CHEMICAL SPECIATION MODELLING OF THE COOLING WATER CIRCUIT AT MATLA POWER STATION

by

Jennifer Anne Reeves

BSc (Wits) BSc (Hons)(UNISA)

A thesis submitted in fulfilment of the requirements of the degree of Master of Science in

Engineering in the Department of Chemical Engineering, University of Natal, Durban.

June 1997

Pollution Research Group

Department of Chemical Engineering

University of Natal

Durban

Abstract

The chemistry of the water used in cooling water systems is extremely complex. In addition, raw water supplies in South Africa are deteriorating due to industrial, urban and rural pollution. Traditional methods for the evaluation of the quality of this water e.g. Langelier Index have proven to be inadequate as insufficient chemical parameters are taken into consideration. MINTEQA2 is a thermodynamic computer model for determining the possible form in which the chemical species can exist in a solution.

Although there is long term experience within Eskom as to the treatment and minimum specifications allowed for cooling water systems, the MINTEQA2 model can assist in interpreting the chemistry of the system, especially for less experienced operators. One of its major advantages is that it can be used to predict at which points of the chemical system precipitation is likely to occur. It can also be used as a teaching tool, particularly in terms of physical chemistry. The model is particularly useful in predicting the chemistry of the micro-elements e.g. silica, barium, copper, manganese, iron, etc. and dissolved organic matter (DOM).

The Matla Power Station cooling system was monitored as the concentration of contaminants increased. The MINTEQA2 model was used to predict the speciation profile of the concentrating cooling water system. The significance of DOM and the presence of an iron hydroxide layer was investigated. The DOM suppresses the precipitation of calcite e.g. in recarbonated cooling water, if the DOM is doubled, the amount of calcite predicted to precipitate is decreased by 12.5 %, and the presence of an iron hydroxide layer results in the adsorption of all copper from solution.

The validity of the outputs of the computer model was confirmed by laboratory techniques and provided that kinetic constraints are taken into account, it has proven to be an acceptable predictive tool in a qualitative rather than quantitative sense.

Declaration of Candidate

I, Jennifer Anne Reeves, declare that unless indicated, this dissertation is my own and that it has not been submitted for a degree at another University or Institution.

J A Reeves

June 1997

Acknowledgements

Table of Contents

Chapter 3

CHEMICAL SPECIATION MODELLING   **3-1**

Chapter 4

EXPERIMENTAL TECHNIQUES   **4-1**

List of Tables

Table   **Page**

List of Figures

Figure   **Page**

Abbreviations

Abbreviation	Explanation
AA	Atomic absorption
AR	Analytical reagent
CCW	Clarified cooling water
CLAR	Clarification
CW	Cooling water
DOM	Dissolved organic matter
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EDAX	Energy dispersive analysis of X-rays
EDF	Electricite De France
EDR	Electrodialysis reversal
EMA	Equivalent mineral acidity
ENEL	Ente Nazionale per l'Energia Electrica
GDL	Glow discharge lamp
GI	General inspection
GO	General overhaul
IAP	Ion activity product
IC	Ion chromatography
ICPOES	Inductively coupled plasma optical emission spectroscopy
IR	Interim repair
LI	Langelier Index
PMV	Predicted MINTEQA2 value
RAW CLAR	Raw water clarifier
RDP	Reconstruction and development programme

Abbreviation	Explanation
RO	Reverse osmosis
RW/CCW	Dual purpose raw and cooling water clarifier
RWE	Rheinisch-Westfalisches Elektrizitatswerk
SEM	Scanning electron microscope
SI	Saturation index
SRB	Sulphate reducing bacteria
TDS	Total dissolved solids
TEPCO	Tokyo Electric Power Company
TOC	Total organic carbon
T-R-I	Technology, Research and Investigations.
TVA	Tennessee Value Authority
USA	United States of America
UV	Ultraviolet
WRC	Water Research Commission
XRD	X-ray diffraction

Nomenclature

Symbol	Explanation
f	number of degrees of freedom
C	number of components
P	number of species with fixed activity and the number of finite solid species

Glossary

Amorphous Noncrystalline; having no molecular lattice structure.

Barite Barium sulphate ($BaSO_4$). A common mineral of wide distribution.

Calcite The thermodynamically stable form of calcium carbonate ($CaCO_3$).

Calcium-Nontronite A form of *stevensite* with calcium substitution $Ca_{0.35}(Mg_{2.88}Mn_{0.02}Fe_{0.02})Si_4O_{10}(OH)_2$.

Calculated Balance A manually calculated cation/anion balance in which trace elements and pH are not taken into account**.**

Chemical Determinand A chemical analyte which makes up part of a water sample, which may either be elemental eg chloride or a group of compounds e.g. dissolved organic matter.

Cleaner Production This is not only the adoption of industrial processes directed at reducing the consumption of natural resources, including raw materials, water and energy, and eliminating the generation of waste materials, but also of practices which ensure that products, throughout their lifecycles, are environmentally compatible.

Cleaner Technology This is a subset of *cleaner production* and involves the improvement of the

thermodynamic efficiency of production processes and which substitutes less hazardous processes, products and activities for more harmful ones, thereby reducing quantities and / or the hazardous nature of waste materials which require treatment and disposal.

Closed System   A system from which carbon dioxide has been excluded.

Diaspore   Hydrogen aluminium oxide mineral, (αAlO.OH or HAlO$_2$) belonging to the Goethite group.

Goethite   Hydrogen iron oxide (HFeO$_2$), the commonest of the ferric oxides after hematite.

Hematite   Iron oxide (Fe$_2$O$_3$), often found admixed with magnetite (Fe$_3$O$_4$), another form of iron oxide.

Leonhardite   Magnesium sulphate with four coordinated water groups (Mg SO$_4$.4H$_2$O).

Magnetite   An iron oxide, (Fe$_3$O$_4$).

Mothballed   When there is a drop in electricity consumption a power station is taken off-line but is kept in readiness to be put on-line in the future.

Noncrystalline   A precipitate in which the aggregation of atoms is not arranged in a definite pattern.

Open System   A system in which carbon dioxide is allowed to equilibrate.

Outage   A shutdown for any length of time for a general overhaul (GO), interrim

repair (IR) or a general inspection (GI).

Quartz   Silicon dioxide, SiO_2.

Speciated Balance   The cation/anion balance calculated by MINTEQA2.

Speciation   A technique whereby chemical constituents are grouped together in the most likely forms in which they will be present in a water sample.

Stevensite $M_{0.35}(Mg_{2.88}Mn_{0.02}Fe_{0.02})Si_4O_{10}(OH)_2$, where M can be calcium, magnesium, sodium or potassium.

Tenorite   Copper oxide (CuO), found naturally but less commonly than cuprite, (Cu_2O).

Tremolite   Calcium, magnesium silicate, a variety of asbestos.

Unit   A unit on a power station consists of one condenser, boiler and turbine etc. which is served by a common water plant and cooling water system.

Chapter 1
INTRODUCTION

Water is essential to life, social development and economic progress (Department of Water Affairs, 1986). The deterioration in water quality is a worldwide phenomenon. In some states of the United States of America e.g. California, it is mandated that reclaimed water (treated sewage) be used in industrial cooling water systems (Puckorius and Strauss, 1995). This results in poorer quality water with more aggressive tendencies being used for industrial purposes.

In this **chapter**, the water situation in South Africa is discussed, followed by water utilisation in the power industry. The power industry in South Africa is compared to its international counterparts and the variability of raw water quality discussed. Following this the requirement to fully understand the water chemistry on power plants with particular emphasis on raw and cooling waters is outlined. The use of chemical speciation modelling to provide this understanding is described. The **chapter** concludes by listing the **Aims** of this thesis and describing the thesis **Outline.**

1.1   SOUTH AFRICAN WATER RESOURCES

The extent of economically viable water resources in South Africa is low since the greater part of the Republic is located in a semi-arid or an arid zone. The average annual rainfall for the Republic of 497 mm is well below the world average of 860 mm (Department of Water Affairs, 1986). The problem of economically utilisable water is complicated by the unfavourable geographical distribution of the low rainfall and the high evaporation rate. The uneven temporal distribution results in prolonged droughts and severe droughts. In addition, the location of the water is not always where it is needed and hence transportation costs are high. Due to increased industrialisation and urbanisation the concentration of pollutants in the raw water is increasing.

