid (usually acetate) is present in a carbon dioxide saturated brine (Garsany et al., 2002). In order to obtain accurate speciation results and accurate remedial action, it is important to determine the carboxylic acids in brines with a high CO_2 content such as TRO brine. The ingress of CO_2 and CO_2 storage for long timescales in brine depends on the contribution of several CO_2 trapping mechanisms (Eke at al. 2009). The mechanisms are as follows;

(i) Physical trapping

$CO_{2\,(gaseous)} \rightarrow CO_{2\,(aqueous)}$

$CO_{2\,(aqueous)} \rightarrow H_2CO_{3\,(aqueous)}$

(ii) Solubility trapping

$H_2CO_{3\,(aqueous)} + OH^- \rightarrow HCO_3^-{}_{(aqueous)} + H_2O$

(iii) Ionic trapping

$HCO_3^-{}_{(aqueous)} + OH^- \rightarrow CO_3^-{}_{(aqueous)} + H_2O$

(iv) Mineral trapping (also known as mineral carbonation or mineral sequestration)

$CO_3^-{}_{(aqueous)} + Ca^{2+} \rightarrow CaCO_{3\,(solid)}$

The CO_2 species in TRO brine may be due to physical trapping of CO_2 from the atmosphere. Thus brines can be used to capture and store CO_2 and therefore reduce emission of gases with greenhouse effects from coal and gas fired power plants (Eke et al.,. 2009).

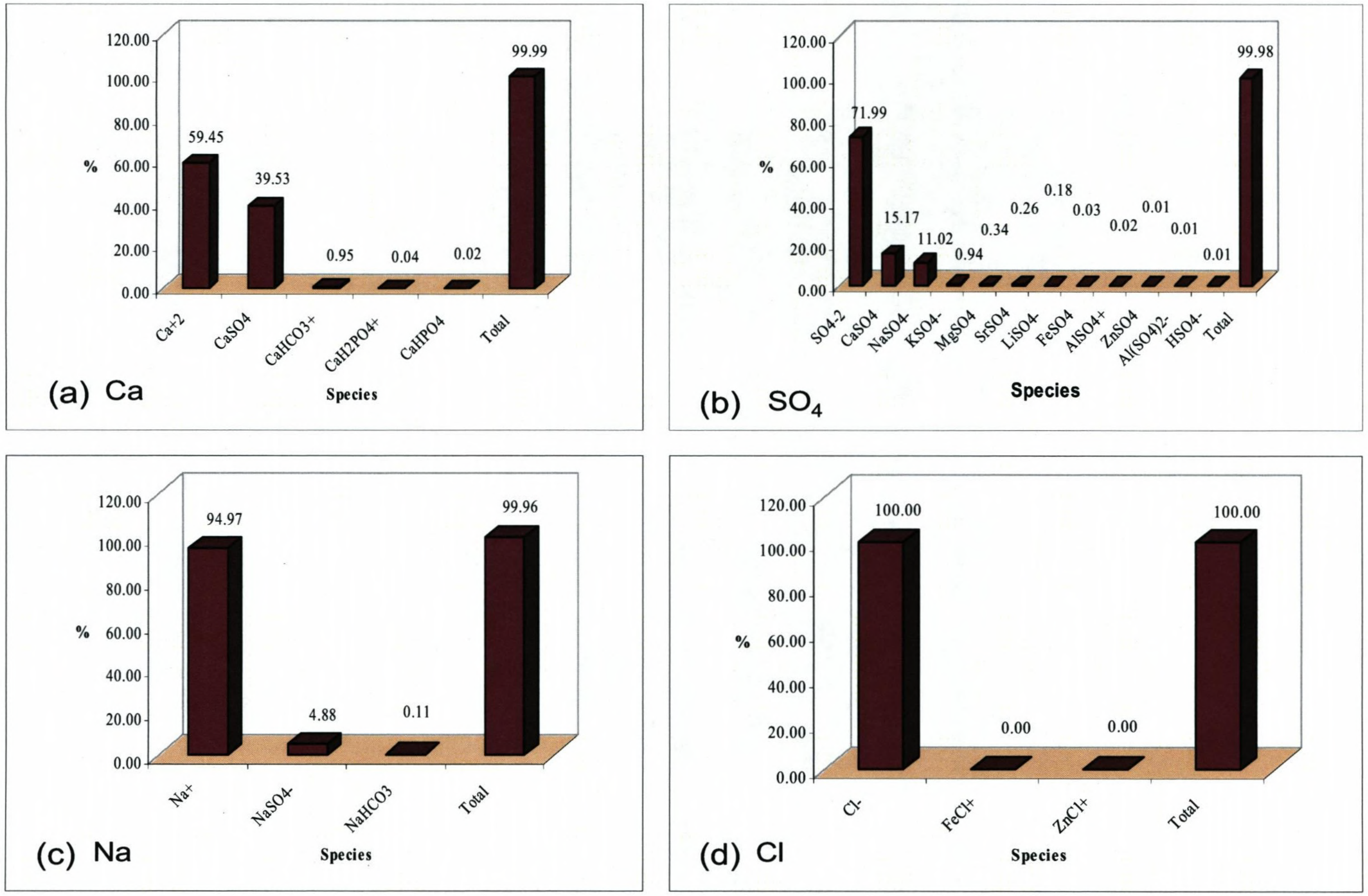
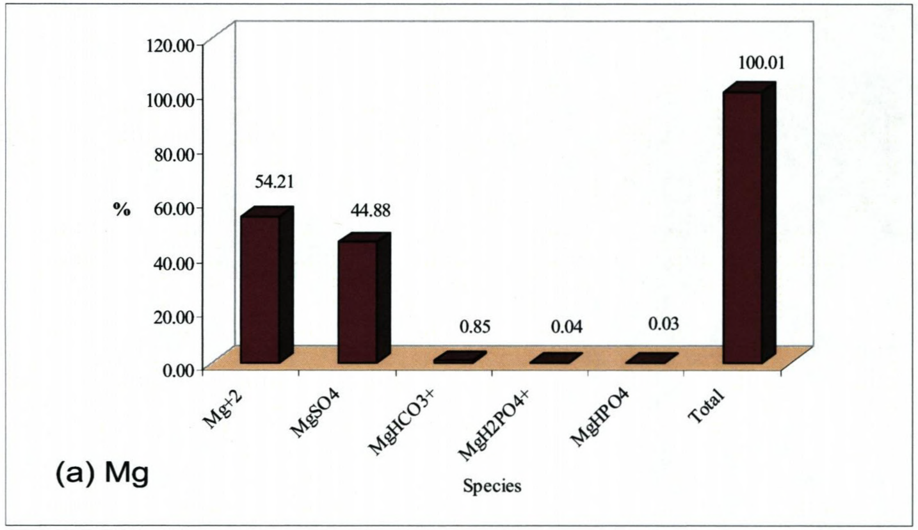
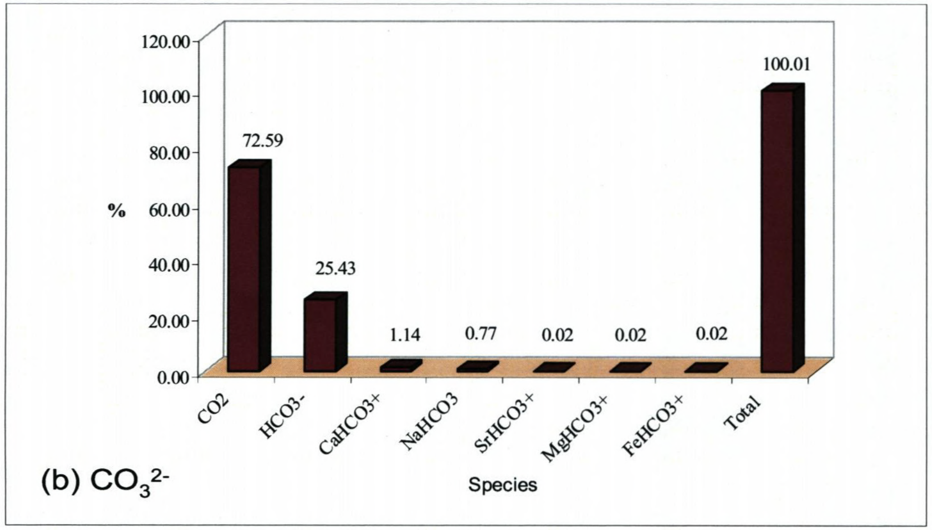


Figure 4.42: Percent major ion species distribution in TRO brine at Sasol.



(a) Mg



(b) CO_3^{2-}

Figure 4.43: Percent major ion species distribution in TRO brine at Sasol.

4.5 Sasol Secunda vs. Tutuka Power Station

Tutuka Power Station and Sasol Secunda have different water treatment layouts (refer to Figs 1.4 and 1.5). Sasol Secunda has a closed loop water treatment circuit whereas Tutuka Power Station has an open end water treatment process. This difference means a difference in the amount of salts in the water being processed at these two sites and therefore scaling and corrosion risks. The similarities and differences will be tabulated in this section.Table 4.2 shows the sources of the highest concentrations in samples taken in 2008 at Sasol Secunda and Tutuka Power Station. It is helpful to know the sources of the highest concentration of cations and anions in a water treatment plant in view of improving the treatment technologies.

Table 4.20: Sources of major ion highest concentration at Sasol Secunda and Tutuka Power Station in samples taken in 2008.

	Sasol Secunda			Tutuka Power Station		
Ion	Conc. (mg/L)	Source	Sample ID	Conc. (mg/L)	Source	Sample ID
Mg	142.01	Mine water	SS908	641.7	VC brine	TP908
Ca	1052.69	FA + FAM	SS708	469.32	Brine after contact with ash	TP608
Na	2355.53	TRO brine	SS308	21656.32	VC brine	TP908
SO_4	4364.88	TRO brine	SS308	36465	VC brine	TP908
Cl	1320.05	Dam penstock overflow	SS1308	11147.3	VC brine	TP908

Key: FA + FAM = Fly ash + fly ash make up
TRO = Tubular reverse osmosis

Table 4.20 shows that the highest concentration of Mg at Sasol Secunda was in mine water (SS908) in samples taken in 2008. Ca is most highly concentrated in fly ash and fly ash make up (20 % slurry) water streams (SS708) and Na and SO_4 were most highly concentrated in TRO brine (SS308) at Sasol Secunda. The highest concentration of Cl at Sasol Secunda was found in dam penstock overflow (SS1308). At Tutuka Power Station, the highest concentrations of Na, SO_4, Cl and Mg were found in VC brine (TP908). Ca at Tutuka Power Station was most highly concentrated in brine after contact with ash (TP608). The Tutuka scenario is straight forward and "normal". The VC brine (TP908) is the most concentrated waste water on the site and it therefore should contain the highest concentrations of major ions.

Ca was most highly concentrated in brine after contact with ash due to ash-brine interactions as discussed in section 4.3.7. At Sasol Secunda the most highly concentrations of Mg were in mine water (SS908), of Ca in FA + FAM (SS708), of Cl in dam penstock overflow (SS1308) and of Na and SO_4 in TRO brine. This is because of the complexity of the water treatment process. However, the similarity between the two sites here is that Ca had highest concentrations in brine streams that had come into contact with ash. Therefore ash can increase the concentration of calcium in brines after mixing.

Mine water is the main intake input at Sasol Secunda and Tutuka Power Station. The salts that end up in all the other water streams originate in mine water, although water treatment chemicals such as flocculants used in clarification and sodium bisulphate used to clean up chlorine before reverse osmosis play a role in the final effluent chemistry. In this study, the major ion chemistry of mine water at Sasol Secunda was compared to that of Tutuka Power Station. Table 4.21 shows the chemistry of the two mine waters as well as their pH.

Table 4.21: Concentration of major ions in mine water from Tutuka Power Station and mine water from Sasol Secunda sampled in 2008.

Ion	Unit	Sasol Secunda	Tutuka Power Station
Mg	mg/L	142.01	55.02
Ca	mg/L	215.85	83.66
Na	mg/L	997.49	905.10
SO4	mg/L	2429.19	1369.43
Cl	mg/L	193.92	430.4
pH		8.05	8.03

Table 4.21 shows that Mg, Ca and SO_4 content in mine water from Sasol Secunda was more than or almost double that in mine water from Tutuka Power Station. The Na content of the two mine waters was almost the same while Tutuka mine water had Cl more than double that of Sasol Secunda mine water. Since mine water is the main input to the water treatment processes at these sites, Sasol Secunda water streams must show higher concentrations than those of Tutuka Power Station because of the higher concentrations in their starting water (SS908). It was found to be true as

shown in Table 4.20. Except for Mg, concentrations of Na, Ca, SO_4 and Cl are higher at Sasol Secunda water streams than at Tutuka Power Station.

It is undesirable to dispose of toxic trace elements into the environment. Table 4.22 shows the sources of the highest concentration of toxic trace elements from water samples taken in 2008 at Sasol Secunda and Tutuka Power Station. Detailed analytical results are presented in Appendices A3 and B3.

Table 4.22: Sources of the highest concentration of toxic trace elements from Tutuka Power Station and Sasol Secunda from samples taken in 2008.