The Water Research Commission (WRC), whose mission includes ... *to contribute effectively to the best possible quality of life for the people of South Africa, by promoting water research and the application of research findings ...* (WRC, 1993) has identified several projects each year related to water quality studies. The gradual deterioration of water quality and the increasing awareness of water quality is a factor determining the full utilisation potential of water. All industry must be prepared to

become involved in the preservation of our natural water sources.

With the new democratic government in South Africa, one of the policies of major importance is the Reconstruction and Development Programme (RDP) which has been defined as ... *an integrated, coherent socio-economic policy framework ...* (African National Congress, 1994). Provisions have been made in the RDP regarding water, with one of the physical targets being *Water security for all - the right to access clean water* (Muller, 1994), where the focus will be on the provision of water to people at the lower levels of socio-economic development. As South Africa moves into this new era the water sector faces major challenges. Absence of adequate services is particularly acute in the former homelands and it is estimated that 12 million of the South African population have inadequate water and 19 million have inadequate sanitation. It has been estimated that there are 12 000 to 15 000 communities with inadequate water and sanitation facilities (Department of Water Affairs and Forestry, DWAF, 1994). Recent government policy stressed that the new water law was strongly based on the principles of the new constitution. The scarcity of water has led to certain controversial principles being included in the law i.e. the loss of private status for groundwater and the preferential access to water is not conferred due to the proximity of a parcel of land (Muller, 1996). In the white paper on Water Supply and Sanitation Policy (DWAF, 1994) the following policy principles are detailed:

- *development should be demand driven and community based,*
- *basic services are a human right,*
- ***some for all*** *rather than* ***all for som****e(sic),*
- *equitable regional allocation of development resources,*
- *water has an economic value,*
- *the user pays,*
- *integrated development, and*
- *environmental integrity.*

Once all of these principles have been implemented and a supply to all South Africans has been achieved there will be increasing demands on industry to reduce water consumption and concommitantly with this to reduce pollution of our raw water sources.

To exacerbate the situation South Africa's population is increasing. This can be ascertained from the following census results:

- 5 March 1985: 23 385 645,
- 7 March 1991: 26 288 390, and
- estimate mid-year 1994: 40 436 000 (Europa World Year Book).

Hence over the six year period from 1985 to 1991 the population had increased by 12.4 % and over the three year period from 1991 to 1994 was estimated to have increased by 53.8 %. This results in a larger rural population living close to the banks of rivers and an increase in urbanisation and informal

settlements. These communities do not have access to sanitation and hence raw sewage is discharged into the water systems causing pollution. This pollution results in a poor quality of life due to the increase in waterborne diseases. (Bothma, 1993). Important parameters to be investigated for an improvement in the quality of life are quality, quantity and location of essential services.

The mechanism of water pollution is complex. Two of the major problems are the buildup of total dissolved solids (TDS) and dissolved organic matter (DOM), in our water systems. At present there is very little information available on the nature of the organic compounds in the raw water supplies as it was previously considered sufficient to carry out total organic carbon (TOC) analyses. However, these figures are insufficient for water treatment purposes. When these two problems are combined with adverse climatic conditions e.g. drought, a water pollution crisis may be anticipated. *Long droughts not only hold serious consequences for the economy but also have a depressing effect on morale ...* due to *... the imposition and orchestration of severe water restrictions.* (Department of Water Affairs, 1986). As water pollution increases, the treatment of the water becomes more problematic and expensive.

The solution to the ever increasing demand for water and its continual deterioration involves a combination of factors;

1.1.1 SUSTAINABLE DEVELOPMENT

Development must be such that there are no detrimental effects on the environment for future generations. *Integrated pollution control* (Western Cape Environmental Monitoring Group, 1993) is now required in which the emphasis is placed on *pollution prevention or waste* reduction. The following actions are included in the concepts of *cleaner production* and *cleaner technology*; prevention or minimisation of waste at source, raw material substitution, resource recovery, recycling, raw material substitution and immobilisation.

1.1.2 MORE STRINGENT WATER LAWS

The existing water laws in terms of effluent discharge and atmospheric emissions from industry, and agricultural pollution are likely to be made more stringent. The need for a new water law has been identified by the Department of Water Affairs and Forestry who have sent out a call for public response in a paper entitled *You and Your Water Rights* (DWAF, 1995).

In this paper it is proposed that there should be a new approach to water pollution control, which involves managing water quality in the catchment areas. However, for this to be viable, other options will have to be made available.

The *polluter pays* principle is now being strongly emphasised. This is an economically efficient option where cost of effluent treatment is low, the polluter will limit its discharges whereas where the costs are high the polluter will probably elect to pay the charge. The drive towards minimising costs will be an incentive to undertake research into more cost effective technologies.

1.1.3 RESEARCH, TECHNOLOGY TRANSFER AND DEVELOPMENT

Research should be carried out into minimising water usage for industrial purposes. Since large quantities of water are used in industry, a small saving will result in more water being available for human consumption. For example, the volume of water consumed by the power industry during 1995 was 230 000 Ml (Eskom, 1994). A reduction in water usage can be addressed by investigating improved methods of water treatment. The effluent load produced by the water treatment processes should also be investigated to reduce the amount of pollutants entering our water systems.

1.2 WATER UTILISATION IN ELECTRIC POWER GENERATION

Throughout the world there are a large variety of ways in which electric power is generated. The main source of power is fossil fuel (which can be either coal, oil or gas) and it is predicted that the major energy producing utilities will continue to be fossil fuel based at least in the foreseeable future (Hewett and Hufton, 1993). There are also a number of nuclear power stations which are beginning to be seen as more environmentally friendly than their fossil fuelled counterparts (Krebs et al., 1993). There is an increasing interest in cleaner forms of energy due to the increase in environmental awareness, these include solar, hydro and wind, geothermal and tidal energy.

At the turn of the 20th century the electric power industry consisted mostly of small municipal lighting companies. With technological progress larger turbines, generators, steam supply systems and ultimately larger plants have been developed.

In the USA the national system is comprised of three interconnected networks. These networks are made up of over 200 privately owned utilities, 1 800 municipal systems, 2 large and almost 200

smaller government controlled systems, and over 900 power co-operatives (Barthold and Wilson, 1988).

In Europe there is a trend to more liberalised energy markets which will embrace technology transfer throughout Europe. This was brought about as it was considered that the national energy markets were still too closed (Maniatopoulos, 1993). However at this stage each country has its own utilities and the types of power stations vary between countries. For example in The Netherlands 37 % of the generation capacity is coal-fired, 57 % generated by gas and 6 % nuclear. (Zijl and Sep, 1993). In Poland, the fuel category for energy production is as follows; 55 % hard coal, 43 % lignite and 2 % hydro (Popczyk and Kedziersli, 1993). In the USA, during 1992, nuclear based stations provided at least 21 % of power generated (Krebs et al., 1993). There were 420 nuclear reactors worldwide in January 1992 most of which were located in western Europe and USA (Herbin, 1993).

Coal-fired thermal power stations with recirculating cooling systems are only used in areas where there is sufficient supply of coal but where water availability is low. Due to the recirculation of water only about 2 % of make-up water is required (Central Electricity Generating Board,1971,a). The total cost per kilowatt per annum is higher for coal-fired power stations than for oil or nuclear power stations. The problems associated with recirculating systems compared to once-through systems are detailed in **Chapter 2.**

1.2.1   ESKOM

Eskom is the major power generating industry in Southern Africa, providing more than 95 % of the electricity consumed in South Africa. In terms of electricity sales Eskom is the fifth largest utility in the world. Eskom's sales by the end of 1993, amounted to a total of 143 800 GWh. A comparison between the sales of electricity per annum by major utilities worldwide is shown in **Fig 1.1** (Eskom, 1994).
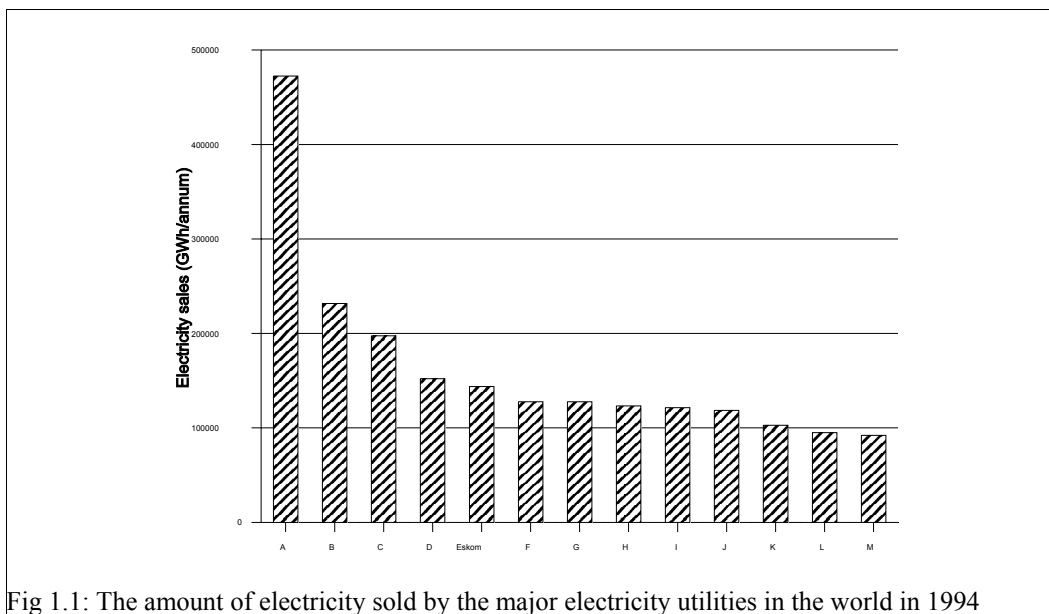
Fig 1.1: The amount of electricity sold by the major electricity utilities in the world in 1994

A = EDF, France
B = TEPCO, Japan
C = ENEL, Italy
D = Hydro-Quebec, Canada
F = Ontario Hydro, Canada
G = Korea Electric Power Co, South Korea

H = Kansai Electric Power Co., Japan
I = RWE, Germany
J = TVA, USA
K = Chubu Electric Power Co., Japan
L = National Power, United Kingdom
M = Taipower, Taiwan

Eskom has prioritised the improvement of productivity, the reducion of operating expenditure and cost containment. Even though Eskom's contribution to the RDP in terms of the electrification programme has been at a high cost, South African industry obtains its electricity at an internationally competitive price e.g. industrial companies pay 38 % less than consumers in North America and 50 % less than consumers in Europe (Eskom, 1994).

The generation of electricity is considered as a strategic activity by the Department of Water Affairs and Forestry. Hence although there is a commitment to supply water for this purpose the DWAF expects Eskom to ... *achieve the most efficient use of water applicable within the limitations imposed by economic and technical considerations.* (Department of Water Affairs, 1986).

The total emissions from power stations form part of Eskom's environmental impact. *The provision of electricity has social, economic and environmental benefits. However, some negative impact on the environment is inevitable, and it is Eskom's aim to maximise the benefits and minimise the negative influences.* (Morgan,1994).

The majority of Eskom power stations are larger than those found in the rest of the world. Many overseas power stations consist of a single unit, whereas Eskom's newer power stations are comprised of 6 units. Each modern Eskom power station has 6 cooling towers, 6 boilers, 6 turbines, etc. Each unit is capable of producing approximately 600 MW on full load. Although there are 6 units, the water used is supplied by 2 integrated water plants. The efficiency of the new stations can be gauged by the fact that in its first full year of operation, 1994, Kendal power station set a world record for a six-unit power station using hard coal by producing an hourly net power of 4 056 MW (Eskom, 1994).

In power generation the basic thermodynamics are governed by condensation and evaporation. Cooling water is used to condense the steam by absorbing heat. In order to reuse the cooling water, it has to be cooled down which is achieved by evaporation. Approximately two thirds of the energy derived from burning coal is required for evaporation of cooling water or as stack losses. In recirculating cooling systems the evaporation of water leads to the concentration and build-up of soluble salts.

Eskom requires large volumes of water for electricity production. Raw water supplies are required for three main purposes :

- to provide make-up water to the water / steam cycle,
- for condensing of the steam for re-use as boiler feed water, and
- general domestic use.

Of the intake water, 90 to 95 % is used to operate cooling water circuits efficiently (Corrosion School '93). The magnitude of the rate of water evaporating from a cooling tower servicing a 600 MW turbine can be likened to an average sized swimming pool evaporating every 2 minutes e.g. The average evaporation rate at Matla power station is 95.32 Ml/day/side. Each side has 3 cooling towers, servicing 3 turbines. The calculation has been worked out on an average pool size of 50 000 l.

It is important to note the difference between regional consumptive and non-consumptive water use i.e. evaporation is consumptive and that which is returned to the ground or river and is available for reuse, is non-consumptive. Ash water is therefore also a consumptive use. Therefore Eskom is mainly a consumptive industry from the South African water perspective. On a *dry ash* system, water is used to condition the ash to form hydrated

minerals thus although consumptive, less water is used than a *wet ash* system.

The bulk of Eskom's electricity is generated by coal-fired power stations, most of which are situated on the Mpumalanga Highveld. High quality coal is mined in South Africa but the majority of this coal is exported to the USA, Europe and Japan for electricity generation. Eskom uses a lower quality coal than international power plants as the plants are designed for this purpose (**Table 1.1**). The choice of site for coal-fired power stations is determined by a trade off between coal transport costs and water transport costs. Eskom has designed some of its plants to utilise a lower grade of coal than is generally used on other plants e.g. Lethabo power station. In many cases on the coalfields there is a shortage of raw water which is frequently of low quality.

TABLE 1.1
Comparison between critical coal analysis values at Duvha (a typical Eskom power station) and Lethabo (extreme example) power stations with internationally accepted standards

Determinand	Lethabo	Duvha	International standards
Ash (%)	35 - 40	23 - 25	10
Calorific Value (MJ/kg)	16 - 18	20 - 22	>25

Eskom has already taken steps to reduce water usage by constructing power stations which are dry-cooled. Matimba power station which is located in the arid area of the Northern Province and Majuba, the newest coal-fired power station, which is located in Mpumalanga close to the border of KwaZulu-Natal, are forced-draught dry-cooled. Kendal power station is natural-draught dry-cooled. Koeberg power station, Eskom's only nuclear power station, located near Cape Town, has a once-through sea water cooling system. Arnot, Duvha, Hendrina, Kriel, Lethabo, Matla and Tutuka power stations are conventional wet-cooled power stations in which the cooling water goes through cycles of concentration and a side-stream of this water is treated in the clarifiers. Komati, Grootvlei, Camden and Ingagane power stations which are currently mothballed are also conventional wet-cooled power stations. Some of these mothballed stations will be recommissioned once the economy improves and electricity demand increases.