	Sasol Secunda			Tutuka Power Station		
Ion	Conc. (mg/L)	Source	Sample ID	Conc. (mg/L)	Source	Sample ID
As	0.07	FAM	SS108	0.02	VC brine	TP908
B	**19.15**	FA + FAM	SS1008	6.84	VC brine	TP908
Cd	0.12	FA, FA + FAM and Dam penstock overflow	SS108,SS1008, SS1308	0.06	VC brine,RO brine,Cooling water	TP908,TP408, TP708
Cr	0.68	FA + FAM	SS1008	0.61	Mine water + cooling water	TP108
Cu	0.14	FA + FAM	SS1008	1	VC brine	TP908
Mo	0.79	Dam toe drain	SS1208	0.03	Mine water + cooling water	TP108
Ni	0.41	Dam toe drain	SS1208	0.71	VC brine	TP908
Pb	0.31	FAM	SS108	0.42	Mine water + cooling water	TP108
Se	0.34	FA + FAM	SS708	0.02	Mine water + cooling water	TP108
Sr	**26.75**	TRO brine	SS308	16.85	VC brine	TP908
V	0.33	FA + FAM	SS1008	0.18	Brine after contact with ash	TP608
Zn	1.92	FAM	SS108	1.26	Brine after contact with ash	TP608

Table 4.22 shows that except for Pb and Ni, Sasol Secunda water streams have higher concentrations of toxic trace elements than Tutuka Power Station. At Sasol Secunda, the highest concentrations of trace elements were found in the brine after contact with ash streams (refer to Fig 4.25) except for Sr which was found in TRO brine (SS308). At Tutuka, V and Zn were the only trace elements found in the highest concentration in brine after contact with ash. At the two sites, brine after contact with ash water streams end up in the ash dams where they have contact with the environment. These toxic elements can in the end affect the environment and biota (see Table 2.9)

As a summary;

(i) Mine water at the two sites cannot be utilised before treatment.

(ii) SAR values of untreated water and effluent streams at the two sites were unacceptable according to TUAS guidelines for water for irrigation. Only desalination product water is suitable for irrigation.

(iii) The water types at Tutuka Power Station water streams were predominantly Na-SO_4 water types (see Appendix A3).

(iv) The water types at Sasol Secunda are Na-SO_4 and Na-Cl water types (see Appendix B3).

(v) The Sasol Secunda water treatment process is more complex than that used at Tutuka Power Station.

(vi) Sasol Secunda produces more concentrated effluent than Tutuka Power Station.

(vii) CO_2 was found to be among the carbonate species in some water streams at both Sasol Secunda and Tutuka Power Station. CO_2, in the presence of an anion of a weak acid such as acetate, accelerates the corrosion of carbon steel. Some water streams at Sasol and at Tutuka also had negative saturation indices, indicating that they are corrosive. There is a risk of plant and equipment corrosion at the two sites.

(viii) High levels of silica were found in cooling water blowdown at Sasol Secunda. The plant is at high risk of siliceous scaling.

(ix) Positive saturations indices with respect to several minerals were reported at both sites. There is high risk of scaling by some common scale-forming minerals such as gypsum, aragonite, anhydrite, calcite and hematite.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The main objective of this study was to characterize and speciate water streams found in the water treatment circuit at Tutuka Power Station and Sasol Synthetic Fuels Complex in Secunda. In addressing the overall objective samples were analysed for composition and physical attributes. The major ion chemistry as shown by ICP-MS and IC analysis of the saline effluents, alkalinity, pH, trace element chemistry, sodium adsorption ratios, evolution of the water streams and brine after contact with ash chemistry were evaluated. Modelling of the water composition data then followed using PHREEQC and Aq.QA where saturation indices of minerals were calculated and species percent distributions determined.

Initially a literature review established that there are alternative ways of utilising the effluent produced in desalination plants in a profitable way, such as the production of chemicals of commercial value. The literature review also established the availability of alternative desalination techniques and brine disposal methods that can be considered for use in South African power utilities. Brines can be harmful and the potential effects of brine to the environment and/or biota were also established through literature review.

In characterizing the water streams, Stiff diagrams and Aq.QA software were utilised. It was found that even though Stiff diagrams are still very useful in fingerprinting and classifying water samples according to the dominant cations and anions, they are limited in cases where other ions besides Cl, SO_4, Na, Ca, Mg, K, CO_3 and HCO_3 are dominant. Aq.QA was found to be a more accurate tool for classifying waters according to dominant ions than Stiff diagrams. However, Stiff diagrams still have the superior advantage of being a mapping tool to easily identify samples of similar composition as well as quickly identify what has been added or what has been removed from a water stream. The water types at Tutuka Power Station were found to be mainly Na-SO_4 water types and those at Sasol Secunda were a mixture of Na-Cl and Na-SO_4 water types. Water treatment chemicals are utilised at the two sites studied in this research. For example, sodium bisulphite is added to clean up residual chlorine before reverse osmosis to prevent membrane damage. Chlorine is used as a biocide during water treatment. At Sasol Secunda, acids are used to regenerate ion exchange resins. These acids lower the pH of effluent streams which become corrosive. Water treatment chemicals play a major role in increasing the salt loads in treatment plants and in changing the character of water streams including introducing elements that were absent in the intake water.

The major ion chemistry at Tutuka Power Station was evaluated. In 2008, it was found that concentrations were as high as 36.5 g/L of SO_4 in the most concentrated saline effluent and as low as 0.05 mg/L of Mg in the least concentrated water streams. The least concentrated water stream at Tutuka Power Station was found to be the vapour compressor product. Desalination by distillation was found to be a more effective way of purifying saline effluents than using TRO in terms of contaminant removal. At Sasol Secunda, major ions varied from 0.01 mg/L of Mg in mine water to 4.6 g/L of SO_4 in tubular reverse osmosis brine from the western plant. It was found that Sasol Secunda water streams are much more heavily contaminated than Tutuka Power Station water streams. The study also found that the mine water utilised at Sasol Secunda is two-fold more polluted than the mine water utilised at Tutuka Power Station although these site are a mere 40 km apart.

Trace elements were evaluated and the toxic trace elements varied from 0.07 mg/L (As) to 26.75 mg/L (Sr) at Sasol Secunda. At Tutuka Power Station the toxic trace elements in brines varied from 0.02 mg/L (As/Se) to 16.85 mg/L (Sr). Sr and B were found to be the most highly concentrated toxic elements. Sr can cause bone growth problems when consumed, especially in children. B affects the stomach, liver, kidneys, the brain and can eventually cause death.

Total alkalinity is of prime importance to the analysis of saline effluents. It is related to the pH and to the bicarbonate concentration, which are both used to predict scale tendency and corrosion potential of saline effluents. The pH of brines at Tutuka Power Station varied from 5.37 to 12.85 from samples taken from 2006 to 2008. The lowest pH was from reverse osmosis permeate and the highest from brine after contact with ash. The total alkalinity of Tutuka Power Station brines ranged from 6.80 to 1147 mg/L $CaCO_3$ in 2008. The lowest total alkalinity was from the vapour compressor product and the highest was from vapour compressor brine. In 2007, the brine after contact with ash at Tutuka Power Station had the highest alkalinity and pH which is 'normal'. At Sasol Secunda, the pH in brines ranged from 2.3 in regeneration effluents to 12.63 in brine after contact with ash. The lowest pH recorded was as a result of acids used to regenerate ion exchange resins. Total alkalinity ranged from 100 to 1200 mg/L $CaCO_3$ in 2008. The lowest total alkalinity was from TRO brine, TRO permeate and SRO permeate while the highest total alkalinity was from the fly ash + fly ash make-up (brine + ash). The study therefore found that the highest alkalinity came from the water streams with the highest pH. When saline effluents at Tutuka Power Station and Sasol Secunda are combined with ash, pH, Ca content and alkalinity of the resulting solution increased.

Water streams studied at Tutuka Power Station and Sasol Secunda were also evaluated for their suitability to be used as irrigation water. The study found that the sodium adsorption ratios of all the water streams at Tutuka Power Station and Sasol Secunda except for desalination product waters were unsuitable for irrigation.

Modelling was an important part in addressing the objectives of this study. It was found that Aq.QA, a very user friendly software programme, is a useful tool for graphing water analysis data. It was capable of calculating the mineral saturation state of water with respect to aragonite and calcite comparably with renowned geochemical model PHREEQC. It is however limited to these two minerals and it can be of no use in calculating saturation indices of other common scale-forming minerals such as gypsum, hematite and anhydrite. It is an excellent tool in characterizing water according to dominant ions. On the other hand, PHREEQC is capable of calculating the saturation state of a large number of minerals. It was therefore utilised to calculate what could potentially precipitate out of different water streams at these two power utilities. In almost pure water streams such as the vapour compressor product, PHREEQC predicted the precipitation of goethite ($FeHO_2$) and hematite (Fe_2O_3). The pH of such waters is low and they are therefore corrosive. In highly concentrated waters from Tutuka Power Station and Sasol Secunda, such as brine after contact with ash, PHREEQC predicted the precipitation of a number of minerals including calcite ($CaCO_3$), barite ($BaSO_4$), aragonite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, hematite (Fe_2O_3) and strontianite ($SrCO_3$). It was found that this high pH, highly contaminated saline effluents have a high scaling potential as predicted by PHREEQC.

Identifying ionic distributions is of particular importance as pollutants affect groundwater and the environment by the chemical behaviour of the ionic species and transformation of species more than by total concentrations. Highly soluble free ions are important in water chemistry because toxicity is related to bioavailability. The ionic distribution of major ion species was evaluated from PHREEQC speciation modelling results. In Tutuka Power Station, all major free ions constituted the largest percentage in their respective species. Free Ca^{2+} existed at 66 % of the entire Ca species and free SO_4 was at 84 %, Cl^- at 100 %, Mg^{2+} at 66 %, HCO_3^- at 94 % and free Na^+ at 97 %. In highly concentrated vapour compressor brine, free SO_4 existed at 58 %, free Na^+ at 85 %, free Cl^- at 100 %, the ionic compound $CaSO_4$ existed at 55 %, $MgSO_4$ at 73 % and $NaCO_3^-$ at 53 %. The study found that waters with lower ion concentration levels had more highly soluble free ions. It was found that the Cl species existed as Cl^- at 100% in all the water streams that were modelled. Therefore the Cl ion is chemically conservative and can be used as a tracer in water chemistry. It is not retarded by reactions.

Modelling results in this study have shown that CO_2 constitutes part of the carbonate species in brines. The amount of CO_2 given as a percentage of the carbonate species, was found to be higher in the most concentrated brines. Ingress of CO_2 from the atmosphere is thought to take place through several different mechanisms. The storage of CO_2 in the brines depends on the contribution of the different trapping mechanisms. Mineral sequestration or mineral carbonation is one of the trapping mechanisms that can fix CO_2 into brines by precipitating a carbonate mineral such as calcite. The other trapping mechanisms are, physical trapping, solubility trapping and ionic trapping. Brines can be used to capture and store CO_2 from coal and gas fired power stations. This would reduce the emission into the atmosphere of gases that have a greenhouse effect. CO_2 is also thought to accelerate the corrosion of carbon steel in pipes when acetate (an anion of a carboxylic acid) is present. In order to obtain accurate speciation results and informed remedial actions, it is important to determine acetate in brines before speciation but this was not done in this study due to the unavailability at the time of sampling, of suitable simple analytical methods and equipment to use in the field. Ash was also found to reduce the amount of major ions at Tutuka Power Station by about 85.9% but much less at Sasol Secunda. The water treatment process at Sasol is a closed loop treatment system and this might reduce the ability of the ash to significantly remove salts from the brine obtained from treating the more concentrated clear ash effluent.

The relationship between pH and saturation indices of calcite, hematite, aragonite, anhydrite and gypsum in Tutuka Power Station water streams was determined. The reader should be aware of the fact that the water streams had different physical and chemical compositions while interpreting this relationship. The saturation indices of these common scale-forming minerals generally increased with increase in pH. As a rule of thumb, a negative saturation index with respect to a given mineral, indicate corrosive water and a positive saturation index indicate water with a scaling potential. To summarize further, the study has contributed knowledge in;

(i) The variation in composition of effluent streams at the two study sites;

(ii) The composition of intake water and the most highly concentrated effluent streams at the two study sites;

(iii) The percent distribution of major ion species in brines including identifying streams with trapped CO_2. These streams will be excellent candidates to be used in determining how brines can be used to capture and store CO_2 from boiler flue gases in future studies;

(iv) What can possibly precipitate out of the water streams. This information is vital in determining the scales likely to be formed in piping and equipment and therefore plan remedial actions accordingly;

(v) The contribution of water treatment chemicals to the chemistry of the effluent streams. This can help find alternative treatment methods;

(vi) Identifying water tracers such as the Cl ion which are not retarded by reactions at the two study sites;

(vii) Understanding the role of fly ash in reducing the amounts of pollutants in brines at the two study sites;

(viii) Identifying corrosive water streams and scaling water streams at the two study sites;

(ix) Capabilities of modelling software through the study and literature review.

5.2 Recommendations

Alkalinity is generally the sum of two primary components, HCO_3^- and carboxylic acids (e.g. acetate), in the brine. Acetate was not determined, which is one of the delimitations in this study. The main reason why carboxylic acids were not analysed, is that there was no simple titration method to use immediately after sampling in the field. Generally, it is necessary to do gas chromatography. The drawback of not considering carboxylic acids in determining total alkalinity, as is generally done in industry, is that the calculated pH in the water will be too high and the scale tendency estimated will be too large. This can cause over treatment for scale, when, in fact, the water is corrosive, due to a low pH. The Brine Consortium has developed easy titrimetric methods to analyse for acetate. It will be recommended to analyse for acetate in future work involving brines.