The advantage of dry-cooled power stations over the wet-cooled ones in terms of water

utilisation can be demonstrated by the following statistics. From January to November 1994 the average net water consumption of a dry-cooled station was 0.17 l/kWh, compared to 1.95 l/kWh for the wet-cooled stations. This represents a water utilisation reduction of over 90 % for dry-cooled power stations (Pozyn, 1994). There are disadvantages to dry cooling which include higher capital costs and a higher coal consumption to produce the same power output, due to a decrease in thermodynamic efficiency. Therefore, the cost of reducing water consumption is an increase in coal use and hence an increase in carbon dioxide, sulphur dioxide and nitrogen oxide production. A balance is therefore needed between the deleterious effects of the production of these atmospheric pollutants and the reduction in water consumption. It is interesting to note that the amount of water consumed by Eskom over this 11 month period was 221 139 Ml (Pozyn, 1994), which is approximately the same amount of water required to supply 1.3 million middle class households.

With the exception of Koeberg power station all of the above-mentioned power stations are coal-fired and as such are located on coal fields. The burning of coal and thereafter the disposal of ash can have an impact on the ground water quality.

1.3 VARIABILITY OF RAW WATER QUALITY SUPPLIED TO ESKOM

Eskom requires reliable high quality water supplies. Security of supplies, reduction of water consumption and pollution prevention are priority issues from both an environmental and operational perspective. (Eskom, 1994)

The quality of raw water supplied to power stations is variable, since raw water is drawn from different sources depending on its availability. The availability and extent of raw water sources is shown in **Fig 1.2**. Raw water supply to Eskom is divided into 5 categories, the Komati river system, the Usutu river system, the Usutu-Vaal system, the Vaal river system and ancillary systems (Pozyn, 1994).
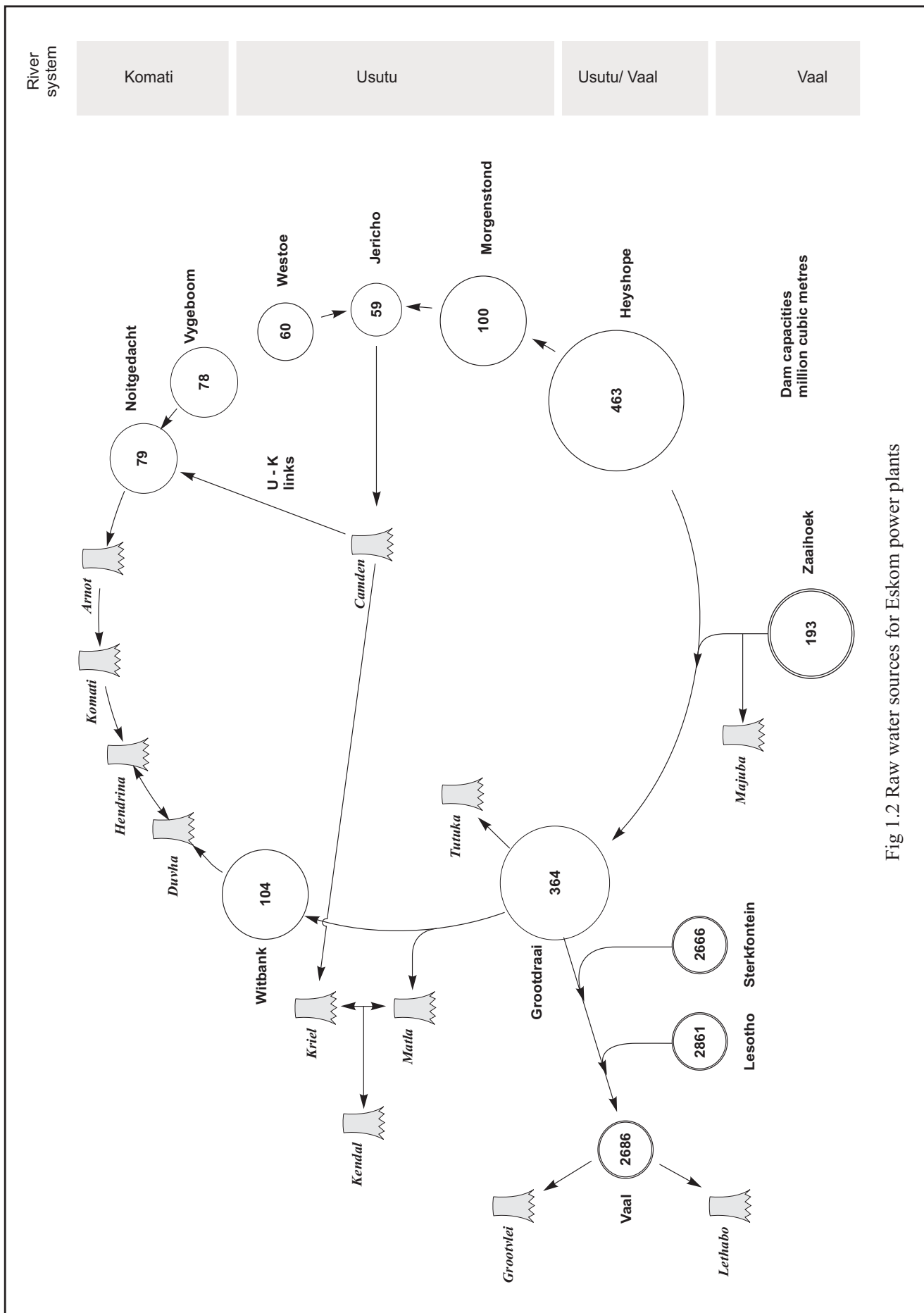
Fig 1.2 Raw water sources for Eskom power plants

During 1994 Arnot, Komati, Hendrina and Duvha power stations received water from the Komati river system; Camden, Kriel, Matla and Kendal power stations from the Usutu river system; Tutuka, Matla, Kriel and Duvha power stations from the Usutu-Vaal river system ; Taaibos, Highveld, Grootvlei and Lethabo power stations from the Vaal river system; and the remaining power stations from ancillary systems. The water utilisation from the ancillary systems is as follows; Matimba power station from Mokolo; Majuba power station from Amersfoort and Zaaihoek dams; Wilge power station from the Bronkhorstspruit dam; and Ingagane power station from the Chelmsford dam.