It is not often easy to analyse highly saline effluents for composition and get acceptable ion balance percentage differences due to CO_2 interacting with samples during sampling. It is recommended that sampling containers should be filled to the brim to exclude air and therefore prevent sample deterioration. The interaction of CO_2 with brines needs to be understood. Experiments need to be undertaken to assess the suitability of brine as a CO_2 sink. CO_2 is produced during power generation at the two sites studied. It is also recommended that geochemical modelling software that can adjust H^+ activity to obtain charge balance be used. MINTEQ is one such package that can obtain charge balance by adjusting the dominant anion before performing speciation calculations. However it is difficult to compare modeling software as it is rare to have models that have the same database and the same input parameters.

Sasol Secunda has a very complex water treatment process. Many sections of the treatment process need to be assessed such as water streams from the evaporators, clarifiers, ion exchange and EDR. It is recommended that more detailed and regular sampling be undertaken in future work.

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APPENDICES

Appendix A1: Chemical composition of water streams at Tutuka Power Station, July 2006

Parameter (mg/L)	TP106	TP206	TP306	TP406	TP506	TP606	TP706	TP806	TP906
Ca	760	46	62	230	0.17	0.96	420	18	140
Mg	240	15	52	92	0.08	0.06	0.08	9.2	58
Na	15400	700	850	5100	40	2	1300	13	3000
Li	0	0	0	0	0.01	0	0	0	0
Be	–	–	–	–	–	–	–	–	–
B	–	–	–	–	–	–	–	–	–
Al	–	–	–	–	–	–	–	–	–
Si	–	–	–	–	–	–	–	–	–
P	780	41	7.8	250	1.8	0.21	71	3.3	130
K	–	–	–	–	–	–	–	–	–
Ti	–	–	–	–	–	–	–	–	–
V	–	–	–	–	–	–	–	–	–
Cr	–	–	–	–	–	–	–	–	–
Mn	–	–	–	–	–	–	–	–	–
Fe	–	–	–	–	–	–	–	–	–
Co	–	–	–	–	–	–	–	–	–
Ni	–	–	–	–	–	–	–	–	–
Cu	–	–	–	–	–	–	–	–	–
Zn	–	–	–	–	–	–	–	–	–
As	–	–	–	–	–	–	–	–	–
Se	–	–	–	–	–	–	–	–	–
Sr	–	–	–	–	–	–	–	–	–
Mo	–	–	–	–	–	–	–	–	–
Cd	–	–	–	–	–	–	–	–	–
Ba	–	–	–	–	–	–	–	–	–
Pb	–	–	–	–	–	–	–	–	–
Cl	8040	370	400	2910	71.2	0.3	780	8.4	1860
NO_3	nd	5.3	0.8	nd	3.9	<0.1	8.1	0.3	15.4
PO_4	–	–	–	–	–	–	–	–	–
SO_4	18890	920	1040	6700	35.6	0.7	1950	19.6	4350
Fluoride as F^-	nd	0.75	3.04	nd	0.25	0	1.7	0.16	5.87
Ammonia as (N)	0	0.1	0.2	0.2	0.2	0.2	2	0	0.1
TDS (Σ)	44110	2098.15	2415.84	15282.2	153.21	4.43	4532.88	71.96	9559.37
Conductivity (µS/cm)	>20000	3440	4050	>20000	200	0	8360	160	11520
pH	8.67	8.38	8.2	7.22	5.37	5.67	11.22	7.54	7.59
TDS (Measured)	>10000	1760	2100	>10000	110	0	4340	80	5960
Temperature (^oC)	48.2	29.7	14.6	27.6	26.8	52.7	30	13.8	19
Ion Balance % Difference	15.84	15.47	15.88	11.87	15.87	76.82	14.77	61.41	6.405
Ion Balance Result	>±5%	>±5%	>±5%	>±5%	>±2meq/L	OK	>±5%	>±2meq/L	>±5%
Water Type	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-Cl	Na-SO_4	Na-SO_4	Ca-SO_4	Na-SO_4
Salinity Hazard	Very High	Very High	Very High	Very High	Low	Low	Very High	Low	Very High
SAR	126	22.9	19.3	72.2	20	523 x 10-3	17.5	621 x 10-3	54
Total Hardness(mg/L $CaCO_3$)	2947	176.15	369.32	960.55	0.7514	2.609	1048	82.775	591.75

NB: – *indicates when a parameter was not measured*
nd *indicates when a parameter was not detected by the instrument*

Legend

TP106	Vapour compressor brine
TP206	Cooling water from evaporation towers.
TP306	Mine water
TP406	SRO brine
TP506	SRO permeate
TP606	Vapour compressor condensate
TP706	SRO brine after contact with ash(after quenching ash in unit 2)
TP806	Cooling water make-up
TP906	Brine at ash dam(used to keep ash damp)

Appendix A2: Chemical composition of water streams at Tutuka Power Station July 2007

Parameter (mg/L)	**TP107**	**TP207**	**TP307**	**TP407**	**TP507**	**TP607**	**TP707**	**TP807**	**TP907**	**TP1007**
Ca	6.64	35.27	4.81	31.78	0.08	489.14	17.59	130.02	490.34	0.16
Mg	33.50	64.71	34.62	319.40	1.34	0.22	38.29	231.40	669.33	0.21
Na	258.65	262.70	190.34	1217.75	7.51	2299.26	985.24	6108.14	22212.13	5.90
Li	0.06	0.07	0.05	0.50	0.00	0.61	0.06	0.33	0.99	0.00
Be	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
B	0.68	0.60	0.65	2.30	0.90	1.28	0.89	1.89	4.82	0.00
Al	0.02	0.03	0.00	0.14	0.01	0.01	0.13	0.21	0.10	0.00
Si	1.82	2.10	1.51	9.89	0.06	1.00	4.08	25.29	54.60	<0.05
P	0.09	0.05	0.03	1.16	0.05	0.00	0.01	1.28	3.20	0.04
K	18.64	7.63	20.15	183.00	1.49	60.42	24.12	148.29	485.33	0.18
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
V	0.00	0.00	0.00	0.03	0.00	0.03	0.01	0.02	0.08	0.00
Cr	0.00	0.00	0.00	0.02	0.00	0.04	0.00	0.02	0.04	0.00
Mn	0.07	0.05	0.02	0.19	0.00	0.01	0.01	0.19	0.27	0.00
Fe	0.04	0.03	0.02	0.49	0.02	1.29	0.13	0.20	0.47	0.01
Co	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.02	0.06	0.00
Ni	0.02	0.02	0.02	0.19	0.00	0.02	0.03	0.16	0.51	0.00
Cu	0.06	0.00	0.06	0.63	0.00	0.03	0.08	0.59	1.14	0.00
Zn	0.03	0.04	0.03	0.34	0.02	0.11	0.05	0.26	0.20	0.01
As	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.03	0.00
Se	0.00	0.00	0.00	0.03	0.00	0.01	0.00	0.02	0.08	0.00
Sr	0.56	3.18	0.61	5.84	0.03	7.18	0.79	5.06	15.36	0.01
Mo	0.01	0.01	0.01	0.09	0.00	0.08	0.01	0.08	0.26	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	nd
Ba	0.01	0.03	0.01	0.09	0.00	0.18	0.02	0.10	0.24	0.00
Pb	0.01	0.00	0.00	0.01	0.00	0.05	0.01	0.01	0.01	0.00
Cl	454.17	504.17	458.33	3600.00	45.33	1960.00	450.00	10266.67	24666.67	2.63
NO_3	2.13	2.25	2.75	16.67	0.81	12.00	1.63	44.00	113.33	0.05
PO_4	0.63	0.63	0.63	5.00	0.05	10.00	0.63	20.00	20.00	0.05
SO_4	1370.83	1437.50	1379.17	11133.33	43.33	6000.00	1258.33	32800.00	76800.00	8.01
TDS (Σ)	2148.65	2321.08	2093.82	16528.93	101.05	10843.00	2782.14	49784.26	125539.60	17.27
Conductivity (µS/cm)	3710.00	4560.00	3700.00	>20000	260.00	>20000	3700.00	19280.00	>20000	0.00
pH	6.51	8.23	6.85	7.47	6.06	12.85	10.14	7.85	9.24	8.54
TDS (Measured)	2150.00	2630.00	2140.00	>10000	150.00	>10000	2090.00	>10000	>10000	20.00
Temperature (^oC)	15.4	13.9	14.4	14.6	14.4	15.3	15	15.5	15.5	15.3
Total Alkalinity(mg/L $CaCO_3$)	62.50	637.50	75.00	537.50	37.50	2375.00	137.50	425.00	1312.50	37.50
Ion Balance % Difference	47.17	49.43	55.65	59.29	59.43	37.06	7.35	53.23	37.00	54.38
Ion Balance Result	>±5%	>±5%	>±5%	>±5%	>±2meq/L	>±5%	>±5%	>±5%	>±5%	>±2meq/L
Water Type	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-Cl	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-HCO_3
Salinity Hazard	Very High	Very High	Very High	Very High	Medium	Very High	Very High	Very High	Very High	Low
SAR	9.06	6.07	6.66	14.30	1.37	28.70	30.20	75.70	16.10	2.28
Total Hardness(mg/L $CaCO_3$)	154.64	354.91	154.70	1411.20	5.71	1213.30	201.85	1325.20	4369.80	1.26

NB: – *denotes when a parameter was not measured*
nd *denotes when a parameter was not detected by the instrument*

Legend

TP107	SRO Feed after pH correction (mine water 90%, cooling water 10%)
TP207	Mine water New Denmark coal mine
TP307	Cooling water + mine water after microfiltration
TP407	SRO brine
TP507	SRO permeate
TP607	Brine after contact with bottom ash
TP707	Cooling water
TP807	Feed for Vapour Compressor (RO Brine)
TP907	Vapour Compressor brine
TP1007	Vapour Compressor product

Appendix A3: Chemical composition of water streams at Tutuka Power Station, May 2008

Parameter (mg/L)	TP108	TP208	TP308	TP408	TP508	TP608	TP708	TP808	TP908	TP1008
Ca	23.04	83.66	22.75	142.25	1.86	469.32	54.30	119.32	467.71	0.23
Mg	32.17	55.02	29.37	201.49	2.49	1.21	25.09	157.08	641.70	0.05
Na	926.65	905.10	906.30	6065.39	128.25	3996.05	995.23	4869.60	21656.32	1.81
Li	0.08	0.07	0.06	0.49	0.01	0.91	0.04	0.39	2.03	0.00
Be	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00
B	1.47	1.30	1.14	1.96	0.83	2.40	1.32	1.87	6.84	0.01
Al	0.21	0.19	0.22	0.46	0.01	0.74	0.45	0.50	0.54	0.01
Si	3.00	0.00	0.00	0.00	0.67	0.00	0.00	0.00	0.00	0.03
P	0.00	0.00	1.57	4.66	0.06	2.94	3.22	4.03	9.47	0.03
K	25.32	7.77	24.17	164.30	3.31	119.05	41.73	137.03	583.08	0.05
Ti	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00
V	0.01	0.00	0.01	0.03	0.00	0.18	0.02	0.03	0.10	0.00
Cr	0.61	0.48	0.10	0.22	0.00	0.23	0.22	0.21	0.28	0.00
Mn	0.37	0.31	0.03	0.16	0.00	0.02	0.04	0.14	0.26	0.00
Fe	3.62	2.85	1.14	2.37	0.02	2.47	2.76	2.35	3.86	0.01
Co	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.04	0.00
Ni	0.33	0.26	0.09	0.29	0.00	0.27	0.16	0.25	0.71	0.00
Cu	0.09	0.01	0.10	0.39	0.01	0.03	0.26	0.37	1.00	0.00
Zn	0.19	0.30	0.33	0.82	0.01	0.30	0.48	0.73	1.26	0.00
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Se	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	0.60	3.60	0.71	4.85	0.05	6.03	0.54	3.85	16.85	0.00
Mo	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.03	0.06	0.00	0.05	0.06	0.05	0.06	0.00
Ba	0.09	0.11	0.11	0.26	0.01	0.52	0.22	0.23	0.46	0.04
Pb	0.42	0.32	0.01	0.03	0.00	0.01	0.01	0.01	0.06	0.00
Cl	471.33	430.40	465.40	3130.03	115.32	2071.37	541.85	2592.23	11147.30	0.54
NO_3	5.00	5.00	5.00	10.00	1.61	10.00	10.00	10.00	38.33	0.05
PO_4	10.00	10.00	10.00	20.00	0.20	20.00	20.00	20.00	25.00	0.10
SO_4	1471.74	1369.43	1548.26	10661.51	132.97	7058.55	1640.20	8376.81	36465.00	3.56
TDS (Σ)	2976.39	2876.21	3016.89	20412.06	387.71	13762.67	3338.21	16297.12	71068.30	6.52
Conductivity (µS/cm)	4460.00	4470.00	4490.00	24500.00	8290.00	19490.00	5180.00	20600.00	71600.00	10.19
pH	10.01	8.03	6.67	7.28	5.91	11.22	8.65	7.36	8.98	8.10
TDS (Measured) *	–	–	–	–	–	–	–	–	–	–
Temperature (°C)	22.00	14.40	23.00	18.00	22.00	43.00	30.00	24.00	51.00	49.00
Total Alkalinity(mg/L $CaCO_3$)	219.5	482	53.5	320.2	16.3	650.3	131	273.4	1147.6	6.80
Ion Balance % Difference	3.144	1.774	2.795	3.936	0.601	6.012	2.536	3.688	2.835	36.548
Ion Balance Result	OK	OK	OK	OK	OK	>±5%	OK	OK	OK	OK
Water Type	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-Cl	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-HCO_3
Salinity Hazard	Very High	Very High	Very High	Very High	Very High	Very High	Very High	Very High	Very High	Low
SAR	29.3	18.9	29.6	77.2	14.4	50.7	28	69.3	15.6	887×10^{-3}
Total Hardness(mg/L $CaCO_3$)	190.01	436.08	177.72	1201.7	14.869	1178.2	238.46	953.8	3962.3	0.77123