The variability of raw water supplies is shown in **Fig. 1.3**, which indicates the amounts of raw water received by the Kriel power station from the Usutu and Usutu-Vaal river systems. In studying this figure it must be borne in mind that the Usutu water is far purer than the Usutu-Vaal water. (**Figs. 1.4** and **1.5**). **Fig 1.4** also shows the chemical analysis results of the Komati and Vaal river systems.
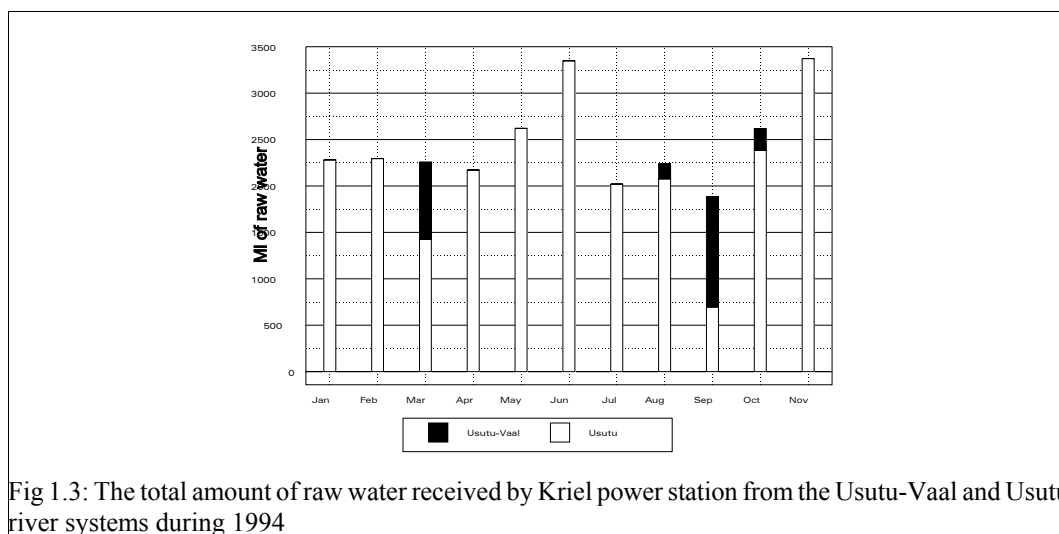
Fig 1.3: The total amount of raw water received by Kriel power station from the Usutu-Vaal and Usutu river systems during 1994
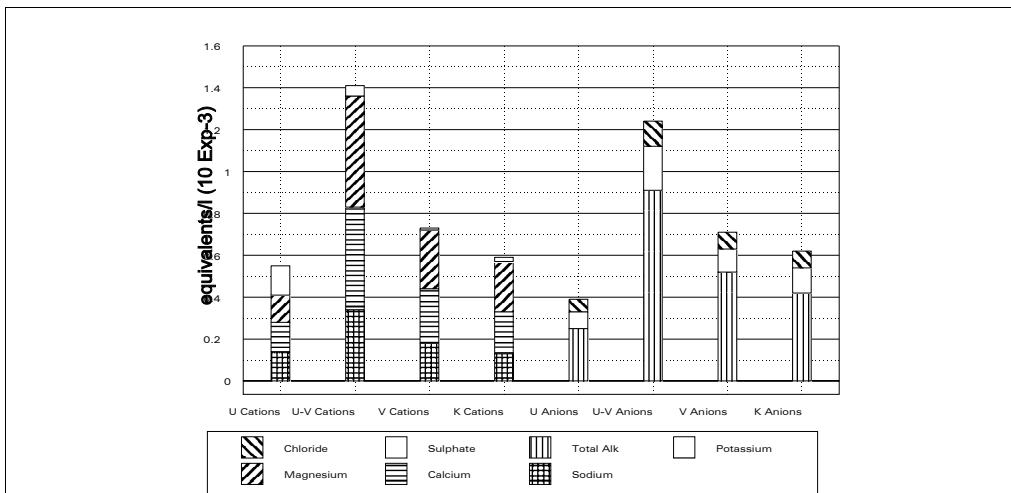
Fig 1.4: Comparison between major cation and anion constituents in the Usutu (U), Usutu-Vaal (U-V), Vaal (V), and Komati (K) river systems during 1994 (**Appendix A2**)
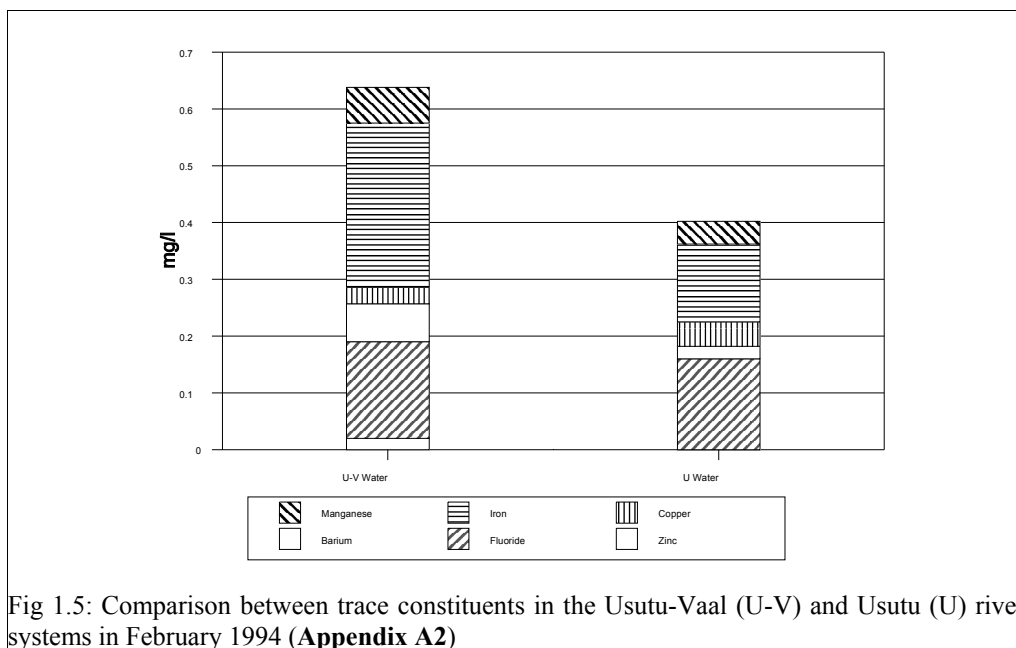
Fig 1.5: Comparison between trace constituents in the Usutu-Vaal (U-V) and Usutu (U) river systems in February 1994 (**Appendix A2**)

Hence water treatment strategies would have had to have been changed particularly in March and September 1994. In addition to changes in the quality of raw water supplies inadequately controlled chlorination techniques result in the organic constituents in the majority of Eskom's chlorinated raw water supplies being highly variable.

Eskom has a policy of zero liquid effluent discharge meaning that no liquid effluents are discharged to the environment, requiring stringent water management techniques. This involves the concentration of effluents which are then absorbed into the ashing system, accompanied by the

recovery of good quality water (Buckley and Winship, 1995).

1.4   THE USE OF TOOLS TO PREDICT CHEMICAL EVENTS

For water treatment purposes it is essential that a fundamental knowledge of the chemistry of the water is available. As the composition of the water changes, previous experiential knowledge such as the relationship between total dissolved solids and conductivity and other relationships e.g. precipitation and corrosion, changes.

Tools are available to provide this knowledge and for the continued smooth running of the plant it is essential that these tools are used. This is particularly relevant when one considers the variability of water quality. Of major significance to the control of cooling water circuits is the aquatic chemistry of these circuits. Aquatic chemistry involves the study of chemical processes which affect the circulation and distribution of chemical compounds in water (Stumm and Morgan, 1981). Apart from the chemical behaviour of water systems, aquatic chemistry embraces fundamental chemical principles and other sciences, especially geology and biology, in order to describe processes involved with water treatment. Useful tools to assist in the understanding of aquatic chemistry are computerised chemical speciation models. Speciated chemical analyses are used for the validation of analytical results, to describe how components are distributed among species and to understand precipitation and adsorption mechanisms.

Chemical speciation involves the distribution of species in solution e.g. iron (Fe) can be found in several different oxidation states and in different complexes in solution e.g. Fe^{2+}, Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)_4^-$. Although there are sensitive analytical techniques for the determination of these different iron oxidation states e.g. ion chromatography, once the water sample is removed from its natural water system, the ratio of its oxidation states can change considerably and hence the analytical result may not be truly representative. It is therefore advantageous to analyse for total iron concentration and allow the speciation program to calculate the species distribution at equilibrium.

Due to the complex nature of cooling water, Langelier Index (LI) calculations are inadequate to predict scaling potential. The rapid and unexpected changes in the raw water quality supplied to some power stations has affected the chemistry in the cooling water circuits. This has emphasised the need for a technique for the quantitative assessment of the chemical state of cooling water at

each point of the cooling water circuit. The chemical speciation modelling program used in this investigation was MINTEQA2, the details of which are provided in **Chapter 3**.

1.5   AIMS

The aims of the thesis are to:
- establish whether MINTEQA2 is a useable tool for predicting occurrences in cooling water circuits, at the Matla power station,
- validate the outputs of MINTEQA2 by comparing them with chemical results, and
- have a readily available tool for plant operators to change treatment conditions when water chemistry changes.