** Instrument malfunctioned*

NB: – *indicates a parameter not measured*

nd *indicates a parameter not detected by the instrument*

Legend

TP108	Cooling Water:Mine Water Mixture at Clarifier outlet (ca. 1:9)
TP208	Mine Water (New Denmark)
TP308	Cooling Water/Mine Water Mixture (after microfiltration, acidifying and chlorine addition)
TP408	RO brine
TP508	RO permeate
TP608	Brine after contact with ash
TP708	Cooling water
TP808	Feed for Vapour Compressor (combined RO Brine)
TP908	Vapor Compressor reject (VC Brine)
TP1008	Vapour Compressor product

Appendix B1: Chemical composition of water streams at Sasol Secunda, July 2006

Parameter (mg/L)	SS106	SS206	SS306	SS406	SS506	SS606	SS706	SS806	SS906	SS1006	SS1106	SS1206	SS1306	SS1406	SS1506
Ca	2.1	34	1000	610	600	810	790	740	860	720	720	150	690	13	620
Mg	0.22	2.6	0.19	370	47	2.1	2	14	2.3	<0.04	59	98	0.16	<0.04	3.1
Na	300	120	2100	2900	2800	2400	2300	7600	2600	1300	4200	1600	1300	1500	1600
Li	0	0	2.4	0	0	5.8	4.8	30	5.2	0	0	0	0	9.3	4.5
Be	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
B	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Al	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Si	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
P	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K	2.6	2.9	190	33	5	240	220	790	240	130	170	48	150	130	180
Ti	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
V	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cr	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Mn	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Fe	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Co	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ni	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cu	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Zn	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
As	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Se	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Sr	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Mo	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cd	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ba	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Pb	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cl	110	13.1	1830	850	160	1570	2260	4570	1940	1060	7980	12	780	1310	1570
NO_3	9.5	0.8	19	<0.1	2.4	nd	24.5	nd	27.2	15.7	nd	nd	nd	nd	31.3
PO_4	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
SO_4	170	410	3630	9950	940	6170	7440	11410	6500	2840	2400	650	1990	800	3860
Fluoride as F	0.99	0.06	5.09	2.45	0.84	9.01	8.31	nd	23.53	17.4	0	0	nd	nd	4.82
Ammonia as (N)	0.2	0.3	60	0.6	0.5	2	19	50	21	80	0.6	0.3	40	70	10
TDS (Σ)	595.61	583.76	8836.68	14715.15	4555.74	11208.91	13068.61	25204	12219.23	6163.1	15529.6	2558.3	4950.16	3832.3	7883.72
Conductivity (µS/cm)	1800	1210	12900	8320	2180	12010	11520	17830	11390	9350	>20000	7330	9010	8490	8900
pH	10.02	2.3	11.6	6.61	3.16	5.09	5.23	5.37	5.26	11.31	9.12	2.82	11.74	11.44	11.24
TDS (Measured)	930	600	5500	4350	1070	6240	5990	9170	5910	4840	>10000	3810	4710	4390	unstable
Temperature (°C)	54.8	21.7	29	26.1	24.9	23	23	50.7	27.6	41.5	59.5	22.5	11.8	18.8	13.2
Ion Balance % Difference	26.47	17.78	3.95	10.35	73.26	6.53	20.12	3.52	8.07	1.71	9.43	72.81	17.97	11.72	8.73
Ion Balance Result	>±2meq/L	>±2meq/L	OK	>±5%	>±5%	>±5%	>±5%	OK	>±5%	OK	>±5%	>±5%	>±5%	>±5%	>±5%
Water Type	Na-SO_4	H-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	Na-Cl	Na-SO_4	Na-SO_4	Na-Cl	Na-SO_4
Salinity Hazard	High	High	Very High	Very High	High	Very High	Very High	Very High	Very High	Very High	Very High	Very High	Very High	Very High	Very High
SAR	52.3	5.34	18.3	23	29.6	23.2	22.6	76	24.4	n/a	40.4	25	13.6	n/a	17.7
Total Hardness(mg/L $CaCO_3$)	6.0653	95.439	2504.1	3070.5	1692.6	2043.3	1995.5	1917.1	2168.7	1790.9	2030.5	777.79	1729.4	32.505	1569.4

NB: – *denotes when a parameter was not measured*

nd *denotes when a parameter was not detected by the instrument*

Legend

SS106	Brine from salt pit – Ash plant feed water
SS206	Cation/anion regeneration effluent
SS306	Fly ash make-up for West Steam Plant-used to collect ash from precipitators
SS406	EDR brine
SS506	Mixture of EDR and RO brine
SS606	TRO from TRO Water Treatment Plant, West
SS706	TRO brine taken at unit 67
SS806	Brine from thermal desalination-Unit 203 feed water
SS906	Brine from Unit 69. TRO treatment of ash water from the dam
SS1006	Fly ash make-up for East Plant-sampled before filters
SS1106	Brine from salt pit Unit 44 West Plant (TRO).
SS1206	Water from neutralizing tank West Plant
SS1306	Penstock Overflow (at ash dam)
SS1406	Ash water in toe drain (Fine ash dam no.5)
SS1506	Clear ash effluent dam no.2

Appendix B2: Chemical composition of water streams at Sasol Secunda, July 2007

Parameter (mg/L)	SS107	SS207	SS307	SS407	SS507	SS607	SS707	SS807	SS907	SS1007	SS1107	SS1207	SS1307	SS1407	SS1507	SS1607
Ca	939.87	588.44	743.14	20.99	6.30	6.57	1129.82	664.57	223.49	918.47	–	17.42	775.64	372.79	583.51	18.31
Mg	0.41	8.05	5.08	0.18	0.06	0.06	0.17	0.18	132.52	0.50	–	0.19	0.17	0.08	387.04	8.29
Na	2247.61	2210.69	2832.58	142.23	103.22	111.88	1897.11	1563.17	982.63	924.74	–	1183.88	1639.60	815.34	8361.48	329.19
Li	10.92	9.24	9.96	0.53	0.35	0.37	8.90	3.79	0.12	5.53	–	7.67	7.27	7.45	108.39	7.85
Be	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00	–	0.00	nd	nd	nd	nd
B	10.88	9.24	7.53	5.79	6.19	6.98	4.02	7.64	0.91	2.61	–	4.66	5.51	5.40	77.99	2.48
Al	0.30	0.05	0.12	0.31	0.29	0.28	0.15	0.07	0.01	0.06	–	5.38	0.05	0.37	0.20	0.11
Si	2.07	2.54	4.44	0.40	0.33	0.52	1.12	3.95	3.31	1.00	–	11.81	1.50	3.69	nd	1.00
P	0.34	0.05	0.29	0.02	0.02	0.01	0.42	0.11	nd	0.16	–	0.08	0.17	0.23	4.91	0.20
K	203.32	206.46	247.47	16.54	11.84	11.99	178.40	107.28	12.40	114.63	–	136.80	135.40	158.26	1971.33	127.21
Ti	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	–	0.00	0.00	0.00	0.05	0.00
V	0.06	0.05	0.06	0.00	0.00	0.00	0.03	0.08	0.00	0.01	–	0.17	0.01	0.15	0.15	0.02
Cr	0.08	0.06	0.09	0.01	0.01	0.01	0.36	0.13	0.01	1.00	–	0.03	0.11	0.44	0.68	0.03
Mn	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.06	0.00	–	0.01	0.00	0.00	1.88	0.16
Fe	0.08	0.02	0.07	0.00	0.01	0.00	0.12	0.08	0.04	0.13	–	0.25	0.06	0.14	2.05	0.26
Co	0.02	0.01	0.03	0.00	0.00	0.00	0.02	0.02	0.01	0.02	–	0.02	0.02	0.03	0.45	0.03
Ni	0.05	0.07	0.09	0.00	0.00	0.00	0.03	0.03	0.01	0.02	–	0.24	0.03	0.07	0.87	0.18
Cu	nd	nd	0.01	0.00	nd	nd	nd	nd	0.10	0.03	–	nd	0.01	0.07	nd	0.00
Zn	0.10	nd	0.13	0.00	0.00	0.01	nd	nd	0.10	0.03	–	0.03	0.01	0.02	2.41	0.03
As	0.05	0.03	0.04	0.00	0.00	0.00	0.04	0.03	0.00	0.03	–	0.04	0.02	0.03	0.31	0.03
Se	0.17	0.13	0.15	0.01	0.01	0.01	0.16	0.12	0.00	0.12	–	0.16	0.10	0.16	0.38	0.06
Sr	31.51	25.00	31.23	0.97	0.29	0.25	47.26	16.58	5.95	56.40	–	2.55	24.55	25.16	67.59	3.50
Mo	0.60	0.67	0.83	0.03	0.01	0.01	0.69	0.37	0.00	0.65	–	1.34	0.39	0.63	2.02	1.45
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	0.00	nd	0.00	nd	0.00
Ba	0.65	0.17	0.22	0.01	0.00	0.00	0.41	0.54	0.02	0.47	–	0.05	0.19	0.23	0.46	0.03
Pb	0.29	0.00	0.00	0.00	0.00	0.00	nd	nd	nd	0.00	–	nd	nd	0.00	nd	nd
Cl	1239.14	1300.00	1706.67	132.33	105.67	103.33	1160.00	820.00	250.00	946.67	–	1120.00	1100.00	1006.67	27466.67	1000.00
NO_3	23.78	18.46	26.53	8.44	7.97	7.91	16.60	22.80	1.90	19.33	–	1.00	30.13	35.60	20.00	1.93
PO_4	0.83	0.79	1.00	0.18	0.05	0.05	1.87	1.00	0.50	1.00	–	1.00	1.00	1.00	20.00	1.00
SO_4	3545.15	3850.00	5400.00	159.00	42.33	37.67	2886.67	2860.00	2773.33	1773.33	–	980.00	3946.67	2246.67	31066.67	926.67
TDS (Σ)	8258.30	8230.22	11017.77	487.98	284.94	287.90	7334.38	6072.54	4387.43	4766.95	0.00	3474.77	7668.62	4680.68	70147.49	2430.01
Conductivity (µS/cm)	12780.00	10040.00	13600.00	940.00	560.00	530.00	11820.00	9740.00	5350.00	12430.00	9810.00	6380.00	10960.00	9340.00	>20000	5660.00
pH	11.42	10.32	5.12	5.34	5.80	5.73	11.57	11.46	7.64	11.78	6.46	11.06	11.31	11.40	8.06	8.25
TDS (Measured)	7420.00	5800.00	7880.00	530.00	320.00	310.00	6870.00	5640.00	3120.00	7180.00	5680.00	3700.00	6400.00	5420.00	>10000	3280.00
Temperature (°C)	17.30	17.30	17.40	17.50	17.90	17.90	17.80	17.60	17.60	18.00	17.00	18.00	17.80	17.90	18.30	17.90
Total Alkalinity(mg/L $CaCO_3$)	375.00	200.00	12.50	5.00	5.00	5.00	1825.00	1200.00	225.00	3400.00	–	900.00	475.00	1250.00	700.00	525.00
Ion Balance % Difference	13.49	5.85	3.24	13.10	26.04	31.93	5.25	0.77	2.46	19.50	–	7.69	3.26	24.72	47.20	46.17
Ion Balance Result	>±5%	>±5%	OK	>±2meq/L	>±2meq/L	>±2meq/L	>±5%	OK	OK	>±5%	n/a	>±5%	OK	>±5%	>±5%	>±5%
Water Type	Na-SO_4	Na-SO_4	Na-SO_4	Na-Cl	Na-Cl	Na-Cl	Na-SO_4	Na-SO_4	Na-SO_4	Ca-CO_3	–	Na-Cl	Na-SO_4	Na-SO_4	Na-Cl	Na-Cl
Salinity Hazard	Very High	Very High	Very High	High	Medium	Medium	Very High	Very High	Very High	Very High	–	Very High	Very High	Very High	Very High	Very High
SAR	20.20	24.90	28.60	8.48	11.20	11.90	15.60	16.70	12.90	8.41	n/a	77.50	16.20	11.60	67.60	16.00
Total Hardness(mg/L $CaCO_3$)	2360.30	1510.00	1889.90	53.10	15.96	16.63	2833.80	1665.60	1106.00	2300.60	n/a	44.34	1946.10	933.21	3210.70	79.90

NB: *–* *denotes when a parameter was not measured*
nd *denotes when a parameter was not detected by the instrument*