1.6   THESIS OUTLINE

The investigation was carried out from January 1992 to December 1994. The period of intense field study was from 28 March to 16 June 1994. **Chapter 1** introduces the project by providing an overview of South African raw water resources, water utilisation in power generation and the need for understanding chemical events. In **Chapter 2** the chemistry of cooling water circuits at power stations is discussed, with a detailed discussion on the cooling water circuit at Matla power station, since this is where the investigation took place. **Chapter 3** outlines the theory and practical applications of chemical speciation modelling. **Chapter 4** constitutes the first experimental section in which method details, samples taken and techniques for the validation of MINTEQA2 are detailed. **Chapter 5** contains the experimental results with each set of results being discussed in detail. **Chapter 6** contains the conclusions while the recommendations are presented in **Chapter 7.**

Chapter 2
COOLING WATER CIRCUITS

There are many ways in which a cooling system can operate, ranging from water intensive once through systems to dry-cooling systems. The different types of cooling are discussed in this **Chapter**, together with the features and procedures required to operate these cooling systems successfully. This includes the design of cooling water treatment plants and the chemicals added to cooling water to prevent corrosion, scaling and fouling. Since the work for this project was carried out at Eskom's Matla power station, a detailed description of the station's cooling water system is given at the end of the **Chapter**.

2.1 DESCRIPTION OF DIFFERENT COOLING WATER CIRCUITS

The essential parts of a typical open recirculating cooling water circuit are illustrated in **Fig. 2.1**.

Fig 2.1 : Schematic diagram of a generalised cooling water circuit
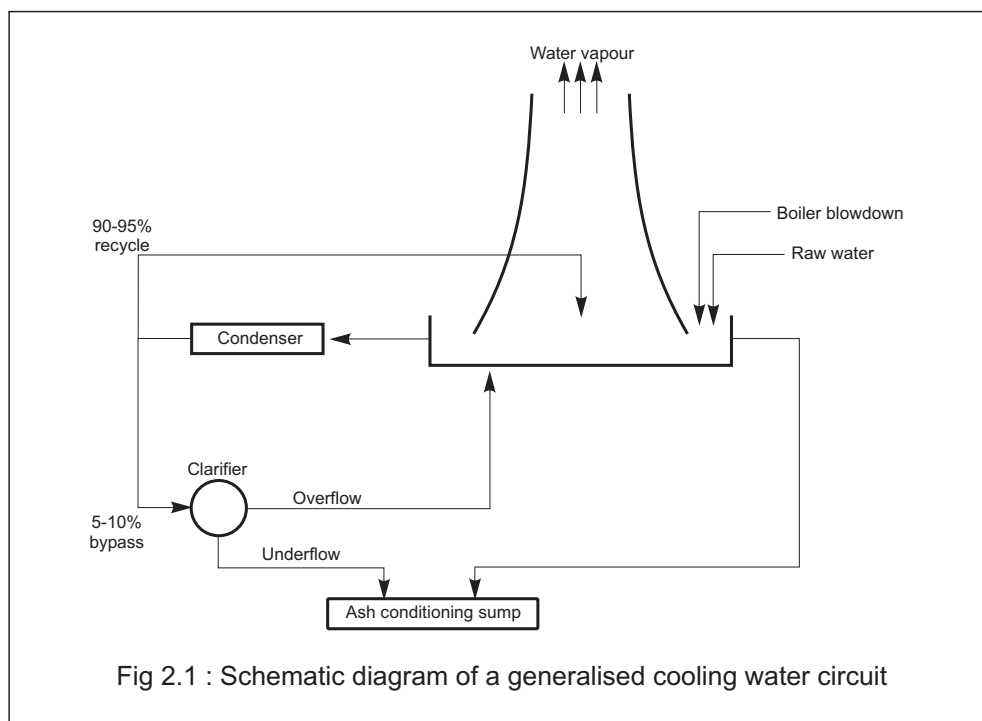
The water from the cooling tower passes through the condenser where it effects the phase change of steam to water with no resulting change in temperature. After passing through the condenser, 90 to 95 % of the cooling water, having a temperature of about 40 $^\circ$C, is returned to the cooling tower and 5 to 10 % is treated in a sidestream clarifier . The clarification process is described in **Sections 2.2.2, 2.2.3** and **2.2.4**. The cooling tower promotes circulation of air and the evaporation of the cooling water, leading to a temperature reduction from 40 to 25 $^\circ$C. Cooling water makeup (CW-makeup) is used to replace the water lost due to evaporation, blowdown and drift. Raw water is used for this purpose (Buckley and Winship, 1995). The sludge from the clarifier and the high total dissolved solids (TDS) cooling water blowdown flow to the ash conditioning sump.

Certain power stations have desalination processes to reduce the volume of the blowdown from the cooling tower. A reverse osmosis (RO) plant has been installed at Lethabo power station. The RO

concentrate is further concentrated in an evaporator. The RO permeate and evaporator condensate is returned to the base of the cooling tower and the brine from the evaporator is pumped to the ash conditioning sump. At Tutuka power station an electrodialysis reversal plant (EDR) is used in place of an RO plant.

Indirect dry cooling systems also make use of cooling towers, however they are generally much smaller than those used for wet cooling systems. This type of cooling is described in **Section 2.3.** Direct dry cooling systems have a completely different appearance, as cooling towers are replaced by dry cooling elements (**Section 2.4**).

2.2   POWER STATION COOLING CIRCUITS

Cooling water acts as an energy sink for the latent heat which is rejected as the steam is condensed to water in heat exchangers or condensers. The condensers consist of condenser tubes through which the cooling water is passed and the steam condenses on the outside of these tubes. After condensing the steam, the cooling water contains heat which must be dissipated. (Nalco, 1988). This is achieved by transferring heat to the environment in different ways depending on the type of cooling system.

2.2.1   PROBLEMS ASSOCIATED WITH COOLING WATERS AND THEIR TREATMENT

Cooling water systems are expected to present difficulties due to the fact that evaporation occurs and large quantities of salt are left behind. The water quality related problems associated with cooling water systems are corrosion, scaling and fouling.

Corrosion

The definition of corrosion is the interaction of a metal with its environment (Corrosion Institute of Southern Africa, 1994). In a cooling water system, corrosion is due to water characteristics and the metals which are present in the cooling water.

Most metal structures which come into contact with water have a tendency to corrode, but the aim is to control the rate of the corrosion to match the service life of a structure. Excessive rates of corrosion lead to premature failure of metals or a reduction in heat transfer efficiency and liquid flow rates.

One of the corrosion phenomena which has been observed at all of the major Eskom power plants is the dezincification of admiralty brass condenser tubing . Attack appears to occur in zinc rich areas where the zinc passes into solution and the copper remains. When dezincification occurs the affected unit is taken offline, the failed tubes are identified and plugged, resulting in poorer turbine efficiency. Eventually the condenser has to be retubed. Dezincification occurs when the sulphate and chloride concentrations in the cooling water exceed 900 and 300 mg/l respectively. Dezincification can be inhibited by dosing in excess of 10 mg/l of tolyltriazole (Woest and Maclons, 1992).

Another cause of corrosion occurring on Eskom power stations is sulphate-reducing bacteria (SRB). The availability of sulphur for the bacteria is high as the element is common and widespread in the form of sulphate ions. SRB's belong to a class of microbes which conduct *dissimilatory sulphate reduction* (Postgate, 1981). Here the sulphate ion acts as an oxidising agent for the breaking up of organic matter into smaller molecules. Only a small amount of reduced sulphur is assimilated by the organism, but the majority is released into the environment in the form of the sulphide ion, mostly hydrolysed to free hydrogen sulphide.

There are three main characteristics of the anaerobic corrosion of iron by SRB's:

- it only occurs in anaerobic environments e.g. the inside of water pipes. Corrosion often occurs more rapidly in areas which are subject to partial or intermittent anaerobic conditions,

- the metal is not evenly corroded, but tends to be pitted resulting in local perforation of pipes, and

- at the point of corrosion the metal is completely removed, often leaving the graphite skeleton of the pipe in its original form. The mechanism whereby this corrosion occurs is cathodic depolarisation.

There are several ways in which SRB corrosion can be controlled e.g. ensuring aerobic conditions, coating the metal using chemical inhibitors to physically prevent access to the metal surface, and implementing cathodic protection.