Legend

SS107	FAM Western plant
SS207	TRO Feed Water Unit 67 Western Plant
SS307	TRO Brine Unit 67 Western Plant
SS407	TRO Permeate Western Plant
SS507	SRO Brine Unit 69 Western Plant
SS607	SRO Permeate Unit 69 Western Plant
SS707	FA and FAM Western Plant
SS807	FAM Unit 243 Eastern Plant
SS907	Feed Water EDR Unit 267 Eastern Plant
SS1007	FA +FAM Eastern Plant
SS1107	Process Cooling Water Blow Down
SS1207	Dam 5 (Outlet 8) Toe Drain
SS1307	Dam 5 Penstock Overflow
SS1407	Dam 4 Penstock Overflow
SS1507	Salty Dam Water
SS1607	Ash Dam 4 Toe Drain

Appendix B3: Chemical composition of water streams at Sasol Secunda, May 2008

Parameter (mg/L)	SS108	SS208	SS308	SS408	SS508	SS608	SS708	SS808	SS908	SS1008	SS1108	SS1208	SS1308	SS1408	SS1508	Blank
Ca	968.06	513.70	699.09	15.35	13.58	0.27	1052.69	649.56	215.85	810.01	–	20.37	164.23	45.27	525.48	0.02
Mg	2.62	22.03	8.46	0.17	0.17	0.01	2.34	2.22	142.01	2.82	–	1.07	24.59	17.71	30.28	0.00
Na	1692.22	1594.32	2355.53	98.65	92.25	1.92	1336.11	1539.93	997.49	1339.87	–	1382.65	1560.33	988.53	1519.61	0.10
Li	10.82	10.96	13.28	0.49	0.45	0.01	5.87	5.03	0.13	7.69	–	7.82	6.59	5.97	11.29	0.00
Be	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.02	–	0.01	0.03	0.01	0.01	0.00
B	10.05	9.34	10.39	6.22	6.16	1.55	17.17	15.07	1.37	19.15	–	6.38	8.76	4.54	10.73	0.01
Al	1.55	0.66	0.61	0.17	0.16	0.00	1.64	1.32	0.22	1.59	–	2.64	3.98	1.49	1.00	0.00
Si	3.47	2.19	3.14	0.00	0.30	0.00	6.88	10.27	3.82	3.20	–	3.71	0.00	0.00	2.19	0.00
P	6.76	4.68	2.68	0.03	0.04	0.01	9.19	7.64	1.58	7.62	–	2.44	6.51	3.36	3.32	0.01
K	205.08	192.61	257.47	14.79	11.97	1.52	129.57	113.33	13.82	198.58	–	144.00	101.97	122.13	186.99	0.00
Ti	0.03	0.02	0.01	0.00	0.00	0.00	0.05	0.03	0.01	0.12	–	0.18	0.08	0.01	0.02	0.00
V	0.12	0.05	0.04	0.00	0.00	0.00	0.05	0.27	0.00	0.33	–	0.03	0.30	0.03	0.03	0.00
Cr	0.55	0.32	0.26	0.01	0.01	0.00	0.38	0.55	0.06	0.68	–	0.18	0.49	0.23	0.21	0.00
Mn	0.19	0.06	0.02	0.00	0.00	0.00	0.28	0.28	0.02	0.08	–	0.12	0.18	0.07	0.11	0.00
Fe	5.93	4.48	2.12	0.03	0.02	0.01	4.90	4.78	0.92	7.78	–	3.12	8.60	2.78	2.80	0.02
Co	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	–	0.00	0.02	0.00	0.00	0.00
Ni	0.32	0.22	0.19	0.00	0.00	0.00	0.25	0.27	0.05	0.31	–	0.41	0.46	0.31	0.16	0.00
Cu	0.10	0.07	0.10	0.00	0.00	0.00	0.10	0.12	0.04	0.14	–	0.04	0.14	0.02	0.07	0.00
Zn	1.92	0.52	0.59	0.03	0.02	0.01	0.79	0.81	0.20	0.82	–	0.83	2.91	0.48	0.77	0.00
As	0.07	0.04	0.03	0.00	0.00	0.00	0.05	0.04	0.00	0.03	–	0.03	0.03	0.03	0.01	0.00
Se	0.14	0.11	0.15	0.01	0.01	0.00	0.34	0.18	0.03	0.24	–	0.15	0.04	0.09	0.09	0.00
Sr	25.06	19.71	26.75	0.55	0.50	0.00	21.34	14.17	5.32	18.80	–	2.02	7.02	4.22	19.46	0.00
Mo	0.41	0.57	0.74	0.02	0.02	0.00	0.74	0.36	0.02	0.20	–	0.79	0.00	0.69	0.29	0.00
Cd	0.12	0.07	0.04	0.00	0.00	0.00	0.10	0.10	0.02	0.12	–	0.05	0.12	0.06	0.05	0.00
Ba	1.15	0.40	0.40	0.01	0.01	0.03	0.85	1.00	0.08	0.82	–	0.20	0.43	0.18	0.27	0.00
Pb	0.31	0.13	0.09	0.00	0.00	0.00	0.04	0.03	0.01	0.03	–	0.02	0.04	0.02	0.03	0.00
Cl	1196.13	1111.07	1643.98	103.91	99.69	1.20	822.82	852.03	193.92	961.93	–	1245.79	1320.05	792.07	1097.85	0.20
NO_3	25.00	10.00	10.00	2.05	2.02	0.05	25.00	25.00	5.00	25.13	–	12.50	25.00	10.00	10.00	0.05
PO_4	50.00	20.00	20.00	0.20	0.20	0.10	50.00	50.00	10.00	50.00	–	25.00	50.00	20.00	20.00	0.10
SO_4	3043.00	3340.15	4364.88	100.15	92.20	0.50	2407.63	2721.92	2429.19	2655.32	–	1032.78	1678.13	1040.97	3295.42	0.50
TDS (Σ)	7251.21	6858.51	9421.01	342.83	319.78	7.20	5897.18	6016.34	4021.18	6113.43	–	3895.32	4971.03	3061.26	6738.55	1.02
Conductivity (µS/cm)	12870.00	9270.00	12750.00	642.00	614.00	14.00	11860.00	9840.00	5670.00	9940.00	11750.00	7030.00	8220.00	5540.00	9050.00	–
pH	12.39	11.30	5.76	5.68	5.65	6.03	12.63	12.05	8.05	12.10	7.63	10.63	10.10	9.64	10.60	–
TDS (Measured) *	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Temperature (°C)	41.00	13.00	25.00	21.00	22.00	25.00	40.00	50.00	14.00	35.00	22.00	22.40	20.40	16.00	15.00	–
Total Alkalinity(mg/L $CaCO_3$)	1600	400	200	100	100	100	2400	1200	1800	300	1200	800	400	400	300	–
Ion Balance % Difference	28.698	1.352	3.118	1.643	0.74	56.314	42.813	27.42	15.508	5.698	n/a	3.299	2.36	0.132	0.386	31.39
Ion Balance Result	>±5%	OK	OK	OK	OK	>±2meq/L	>±5%	>±5%	>±5%	>±5%	n/a	OK	OK	OK	OK	OK
Water Type	Na-OH	Na-SO_4	Na-SO_4	Na-Cl	Na-Cl	B-HCO_3	Na-OH	Na-OH	Na-SO_4	Na-SO_4	n/a	Na-Cl	Na-Cl	Na-Cl	Na-SO_4	Na-SO_4
Salinity Hazard	Very High	Very High	Very High	Medium	Medium	Low	Very High	Very High	Very High	Very High	n/a	Very High	Very High	Very High	Very High	Low
SAR	14.9	18.8	24.3	6.87	6.82	$986x10^{-3}$	11.3	16.5	13	12.9	n/a	81	30.1	31.6	17.5	$194x10^{-3}$
Total Hardness(mg/L $CaCO_3$)	2421.1	1379.8	1787.8	38.96	34.54	0.71325	2629.1	1618.8	1126.4	2031.2	n/a	55.304	512.31	186.21	1442.9	0.05

** Instrument malfunctioned*

NB: – *indicates a parameter was not measured*

nd *indicates a parameter not detected by the instrument*

Legend

SS108	FAM Western Plant (U43)
SS208	TRO Feed Water (U67) Western Plant
SS308	TRO Brine (U67) Western Plant
SS408	TRO Permeate Western Plant
SS508	SRO Brine (U69) Western Plant
SS608	SRO Permeate (U69) Western Plant
SS708	FA & FAM Eastern Plant
SS808	FAM (U243) Eastern Plant
SS908	Feed Water EDR (U267) Eastern Plant Mine Water
SS1008	FA & FAM Western Plant (slurry)
SS1108	Process Cooling Water Blowdown
SS1208	Dam 5 (Outlet 8) Toe Drain
SS1308	Dam 5 Penstock Overflow
SS1408	Dam 4 Penstock Overflow
SS1508	Salty Dam Water (Clear Ash Effluent)
SS1608	Ash Dam 4 Toe Drain
Blank	Ultrapure Water

Appendix C: Chemical composition of Muizenburg sea water and ultrapure water

Parameter (mg/L)	Muizenburg Sea Water	ENS Lab Ultrapure Water
Ca	394.7	nd
Mg	1234	0
Na	10168.3	nd
Li	0.00	0.00
Be	0.01	0
B	3.52	nd
Al	0.19	nd
Si	14.02	18.98
P	nd	nd
K	396.8	0
Ti	–	–
V	0	0
Cr	nd	nd
Mn	0	0
Fe	0.08	nd
Co	nd	nd
Ni	nd	nd
Cu	0.02	nd
Zn	0.1	1
As	0	nd
Se	0.01	0.1
Sr	7.73	nd
Mo	0.01	0
Cd	0.01	0
Ba	–	–
Pb	0	0
Cl	19833.3	0.8
NO_3	4	0
PO_4	10	0.1
SO_4	2733	0.1
TDS	>10000	–
Conductivity (µS/cm)	>20000	–
pH	7.89	–
Temperature	21	–
Alkalinity	1200	–
Ion Balance % Difference	5.242	97.992
Ion Balance Result	>±5%	>±2meq/L
Water Type	Na-Cl	Si-Cl
Salinity Hazard	Very High	Low
SAR	57	–
Total Hardness(mg/L $CaCO_3$)	6100.8	n/a

Appendix D1: Sasol Secunda cooling water blow down historic data from 2004 to 2007

Parameter	Unit	2004-01-01	2004-02-01	2004-03-01	2004-04-01	2004-05-01	2004-06-01	2004-07-01	2004-08-01	2004-09-01	2004-10-01	2004-11-01	2004-12-01	2005-01-01	2005-02-01	2005-03-01	2005-04-01	2005-05-01	2005-06-01	2005-08-01	2005-09-01
Ca	mg/L	19.0	31.3	35.9	38.4	19.0	14.0	9.8	15.5	13.1	15.8	20.6	20.5	13.1	27.5	18.5	18.3	13.2	21.4	9.5	17.2
Mg	mg/L	20.0	24.5	18.4	21.7	14.5	11.9	7.8	12.8	15.4	14.5	15.1	13.0	21.8	23.5	24.8	19.4	11.4	16.2	13.9	16.9
Si	mg/L	135.3	131.5	94.8	103.3	123.1	80.4	59.9	57.3	97.9	119.4	169.0	177.8	196.5	114.4	173.6	151.7	152.3	147.3	243.1	120.2
Fe	mg/L	11.0	8.6	7.2	6.4	7.3	8.5	5.1	6.1	11.3	13.2	16.3	13.2	12.6	13.6	21.3	16.1	10.0	17.0	19.4	22.5
Cl	mg/L	335.0	328.6	204.8	216.2	284.1	258.1	229.3	240.0	335.4	293.3	303.6	332.2	326.1	283.6	276.2	262.1	311.8	471.4	502.3	505.8
SO_4	mg/L	2012.5	1579.5	1072.5	1280.3	2297.5	2009.2	1595.2	2050.0	2093.7	1351.6	2156.3	2463.0	2371.3	2267.8	2339.9	2583.6	2528.1	3725.0	3627.5	3910.9
Fluoride (as F)	mg/L	344.9	266.5	214.2	304.3	324.8	302.3	303.2	334.7	369.6	432.9	363.1	357.8	395.1	221.7	312.5	342.2	395.0	454.1	477.1	379.0
Conductivity (µS/cm)	µS/cm	7206.3	5547.5	4871.9	5106.3	6167.2	6475.0	5623.8	5818.1	7624.7	6880.9	7973.1	7770.6	8424.1	7338.4	8162.8	7366.9	7636.9	12631.6	11957.8	12311.3
pH		7.07	7.24	7.20	7.01	7.22	7.19	7.35	7.36	7.37	7.12	7.10	6.91	6.93	6.39	6.95	6.72	7.07	7.09	6.95	7.26
COD	mg/L	2531.3	1310.9	1209.4	1503.1	1814.1	1875.0	1751.6	1746.9	1873.4	2156.3	2818.8	3881.3	2700.3	1893.8	2206.4	1928.1	2551.6	2007.5	2753.1	3628.3
Total Alkalinity	mg/L (as $CaCO_3$)	382.5	293.5	518.7	224.9	378.1	426.4	386.5	310.5	450.7	181.1	204.6	225.4	438.9	179.6	381.0	271.7	214.3	281.6	301.0	295.1