Scaling

Scaling is a result of the precipitation of compounds which have become insoluble due to a variety of factors, namely water composition, temperature and pH value. Scaling interferes with heat transfer and reduces flow. Calcite ($CaCO_3$) is one of the major scaling deposits on power stations. There is a fine balance between scaling and corrosion and in order to minimise the risk of either occurring the water should be just saturated with calcium carbonate. An undersaturated solution of calcium carbonate is potentially corrosive and conversely an oversaturated solution is potentially scaling (Central Electricity Generating Board, 1971b).

The Langelier Index (LI) of a solution is calculated by relating temperature, total dissolved solids, total alkalinity, calcium hardness and pH value. A positive LI indicates a potentially scaling water, whereas a negative LI indicates a potentially corrosive water. However, it is considered preferable to have a slightly positive LI since a certain amount of supersaturation can usually occur without scale formation occuring (Central Electricity Generating Board, 1971b).

The solubility of calcium carbonate in pure water is very low in the absence of carbon dioxide. Its solubility is 14 mg/l at 25 $^{\circ}$C. In the presence of carbon dioxide the following reaction occurs:

$$CaCO_3 + CO_2 + H_2O \div Ca(HCO_3)_2$$

Calcium bicarbonate, $Ca(HCO_3)_2$ has a much higher solubility of 300 to 400 mg/l at a temperature of 25 $^{\circ}$C. When a water which contains $Ca(HCO_3)_2$ is heated the following reaction occurs :

$$Ca(HCO_3)_2 \, ^* \, CaCO_3 - + CO_2 , + H_2O$$

Hence $CaCO_3$ precipitation is accompanied by the release of CO_2 from solution (Drew, 1979).

Another deposit causing scaling problems in cooling water circuits is calcium phosphate due to the popularity of phosphate-based treatment programmes. Other forms of scale in descending order of frequency are silica, calcium sulphate and calcium fluoride (Puckorius and Strauss, 1995).

Fouling

Since cooling water is obtained from the sea or rivers, microbial material will be present. Fouling is caused by the settling out of suspended solids, the build up of corrosion products and growth of microbial masses. Fouling also interferes with heat transfer and reduces flow. In addition, fouling promotes severe corrosion under the deposits (Nalco, 1988), (British Electricity International, 1992).

Fouling caused by suspended solids is a form of sedimentation and hence is related to the velocity of the water. The higher the velocity the lower is the tendency for the suspended solids to settle and adhere to the surfaces (Drew, 1979).

In the past few years there has been an increase in microbial fouling. This has been attributed to a variety of factors:

- cooling water systems are run on a higher pH regime normally in the range of 8 to 9. This reduces the effectiveness of chlorine and some of the non-oxidising substitutes,

- for environmental reasons chromate is no longer being used and has been replaced by phosphates, phosphonates and polymers. These replacement chemicals serve as nutrients for micro-organisms, and

- there is an increasing tendency to use treated wastewaters which are rich in nutrients as a source of cooling tower makeup (Puckorius and Strauss, 1995), (British Electricity International, 1992).

Microbiological control is achieved in several different ways. The most commonly used toxicant is still chlorine. Biocides and biodispersants are also used extensively.
In order to treat the problems of scaling, corrosion and fouling, it is important to first identify which of the problems is occurring. It is of importance that there is also an understanding of the process and water side of the system. The two types of open cooling water systems which are in use in Eskom are once-through cooling and open recirculating.

Treatment of once-through cooling water systems

As mentioned in **Chapter 1**, once-through cooling is only used at the Koeberg nuclear power station and hence will only be dealt with briefly. In once-through systems cool water is withdrawn from its source, heated and the returned to the receiving source which

subsequently increases in temperature. Hence in these systems large quantities of water are used for cooling.

Corrosion control in once-through systems is complicated due to high costs and the effects that inhibitors may have on the environment. Therefore materials of construction are chosen to minimise corrosion. Control can be achieved by using inorganic phosphates which may be combined with zinc and / or silica. They are capable of reducing corrosion rates by up to 90 % (Nalco, 1988). Polyphoshates are used extensively as they can provide protection against corrosion and scale through a mechanism called threshold stabilisation. Low concentrations of inhibitors can be used, as corrosion is not normally severe in once-through systems (Drew, 1979).

Scale in once-through systems is normally the result of calcium carbonate build up. The other forms of scale mentioned above are rarely a problem in once-through systems since the salts are more soluble and there is no concentration effect. Scaling can be reduced by the addition of polyphosphates, phosphonates and acrylate polymers. These inhibitors interfere with the potentially scaling ions and prevent crystal growth. They also condition crystal nuclei to prevent their growth on heat transfer surfaces (Nalco, 1988).

The quality of water used has a direct bearing to fouling in once-through systems. One approach is to condition foulants by applying specific polymers which results in the conditioned material being carried out of the system. A more widely used approach involves the dispersion of suspended solids into smaller particles which prevents their agglomeration and settling. The choice of dispersants includes surfactants and low molecular weight polymers. The majority of fouling problems are complicated by microbial activity resulting in slime deposits on tubes. In sea water the growth of macro-organisms such as mussels will occur (British Electricity International, 1992). By-products of bacterial activity affect water chemistry, including the tendency for scale to form and metal to corrode. A programme of biocide and biodispersant dosing can go a long way towards solving this scaling problem (Nalco,1988).

Treatment of open recirculating systems

An open recirculating system incorporates a cooling tower to dissipate heat. The water is taken from a cooling tower basin, passed through the condensers where it effects cooling and then returns to the cooling tower where the water that evaporates cools the water that remains. This cycle is continually repeated with sufficient water makeup added to balance the water evaporated and that blown down from the system. This is carried out not only to maintain the correct amount of water to run an efficient system, but also to ensure that the chemical composition of the water is maintained within certain specified limits. This greatly reduces water demand and discharge. Cooling towers are designed to evaporate water by promoting the contact of water with air. The types of cooling towers used in Eskom are called hyperbolic cooling towers. (**Fig. 2.2**) These are natural draught cooling towers, where due to the hyperbolic shape, an upward airflow is created which is in counterflow to the falling water.The material used for the construction of the cooling towers in Eskom is reinforced concrete, which has the following advantages over other materials; its strength, low maintenance and the design flexibility (McKelvey and Brooke, 1959).

Fig 2.2 : Schematic view of a hyperbolic cooling tower
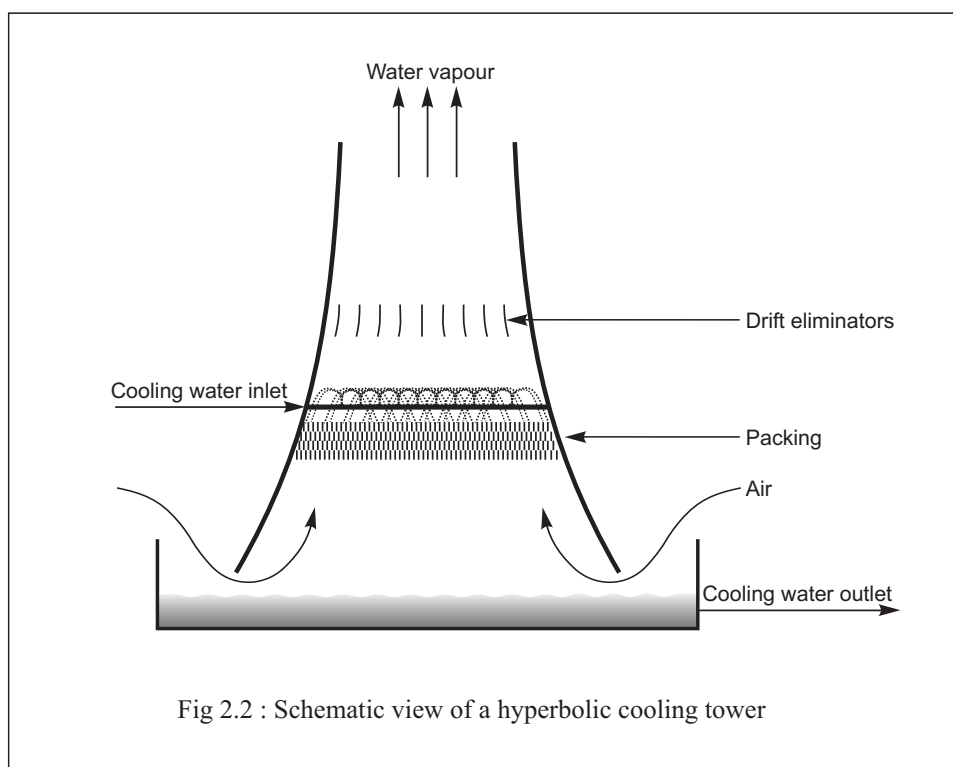
In every cooling water system there is a unique combination of equipment, water chemistry, contaminants, blowdown, and control considerations. There are five main categories which have to be considered : cooling system data, cooling water chemistry, heat transfer, effluent regulations and existing treatment and control methods (Nalco, 1988).