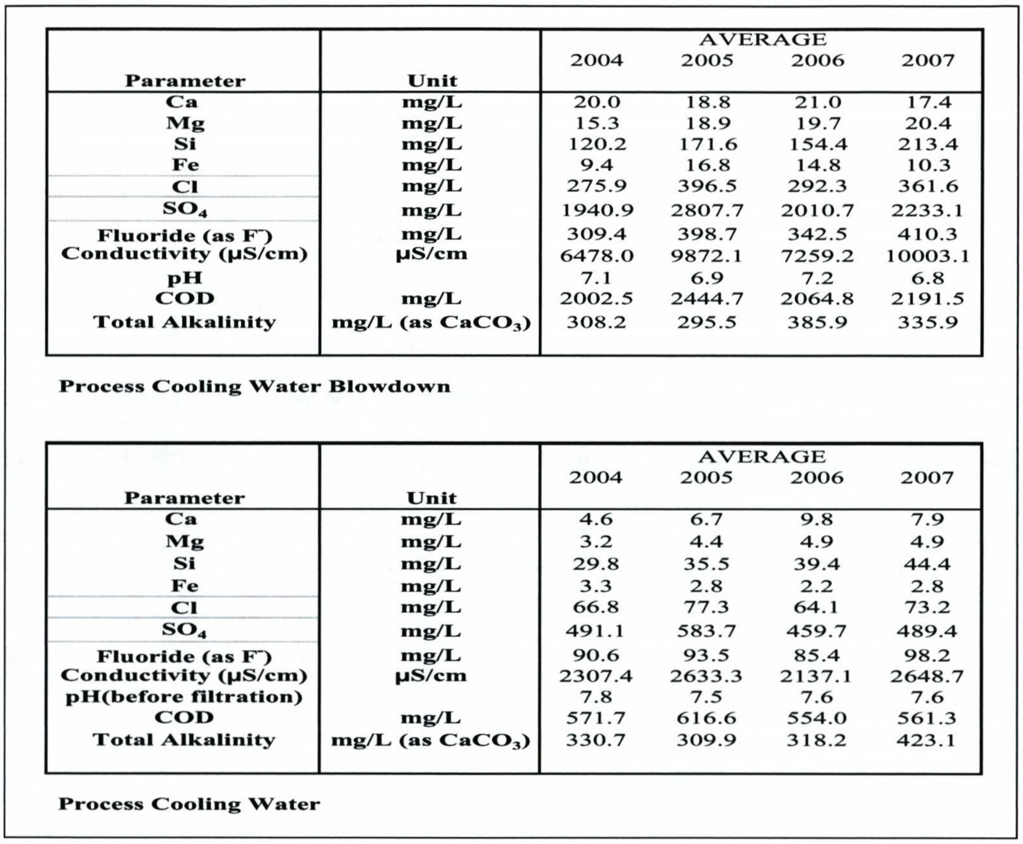
Parameter	Unit	2005-10-01	2005-11-01	2005-12-01	2006-01-01	2006-02-01	2006-03-01	2006-04-01	2006-05-01	2006-06-01	2006-08-01	2006-10-01	2006-12-01	2007-01-01	2007-02-01	2007-03-01	2007-04-01	2007-05-01	2007-06-01	2007-07-01	2007-07-31
Ca	mg/L	22.2	14.2	10.7	15.5	24.9	19.3	34.3	21.4	14.3	14.7	24.5	13.4	15.1	19.1	19.3	19.2	22.9	19.1	8.1	18.3
Mg	mg/L	21.5	19.8	11.9	14.4	27.4	16.2	27.1	22.2	15.2	18.9	18.0	14.0	14.6	20.2	21.2	21.3	15.6	24.0	14.8	20.8
Si	mg/L	175.1	175.7	164.8	45.6	130.9	124.5	180.8	178.4	137.7	82.2	122.0	227.8	272.4	280.0	183.3	224.7	222.6	204.2	142.2	243.1
Fe	mg/L	12.5	18.9	11.6	9.6	10.1	13.9	9.9	19.4	9.9	11.6	21.3	18.8	25.2	13.6	7.9	19.1	13.7	6.8	4.3	10.9
Cl	mg/L	423.4	520.1	405.6	244.2	228.8	191.6	255.9	263.3	330.0	314.3	357.0	302.4	329.4	390.6	309.3	264.5	390.8	340.0	290.5	424.3
SO_4	mg/L	2916.7	2915.0	3276.6	2103.7	1835.9	1703.2	1884.4	2135.3	2613.9	1703.1	2348.8	956.9	2065.0	2046.9	2229.3	2112.5	2835.0	2826.0	1573.8	3150.0
Fluoride (as F)	mg/L	472.7	492.7	435.4	273.1	206.9	321.8	275.2	322.5	252.1	436.0	398.4	384.1	371.3	445.2	329.3	396.3	446.0	329.3	393.5	470.0
Conductivity (µS/cm)	µS/cm	10558.8	11443.4	9911.3	6973.0	6258.1	5847.5	5697.0	6233.1	7211.3	6825.3	9317.2	7662.2	8813.1	9911.9	7800.0	8052.5	11162.5	9000.0	8290.0	10705.0
pH		6.69	6.54	6.70	7.27	6.73	7.05	7.27	6.67	7.51	8.81	8.13	7.10	7.03	6.80	6.60	6.80	5.40	6.80	7.00	6.80
COD	mg/L	1912.5	1801.6	2646.7	1755.7	1303.1	1134.4	1875.0	1406.2	2151.6	2559.4	2840.6	2256.3	2765.6	1868.8	2050.0	2100.0	5600.0	2100.0	1800.0	2225.0
Total Alkalinity	mg/L (as $CaCO_3$)	275.4	163.1	258.9	308.4	122.2	445.8	205.8	351.6	291.1	757.1	1032.7	305.0	248.9	284.5	222.1	202.3	1152.1	622.4	215.3	244.6

Appendix D2: Sasol Secunda cooling water historic data from 2004 to 2007

Parameter	Unit	2004-01-01	2004-02-01	2004-03-01	2004-04-01	2004-05-01	2004-06-01	2004-07-01	2004-08-01	2004-09-01	2004-10-01	2004-11-01	2004-12-01	2005-01-01	2005-02-01	2005-03-01	2005-04-01	2005-05-01	2005-06-01	2005-08-01	2005-09-01	2005-10-01
Ca	mg/L	7.0	2.6	4.5	6.7	6.3	3.6	2.4	3.9	3.1	5.6	5.0	4.6	5.1	6.0	7.2	4.8	5.3	8.1	7.6	4.5	4.7
Mg	mg/L	5.6	2.3	3.3	4.4	5.2	3.0	1.7	3.0	2.8	4.8	4.1	2.3	3.2	3.4	4.2	4.5	2.4	4.2	3.4	3.3	3.2
Si	mg/L	32.2	29.1	27.8	33.2	33.7	21.9	13.6	15.1	8.7	34.6	40.2	39.0	44.9	21.1	32.8	34.3	32.4	33.1	42.1	37.7	35.0
Fe	mg/L															3.6	3.0	3.4	3.5	7.9	4.3	1.3
Cl	mg/L	113.7	57.6	51.5	65.9	73.0	63.9	59.7	77.5	77.5	73.3	67.3	65.4	62.2	48.3	37.8	59.3	61.4	96.4	80.8	94.6	80.9
SO_4	mg/L	511.9	414.0	292.2	371.2	700.0	563.5	390.0	587.5	448.2	556.3	504.7	530.8	599.6	475.4	521.4	431.5	568.1	673.8	829.3	604.0	763.1
Fluoride (as F^-)	mg/L	91.4	79.9	60.4	83.0	90.5	90.4	85.9	91.2	94.1	108.8	99.4	91.1	96.1	73.7	78.9	85.4	96.0	98.8	93.1	112.9	111.4
Conductivity (µS/cm)	µS/cm	2411.3	1955.8	1963.5	2135.0	2325.8	2401.3	2100.0	2394.0	2623.0	2699.8	2666.4	2416.3	2536.7	2186.3	1872.5	2105.3	2059.7	3518.4	2946.3	3088.4	2681.3
pH		7.98	7.58	8.01	7.76	7.92	7.56	7.82	7.72	7.76	7.62	7.70	7.73	7.64	7.48	7.44	7.49	7.25	7.70	7.53	7.90	7.50
COD	mg/L	640.0	780.0	465.0	400.0	600.0	490.0	430.0	547.5	577.5	675.0	745.0	730.0	515.0	635.0	605.0	670.0	810.0	790.0	582.5	506.5	445.0
Total Alkalinity	mg/L (as $CaCO_3$)	273.0	341.8	375.0	304.0	340.9	391.9	341.5	326.0	366.4	311.0	304.4	246.7	341.0	343.0	164.0	271.4	308.5	360.0	358.6	343.4	283.3

Parameter	Unit	2005-11-01	2005-12-01	2006-01-01	2006-02-01	2006-03-01	2006-04-01	2006-05-01	2006-06-01	2006-07-01	2006-08-01	2006-10-01	2006-11-01	2006-12-01	2007-01-01	2007-02-01	2007-03-01	2007-04-01	2007-05-01	2007-06-01	2007-07-01	2007-07-31
Ca	mg/L	5.5	4.3	10.1	10.8	11.7	12.4	13.2	8.7	12.6	5.0	8.0	9.8	9.7	6.8	9.1	9.1	5.1	8.7	3.7	6.9	4.5
Mg	mg/L	4.2	2.8	6.7	4.9	4.5	5.2	6.6	4.9	5.7	2.7	5.3	4.3	4.9	4.0	4.2	5.6	2.7	5.1	3.3	5.1	3.1
Si	mg/L	42.3	32.5	36.3	23.5	25.1	32.7	45.1	38.0	37.3	50.0	44.7	40.5	51.0	41.1	42.1	56.9	26.6	37.2	34.1	45.8	39.9
Fe	mg/L	4.2	2.1	2.8	1.6	0.9	1.5	2.9	1.9	2.6	2.5			5.4	2.6	3.1	2.6	1.3	1.4	1.3	2.0	1.2
Cl	mg/L	101.9	63.8	90.2	45.5	42.1	50.6	55.7	83.2	62.6	67.3	76.9	61.5	83.6	77.3	49.5	62.0	74.5	88.8	63.0	75.0	68.5
SO_4	mg/L	544.5	644.7	622.1	380.0	384.2	308.6	622.1	535.2	446.5	481.4	518.7	148.7	534.5	427.5	504.6	561.0	551.5	473.8	405.0	491.0	386.9
Fluoride (as F^-)	mg/L	112.4	93.5	111.0	55.6	68.6	79.7	77.0	77.4	84.7	86.2	93.9	88.3	103.2	99.1	79.2	111.5	102.7	111.3	85.6	107.8	97.2
Conductivity (µS/cm)	µS/cm	2722.5	2450.0	3696.3	1638.7	1540.7	1689.7	1545.2	2544.4	1829.4	2221.3	2552.2	2179.1	2671.6	2681.6	2410.0	2537.5	3157.5	2717.5	2572.5	2820.0	2777.5
pH		7.47	7.82	7.99	7.47	7.34	7.80	7.44	7.98	7.91	7.28	8.02	7.40	7.43	7.57	7.60	7.90	6.00	7.60	7.80	7.65	7.74
COD	mg/L	490.0	489.5	845.0	425.0	440.0	615.0	460.0	600.0	530.0	490.0	580.1	870.0	790.0	555.0	480.0	460.0	1250.0	460.0	520.0	520.0	380.0
Total Alkalinity	mg/L (as $CaCO_3$)	243.0	314.1	372.6	181.9	291.6	454.4	350.4	607.4	265.6	292.0	458.3	300.0	307.8	428.8	312.0	506.9	514.4	430.5	651.9	287.5	289.8

Appendix E: Sasol Secunda process cooling water and process cooling water blowdown yearly averages



Parameter	Unit	AVERAGE 2004	2005	2006	2007
Ca	mg/L	20.0	18.8	21.0	17.4
Mg	mg/L	15.3	18.9	19.7	20.4
Si	mg/L	120.2	171.6	154.4	213.4
Fe	mg/L	9.4	16.8	14.8	10.3
Cl	mg/L	275.9	396.5	292.3	361.6
SO_4	mg/L	1940.9	2807.7	2010.7	2233.1
Fluoride (as F^-)	mg/L	309.4	398.7	342.5	410.3
Conductivity (µS/cm)	µS/cm	6478.0	9872.1	7259.2	10003.1
pH		7.1	6.9	7.2	6.8
COD	mg/L	2002.5	2444.7	2064.8	2191.5
Total Alkalinity	mg/L (as $CaCO_3$)	308.2	295.5	385.9	335.9

Process Cooling Water Blowdown

Parameter	Unit	AVERAGE 2004	2005	2006	2007
Ca	mg/L	4.6	6.7	9.8	7.9
Mg	mg/L	3.2	4.4	4.9	4.9
Si	mg/L	29.8	35.5	39.4	44.4
Fe	mg/L	3.3	2.8	2.2	2.8
Cl	mg/L	66.8	77.3	64.1	73.2
SO_4	mg/L	491.1	583.7	459.7	489.4
Fluoride (as F^-)	mg/L	90.6	93.5	85.4	98.2
Conductivity (µS/cm)	µS/cm	2307.4	2633.3	2137.1	2648.7
pH(before filtration)		7.8	7.5	7.6	7.6
COD	mg/L	571.7	616.6	554.0	561.3
Total Alkalinity	mg/L (as $CaCO_3$)	330.7	309.9	318.2	423.1

Process Cooling Water

Appendix F1: Tutuka Power Station Mine Water Quality (1989 to 2004) (a)

Date	pH	EC	TDS	P.Acid	M ALK	Ca	Mg	Na	K	SO4	Cl	F	Fe	Mn	Al
10-Jan-89	8.09	269.00						598.00		290.00	420.00	6.20			
24-Jan-89	7.80	263.00						588.00		305.00	359.00	6.20			
09-Jul-91	8.42	384.00	2358.00		526.00	30.00	23.00	800.00		536.00	650.00	4.40	4.10		
06-Aug-91	8.96	338.00	2248.00		566.00	16.00	13.60	752.00		480.00	670.00	7.88	0.12		
05-Nov-91	8.26	356.00	2318.00		486.00	28.80	16.80	856.00	4.70	510.00	665.00	5.40	0.47	0.09	
12-Nov-91	8.19	340.00	2090.00		492.00	27.20	15.60	778.00	4.30	360.00	570.00	5.72	0.35	0.06	
03-Dec-91	8.70	340.00	2242.00		494.00	26.40	14.10	834.00		432.00	705.00	4.30	0.38		
10-Dec-91	7.91	349.00	2634.00		502.00	26.40	14.60	716.00	5.20	980.00	635.00	5.40	0.27	0.08	
07-Jan-92	8.45	386.00	2758.00		444.00	280.30	243.00	776.00	5.20	520.00	720.00	4.04	0.37	0.08	
28-Jan-92	8.82	381.00	2588.00		510.00	30.40	19.00	920.00		5.70	775.00	3.82	0.35		
11-Feb-92	8.56	345.00	2240.00		580.00	11.20	13.60	796.00		490.00	595.00	1.92	0.21		
18-Feb-92	7.97	314.00	2308.00		482.00	25.60	12.20	912.00		510.00	558.00	4.96	0.48		
03-Mar-92	8.18	282.00	1918.00		442.00	32.00	13.10	608.00		550.00	515.00	5.88			
10-Mar-92	8.07	346.00	2464.00		470.00	51.30	14.50	838.00		680.00	665.00	6.00	1.04		
17-Mar-92	7.64	359.00	2444.00		504.00	43.20	36.90	920.00		660.00	660.00	5.24	0.37		
24-Mar-92	7.99	359.00	2472.00		464.00	39.20	24.80	880.00		680.00	625.00	5.30	0.36		
30-Mar-92	8.05	383.00	2854.00		382.00	50.40	28.10	880.00	5.10	980.00	705.00	4.68	0.33	0.24	
02-Apr-92	7.68	384.00	2718.00		484.00	47.20	24.30	920.00	6.40	790.00	695.00	4.26	0.35	0.30	
07-Apr-92	8.15	373.00	2620.00		492.00	48.80	25.30	892.00	5.70	540.00	655.00	3.80	0.29	0.28	
05-May-92	8.08	339.00	2538.00		536.00	37.60	19.40	840.00	6.60	820.00	520.00	6.80	0.32	0.21	
19-May-92	8.06	380.00	2638.00		494.00	53.60	22.80	780.00	5.90	850.00	655.00	6.36	0.13	0.35	
23-Jun-92	8.71	607.00	3842.00		328.00	48.00	67.60	1230.00	7.60	109.00	1095.00	6.20	0.20	0.07	
16-Jul-92	8.37	421.00	2720.00		452.00	51.20	27.20	900.00	6.00	800.00	690.00	6.56	0.25	0.30	
11-Aug-92	8.38	339.00	2370.00		490.00	43.20	21.30	798.00	6.60	564.00	540.00	5.68	3.09	0.31	
01-Sep-92	8.60	309.00	2130.00		474.00	34.40	20.40	660.00	4.70	610.00	490.00	4.80	0.44	0.21	
10-Nov-92	7.60	386.00	2210.00		450.00	31.30	22.10	402.00	90.00	105.40	425.00	0.10	3.10	0.10	0.10
03-Dec-92	8.20	389.00	2624.00		436.00	55.30	25.80	816.00	5.90	940.00	545.00	5.40	0.20	0.20	
30-Dec-92	8.20	389.00	2624.00									5.40			
31-Dec-92	6.50	521.00	2398.00		535.00	21.60	23.30	571.30	4.60	896.00	66.00		0.00	0.00	1.80
04-Feb-93	7.60	307.00	2340.00		460.00	54.50	18.80	882.50	8.20	688.00	320.00		17.20	0.40	
13-Apr-93	7.60	404.00	2590.00		454.00	44.80	18.30	900.00	5.50	670.00	660.00	0.70	1.10	0.10	1.40
13-May-93	7.60	405.00			416.00	52.10	22.60	1020.30	10.20	736.00	650.00	0.10	1.10	0.40	
15-Jun-93	7.60	412.00			438.00	73.40	35.40	904.00	5.60	36.00	18.00	0.10	0.20	0.70	
15-Jul-93	8.20	397.00			440.00	85.80	33.30	886.80	5.30	764.00	640.00	0.10	9.40	0.60	
12-Aug-93	7.50	464.00			450.00	58.50	29.20	1026.00	0.60	600.00	720.00	0.30	1.60	0.50	
14-Oct-93	7.50	464.00	3043.00		492.00	77.00	29.80	993.00	2.50	823.00	860.00	0.20	0.13	0.44	
11-Nov-93	8.60	411.00			494.00	65.60	27.70	761.00	6.40	834.00	555.00	1.00	0.10	0.30	
13-Dec-93	7.60	349.00	2444.00		462.00	65.00	31.00	833.00	5.70	783.00	476.00	1.30	0.10	2.00	
12-Jan-94	6.90	391.00	2634.00		474.00	68.20	30.40	831.00	4.60	802.00	592.00	1.00	0.70	0.70	
10-Feb-94	8.50	404.00	2768.00		458.00	77.80	35.20	790.00	5.20	860.00	620.00		0.10	0.50	0.10
17-Mar-94	6.20	331.00	2138.00		500.00	48.60	25.50	733.00	3.80	498.00	508.00	0.20	0.40	0.30	
13-Apr-94	6.00	308.00	2343.00		550.00	58.00	28.70	697.00	8.50	779.00	422.00	0.20	0.01	0.20	
16-May-94	6.60	308.00	2789.00		438.00	79.60	33.20	788.00	10.10	901.00	698.00	0.40	2.70	0.40	
14-Jun-94	6.90	41.00	269.00		100.00	34.70	11.00	33.80	9.80	60.00	46.00	0.10	0.10	1.00	
14-Jul-94	7.70	369.00	2394.00		516.00	49.40	23.70	792.00	8.90	669.00	560.00	0.40	0.03	0.30	
11-Aug-94	7.70	373.00	2389.00		520.00	61.30	19.70	794.00	7.70	624.00	542.00	0.30	0.20	0.40	
15-Sep-94	7.80	410.00	2795.00		430.00	85.60	45.30	780.00	9.50	1054.00	540.00	0.40	0.01	0.01	
11-Oct-94	7.40	356.00	2347.00		346.00	76.90	48.70	631.00	15.30	874.00	466.00	0.20	0.70	0.01	
15-Nov-94	6.80	47.00	271.00		72.00	24.60	9.50	39.30	4.70	96.00	36.00	0.01	0.10	0.20	
01-Dec-94	7.30	506.00	3127.00		370.00	82.00	39.00	1032.00	9.20	864.00	850.00	0.20	0.01	0.10	0.01
26-Jan-95	7.60	586.00	3289.00		354.00	72.20	32.40	998.00	9.20	921.00	1020.00	0.20	0.50	0.60	
16-Feb-95	7.60	531.00	3058.00		418.00	63.80	26.00	953.00	9.60	658.00	1070.00	0.20	0.10	1.00	
16-Mar-95	6.80	63.00	401.00		160.00	35.10	15.10	85.50	6.60	89.00	50.00	0.10	0.03	0.10	
11-Apr-95	7.00	38.00	331.00		208.00	31.60	14.80	39.20	4.60	52.00	44.00	0.10	0.01	0.01	
09-May-95	7.40	37.00	217.00		120.00	15.60	10.10	33.10	2.00	38.00	32.00	0.01	0.02	0.01	
06-Jul-95	7.70	434.00	2966.00		432.00	113.70	54.70	767.00	9.80	1145.00	615.00	0.20	0.90	0.10	
08-Aug-95	7.40	453.00	2982.00		384.00	81.71	54.80	886.60	6.69	1230.00	530.00	0.20	0.14	0.01	
14-Sep-95	7.00	341.00	1807.00		580.00	26.18	27.86	549.80	4.73	547.00	340.00	0.10	0.43	0.07	0.00
12-Oct-95	7.90	597.00	3211.00		418.00	121.58	47.08	1240.00	9.03	719.00	1180.00	0.10	0.29	1.97	0.01
14-Nov-95	7.20	576.00	4567.00		350.00	150.67	70.38	1072.89	6.35	1707.00	1140.00	0.30	0.09	1.27	
04-Dec-95	7.00	520.00	3594.00		480.00	50.08	48.58	1158.30	11.11	1352.00	780.00	0.20	0.37	0.23	
15-Jan-96	6.60	472.00	3036.00		538.00	72.81	44.48	795.60	15.82	1186.00	690.00	0.20	0.37	0.69	0.00
13-Mar-96	7.90	586.00	3598.00		436.00	95.15	31.21	1077.00	9.75	1151.00	1300.00	0.01	0.41	0.08	
15-Mar-96	8.00	553.00	3597.00		558.00	25.00	29.50	1232.00	11.70	1224.00	870.00	0.20	0.30	0.30	0.00
18-Apr-96	7.70	520.00	3089.00		430.00	56.63	15.16	949.50	3.56	1233.00	790.00	0.30	0.23	0.03	
08-May-96	7.30	35.00	192.00		80.00	17.39	20.40	18.83	7.75	37.00	26.00	0.01	0.37	0.40	
13-Jun-96	7.50	506.00	3482.00		466.00		22.96	1318.00	5.03	1322.00	710.00	2.20	0.25	0.16	
11-Jul-96	7.30	455.00	2824.00		490.00	152.40	113.10	602.70	8.18	981.00	838.00	0.20	0.11	0.31	
27-Aug-96	7.20	459.00	3103.00		486.00	216.70	42.04	817.50	8.85	1093.00	712.00	0.40	0.14	0.39	
17-Sep-96	7.80	582.00	2997.00		278.00	70.38	53.35	1073.00	10.71	1095.00	720.00	0.30	0.61	2.44	

Appendix F2: Tutuka Power Station Mine Water Quality (1989 to 2004) (b)

Date	pH	EC	TDS	P.Acid	M ALK	Ca	Mg	Na	K	SO4	Cl	F	Fe	Mn	Al
29-Oct-96	6.90	523.00	3447.00		486.00	27.64	53.69	1228.00	9.76	1247.00	770.00	0.80	0.25	0.01	0.01
09-Dec-96	8.10	497.00	3258.00		474.00	37.97	52.64	1507.00	11.60	1246.00	900.00	1.70	0.13	0.42	0.01
10-Dec-96	8.00	441.00	3136.00	14.00	462.00	98.91	63.92	1192.80	8.13	1125.00	940.00	0.40	0.01	0.22	0.54
13-Jan-97	8.00	424.00	2738.00	36.00	548.00	20.47	37.39	961.80	6.27	891.00	564.00	0.30	0.48	0.20	0.01
20-Feb-97	7.60	392.00	2983.00	38.00	534.00	52.89	42.41	873.40	7.96	754.00	658.00	0.30	0.09	1.38	0.01
24-Mar-97	7.60	308.00	1987.00	198.00	470.00	56.72	37.86	775.20	4.14	698.00	378.00	0.30	0.16	0.16	0.01
24-Apr-97	7.50	268.00	1963.00	14.00	368.00	36.97	25.21	572.50	5.10	657.00	466.00	1.80	0.09	0.33	0.01
22-May-97	7.70	414.00	2536.00	14.00	340.00	71.94	37.02	869.00	9.65	841.00	642.00	4.20	0.08	0.86	0.01
19-Jun-97	7.50	305.00	1983.00	36.00	610.00	17.90	23.60	774.40	1.34	707.00	274.00	2.60	0.04	0.00	1.70
23-Jul-97	7.60	391.00	3404.00	48.00	372.00	147.80	58.78	883.60	11.19	1665.00	660.00	4.40	0.01	0.78	0.01
29-Aug-97	7.20	445.00	3273.00	18.00	448.00	159.00	75.41	787.30	8.31	1583.00	594.00	2.80	0.19	0.42	0.01
10-Sep-97	7.80	425.00	3657.00	26.00	96.00	106.10	60.63	839.00	11.58	1716.00	654.00	4.40	0.42	1.08	0.01
15-Oct-97	7.80	420.00	3533.00	2.00	424.00	118.90	64.52	1145.00	14.26	1685.00	656.00	4.22	0.14	0.01	0.01
15-Dec-97	7.20	561.00	3278.00	30.00	324.00	122.40	54.38	849.30	10.55	1517.00	734.00	2.06	0.59	1.28	0.03
08-Jan-98	7.40	362.00	2738.00	34.00	400.00	80.39	38.41	866.00	8.73	1132.00	660.00	3.60	0.15	0.55	0.01
11-Feb-98	7.80	481.00	3833.00	52.00	518.00	95.91	51.95	1124.00	11.91	1785.00	772.00	3.72	0.72	0.78	0.01
12-Mar-98	7.60	593.00	4094.00	14.00	544.00	133.28	70.51	1088.61	9.97	1698.00	1048.00	3.64	0.13	6.84	0.02
08-Jun-98	7.70	221.00	1865.00	10.00	294.00	44.82	37.26	475.29	7.62	727.00	350.00	2.00	0.01	0.01	0.01
15-Jun-98								901.42		2277.00	788.00	2.70			
22-Jun-98								1115.53		1727.00	870.00	3.48			
29-Jun-98								1100.90		1770.00	922.00	2.19			
14-Jul-98	7.40	500.00	3740.00	20.00	496.00	228.97	91.00	988.73	7.68	1612.00	718.00		0.10	0.43	0.05
07-Aug-98	7.50	518.00	3822.00	26.00	500.00	118.40	88.27	915.00	11.19	1538.00	666.00		0.06	0.06	0.01
11-Sep-98	7.40	559.00	3677.00	20.00	528.00	67.60	63.80	1240.00	10.30	1292.00	868.00		0.01	0.01	0.01
13-Oct-98	7.40	597.00	3845.00	18.00	476.00	67.62	53.82	950.68	15.52	1306.00	908.00		0.01	0.01	0.10
10-Nov-98	7.00	527.00	3784.00	16.00	422.00	99.00	55.83	953.91	17.95	1419.00	868.00		0.02	0.02	0.06
12-Dec-98	7.70	552.00	3848.00	16.00	428.00	99.83	43.58	966.00	12.65	1130.00	1036.00		0.25	0.01	0.04
13-Jan-99	7.70	648.00	4272.00	6.00	454.00	113.99	58.70	1114.23	16.80	1495.00	973.00		0.92	0.68	0.01
15-Feb-99	7.30	736.00	4885.00	20.00	434.00	170.04	87.07	1068.70	19.29	2154.00	810.00		0.01	0.01	0.01
15-Mar-99	7.80	526.00	3812.00	14.00	372.00	113.07	57.66	889.59	15.00	1462.00	846.00		0.20	0.66	0.01
15-Jun-99	8.00	629.00	3384.00	8.00	418.00	78.96	43.44	1064.70	11.60	1421.00	840.00		0.01	0.01	0.08
13-Aug-99	8.20	647.00	3373.00	16.00	502.00	54.13	28.97	1178.55	12.66	811.00	1220.00		0.09	0.06	0.05
14-Sep-99	8.10	711.00	3918.00	12.00	520.00	67.56	34.85	1254.26	14.77	1023.00	1300.00		0.03	0.20	0.05
10-Nov-99	7.94	603.00	4569.00	36.00	526.00	133.05	66.24	1316.21	18.09	1445.00	934.00		0.01	0.20	0.04
17-Nov-99	7.70	633.00	4142.00	44.00	508.00	107.80	53.47	936.16	10.56	1451.00	854.00		0.01	0.01	0.04
14-Dec-99	7.70	644.00	4174.00	62.00	480.00	83.88	43.34	1085.49	12.59	1205.00	1130.00		0.01	0.03	0.05
12-Jan-00	8.20	580.00	3552.00	58.00	416.00	84.70	44.72	895.42	10.82	1076.00	998.00		0.01	0.01	0.01
16-Feb-00	7.80	586.00	3581.00	30.00	424.00	79.32	46.47	915.94	11.68	1069.00	1010.00		0.01	0.13	0.03
14-Mar-00	7.55	610.00	3471.00	36.00	414.00	96.73	42.47	1035.12	10.26	1169.00	952.00		0.10	0.29	0.02
15-Apr-00	7.64	352.00	4603.00	34.00	320.00	175.73	77.75	997.81	10.06	2000.00	705.00		0.04	0.01	0.02
17-May-00	7.59	593.00	4253.00	78.00	330.00	149.51	71.30	932.73	9.12	1986.00	662.00		0.06	0.02	0.01
14-Jun-00	7.32	637.00	4691.00	94.00	250.00	261.21	113.01	955.80	17.98	2328.00	532.00		0.01	0.04	0.01
10-Aug-00	7.46	539.00	3730.00	50.00	362.00	103.43	49.58	768.63	13.47	1313.00	798.00		0.07	0.04	0.06
12-Oct-00	8.06	644.00	4060.00	402.00	4.00	105.83	56.19	932.48	14.84	1299.00	948.00		0.01	0.02	0.01
28-Feb-01	7.88	627.00	4082.00		388.00	142.00	62.00	1030.00	11.40	1478.00	1005.00	3.74	0.00	0.00	0.00
30-Mar-01	8.09	667	4402	3.8	292	183	83.9	989	12.9	1480	1010	4.0	0	0	0
23-Apr-01	8.37	58.80	475.00	0.00	201.00	34.83	34.96	47.44	1.78	122.00	48.00		0.06	0.01	0.10
04-May-01	6.682	736	4813	37	416	174.24	74.281	1168.86	11.688	1866	906		0.033	1.272	0.086
21-May-01	7.82	566	5153	112	420	154.307	61.657	1491.71	10.47	1789	1390		0.242	1.444	0.062
16-Jul-01	7.314	715	5213	72	473	163.022	80.302	1088.71	12.834	2086	818		0.118	0.89	0.056
14-Jan-02	7.659	686	4501	41	485	154.991	70.974	820.472	12.602	1857	854		0.074	0.095	0.013
14-Feb-02	7.327	569	4516	63	492	146.772	72.127	1583.07	22.673	2187.5	892		0.141	0.133	0.019
15-May-02	7.419	682	3131	12	441	145.539	70.465	1119.96	12.209	1799	882		0.608	0.406	0.01
28-Jun-02	7.623	765	4918	27	522	174.958	88.375	1105.98	13.422	1985	916		0.337	0.571	0.12
27-Aug-02	7.653	543	3958	29	473	111.562	60.65	883.476	9.731	1589	674		0.169	0.259	0.058
30-Sep-02	7.168	501	3769	18	490	111	58.8	1044	7.77	1343	715		0.01	0.21	0.02
28-Nov-02	7.796	470	3421	20	511	77.3	39.6	930	8.29	1192	650		0.01	0.24	0.01
11-Dec-02	8.302	34.32	269	43	107	21.1	12.7	33.2	2.21	43	14		0.01	0.01	0.01
24-Jan-03	7.738	622	4332	24	586	122	65.4	987	11.7	1550	624		0.01	4.23	0.07
25-Feb-03	7.534	511	4896	46	469	102.467	59.13	799.796	9.732	1380	540		0.058	3.573	0.038
20-Mar-03	6.875	414	3666	224	105	109.09	74	921.02	2.82	1520	486		0.01	0.01	0.015
15-Apr-03	7.537	504	4489	82	582	124.371	63.148	990.356	10.366	1270	616		0.01	0.01	0.038
19-May-03	7.42	515	4537	195	583	131.41	58.145	977.354	9.823	1480	470		0.01	0.01	0.057
24-Jun-03	7.5	560	4211	978	564	108.173	59.901	786.72	8.67	1630	602		0.139	0.01	0.12
21-Jul-03	7.68	516	4312	29	584	162.387	73.592	1137.33	11.738	1540	526		0.021	0.01	0.014
18-Aug-03	7.432	430	3913	84	588	155.96	56.455	891.63	8.625	1680	594		0.01	0.01	0.083
29-Sep-03	8.25	498	3775	0	576	85.851	39.57	824.092	7.39	1090	504		0.01	0.142	0.071
16-Oct-03	8.181	527	3727	34	608	115.337	57.362	940.468	9.204	1610	498		0.01	0.01	0.01
05-Jan-04	7.914	466	4136	57	525	101.169	48.105	840.72	7.487	1180	468		0.01	0.353	0.01
26-Jan-04	8.077	456	3908	25	497	102.104	47.054	927.641	7.78	1340	386		0.118	0.27	0.01

Appendix G1: Minerals with SI > 0 in Tutuka Water Streams (a)

Mineral	SI	Formula
Aragonite	1.09	$CaCO_3$
Barite	0.88	$BaSO_4$
Calcite	1.24	$CaCO_3$
Chlorite(14A)	14.65	$Mg_5Al_2Si_3O_{10}(OH)_8$
Chrysotile	7.65	$Mg_3Si_2O_5(OH)_4$
Dolomite	2.95	$CaMg(CO_3)_2$
$Fe(OH)_3$(a)	2.62	$Fe(OH)_3$
Goethite	8.4	FeO_2H
Hausmannite	6.11	Mn_3O_4
Hematite	18.8	Fe_2O_3
K-mica	2.72	$KAl_3Si_3O_{10}(OH)_2$
Manganite	1.96	MnO_2H
Rhodochrosite	1.01	$MnCO_3$
Sepiolite	3.1	$Mg_2Si_3O_{7.5}OH:3H_2O$
Sepiolite(d)	0.28	$Mg2Si_3O_{7.5}OH:3H_2O$
Strontianite	0.17	$SrCO_3$
Talc	9.03	$Mg_3Si_4O_{10}(OH)_2$
Willemite	1.67	Zn_2SiO_4

TP108

Mineral	SI	Formula
Alunite	6.16	$KAl_3(SO_4)_2(OH)_6$
Barite	0.98	$BaSO_4$
$Fe(OH)_3$(a)	0.82	$Fe(OH)_3$
Gibbsite	2.69	$Al(OH)_3$
Goethite	6.64	FeO_2H
Hematite	15.29	Fe_2O_3

TP308

Mineral	SI	Formula
Alunite	1.72	$KAl_3(SO_4)_2(OH)_6$
Gibbsite	1.25	$Al(OH)_3$
Goethite	2.88	FeO_2H
Hematite	7.75	Fe_2O_3
K-mica	2.39	$KAl_3Si_3O_{10}(OH)_2$
Kaolinite	1.46	$Al_2Si_2O_5(OH)_4$

TP508

Mineral	SI	Formula
Alunite	6.37	$KAl_3(SO_4)_2(OH)_6$
Barite	1.55	$BaSO_4$
$Fe(OH)_3$(a)	2.48	$Fe(OH)_3$
Gibbsite	2.71	Al(OH)3
Goethite	8.12	FeO_2H
Hematite	18.22	Fe_2O_3
Hydroxyapatite	1.37	$Ca_5(PO_4)_3OH$
Jarosite-K	2.95	$KFe_3(SO_4)_2(OH)_6$
Siderite	0.08	$FeCO_3$
Vivianite	0.52	$Fe_3(PO_4)_2:8H_2O$

TP408

Appendix G2: Minerals with SI > 0 in Tutuka Water Streams (b)

Mineral	SI	Formula
Aragonite	1.82	$CaCO_3$
Barite	1.46	$BaSO_4$
Calcite	1.95	$CaCO_3$
$Cd(OH)_2$	0.14	$Cd(OH)_2$
Dolomite	1.58	$CaMg(CO_3)_2$
Goethite	6.17	FeO_2H
Gypsum	-0.01	$CaSO_4{:}2H_2O$
Hausmannite	16.81	Mn_3O_4
Hematite	14.43	Fe_2O_3
Hydroxyapatite	14.96	$Ca_5(PO_4)_3OH$
Manganite	4.28	MnO_2H
Pyrolusite	6.17	$MnO_2{:}H_2O$
Strontianite	0.46	$SrCO_3$

TP608

Mineral	SI	Formula
Alunite	4.64	$KAl_3(SO_4)_2(OH)_6$
Barite	1.37	$BaSO_4$
$Fe(OH)_3(a)$	2.74	$Fe(OH)_3$
Gibbsite	2.38	$Al(OH)_3$
Goethite	8.6	FeO_2H
Hematite	19.21	Fe_2O_3
Hydroxyapatite	1.93	$Ca_5(PO_4)_3OH$
Jarosite-K	3.76	$KFe_3(SO_4)_2(OH)_6$
Siderite	0.06	$FeCO_3$
Vivianite	0.38	$Fe_3(PO_4)_2{:}8H_2O$

TP808

Mineral	SI	Formula
Aragonite	0.5	$CaCO_3$
Barite	1.16	$BaSO_4$
Calcite	0.64	$CaCO_3$
Dolomite	1.31	$CaMg(CO_3)_2$
$Fe(OH)_3(a)$	2.86	$Fe(OH)_3$
Gibbsite	0.8	$Al(OH)_3$
Goethite	8.92	FeO_2H
Hematite	19.88	Fe_2O_3
Hydroxyapatite	7.66	$Ca_5(PO_4)_3OH$
Otavite	0.6	$CdCO_3$

TP708

Mineral	SI	Formula
Goethite	6.13	$FeOOH$
Hematite	14.38	Fe_2O_3

TP1008

Appendix H: Department of Water Affairs and Forestry Elemental Limits in Waters

Element	Domestic Use (mg/L)	Plant Irrigation (mg/L)
Al	0.15	0.5
As	10	0.1
Be		0.1
B		0.5
Cd	5	0.01
Ca	32	
Cl	100	100
Cr	0.05	0.1
Co		0.05
Cu	1	0.2
F	1	2
Fe	0.1	5
Pb	10	0.2
Li		2.5
Mg	30	
Mn	0.05	0.02
Mo	1	0.01
Ni		0.2
N		5
Hg	1	
pH	9-Jun	6.5-8.4
K	50	
Se	20	0.02
SAR		2***
Na	100	70
V	0.1	0.1
Zn	3	1
NO3	6	
SO4	200	
EC	70**	40**
Total hardness	50	

** µs/cm *** no units SAR = [Na] ÷ ([Ca] + [Mg])0.5

Total hardness (mg/L CaCO3) = 2.497 x mg/L Ca + 4.118 mg/L Mg