The purpose of the blowdown procedure is the removal of concentrated water, which mainly results in the maintenance of the solids content of the water within specified limits (Betz, 1980).

The cooling system data includes the physical and engineering aspects such as type of heat exchanger, construction materials, temperatures of operation at different parts of the circuit, and system characteristics such as velocities, makeup, bleed-off, etc. (Nalco, 1980).

The cooling water chemistry defines the chemical environment of the system. This would include the chemical composition of the cooling, clarified cooling and makeup waters and their treatment. The causes of poor makeup water and persistent sources of contamination should be investigated (Nalco, 1980), (British Electricity International, 1992).

The heat transfer activities can be considered in four parts; heat transfer coefficients monitoring; heat transfer control; conditions which affect the physical condition of the heat exchange equipment; and the cleaning procedure which includes both mechanical and chemical cleaning procedures (Nalco, 1988).

When considering chemical treatment, plant effluent regulations must be taken into account as the treatment chemicals will impact on the effluent quality. It is important to know how a chemical treatment regime will affect effluent treatment.

Chemical control, monitoring of results, and corrective action are required for an effective cooling water treatment programme (Nalco, 1988). In order to maintain chemical control the following types of analyses have to be carried out ; water analyses, deposit analyses, corrosion and deposition monitoring, metallographic analyses and microbiological analyses. The important variables which require controlling are calcium and magnesium hardness which affect scaling; total alkalinity, pH and temperature which affect the

concentrations of carbonate and bicarbonate ions in the water; and most important the solubility of calcium carbonate. Sulphate, silica and phosphate concentrations must also be maintained at reasonable levels to prevent the formation of gypsum, silica and phosphate scale. High concentrations of sulphate are detrimental to the concrete structures in the cooling water system i.e. the cooling towers.

Since cooling towers scrub the air passing through them, the atmosphere has a large effect on the efficiency of the cooling system. In areas where dust presents a problem, side-stream filtration is required. The presence of alkaline or acidic gases in the atmosphere is a more complex problem as they affect the pH of the system which in turn may be affected by the wind direction. Carbon dioxide is one of the most prominent of the acidic atmospheric gases and its content in the cooling towers varies according to local atmospheric conditions. The carbon dioxide content is related to the alkalinity and the pH and hence, if it varies, the alkalinity has to be altered in order to maintain the pH at the correct level. So, under varying atmospheric conditions it becomes difficult to predict what alkalinity is required for correct pH maintenance.

Inorganic or organic inhibitors are used for corrosion control in open recirculating cooling water systems. Inorganic inhibitors include zinc, orthophosphate and polyphosphate. Organic inhibitors include organic phosphorous compounds, specific synthetic polymers, organic nitrogen compounds and long-chain carboxylic acids.

Deposit control in cooling water systems is essential for maintenance of heat transfer rates (Nalco, 1988). Since cooling water systems are alkaline, control of deposits is more difficult than in lower pH systems. These deposits have three different sources namely raw water, airborne and in the recirculating water itself. The nature of the deposit must be accurately determined in order to choose the correct dispersant.

2.2.2   THE CLARIFICATION PROCESS

After cooling water has been passed through the condensers approximately 5 to 10 % is bled off to the clarifiers with the remainder flowing back to the cooling towers. The flow through the cooling water clarifiers varies in order to keep the alkalinity within specification. Maximum efficiency of the clarifier, in terms of alkalinity removal is known

to be approximately 50 %. At certain power stations control of the clarifiers is made difficult by the fact that lime addition is not automated and that the retention time in the clarifier is approximately 8 h, while lime dosage may require adjusting every 2 h.

The clarification process is made up of three distinct procedures; coagulation, flocculation and sedimentation (Drew, 1979). If any one of these three processes is adversely affected the clarification process will not be optimal. Coagulation involves the addition and rapid mixing of a chemical coagulant with the water. This results in a chemical reaction which neutralises colloidal charges and forms a precipitate which is called a floc. Flocculation takes place after coagulation and involves the joining of all the individual flocs together which is necessary because larger particles have faster settling speeds. This is achieved using gentle agitation which has to be carefully controlled to prevent breaking up of the newly formed flocs. In the sedimentation process the aggregated flocs are allowed to settle, the clarified water rises which affects the waters separation from the sediment. The sediment is removed as sludge.

2.2.3 THE TYPE OF CLARIFIERS USED IN ESKOM

The clarifiers used in Eskom are designed in such a way that the three procedures take place in one unit. The type of clarifier used is called a sludge blanket clarifier. In this type of clarifier the floc solids are maintained in a fluidised blanket through which the water flows. As the sludge passes through the blanket the larger floc settles to the bottom due to gravity and the remaining finer floc is removed by straining and adsorption. Flocculation and solids concentration in the reaction zone is controlled by variable speed mixers.

2.2.4 THE LIME SOFTENING PROCESS

Cold lime softening is one of the major precipitation softening procedures used in Eskom. It is called cold lime softening because the procedure is carried out at ambient temperatures. Hydrated lime, $Ca(OH)_{2(s)}$ also called portlandite is added to the water, resulting in the following reactions taking place;

$$CO_2 + Ca(OH)_2 \div CaCO_{3(s)} + H_2O$$
$$Ca(HCO_3)_2 + Ca(OH)_2 \ddot{y} \ 2CaCO_{3(s)} + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \ddot{y} \ Mg(OH)_{2(s)} + 2CaCO_{3(s)} + 2H_2O$$
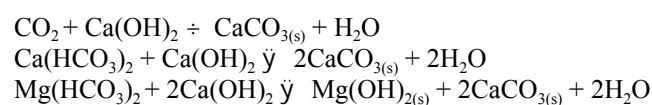
Lime addition forces the precipitation of calcium carbonate ($CaCO_{3(s)}$), thereby reducing

the amount of calcium bicarbonate in the water. Lime addition also has the affect of removing magnesium alkalinity. However, twice the amount of lime is required to remove magnesium alkalinity compared to the amount required to remove calcium alkalinity and the calcium will increase to the extent of the magnesium reduction. The added benefit is the reduction in total dissolved solids.

2.3   INDIRECT DRY COOLING SYSTEMS

The Kendal and Majuba power stations utilise indirect dry cooling systems. For each unit there is one cooling water system which includes a cooling tower containing tubular heat exchangers, three circulating pumps, one hot and one cold duct and a condenser. The circulating water cools the condensate in the condenser. Once it has cooled the condensate, the circulating water (now at 49 $^{\circ}$C) flows to the cooling tower along the hot duct. It is then cooled in the heat exchangers by the natural draught created within the cooling tower. The cooled water then flows through downcomers from the tube bundles. The circulating water (now at 34 $^{\circ}$C) is then returned to the condenser via the cold duct thus completing the closed circuit (Anon, Chemistry Standards and Procedures For the Closed Cooling Systems at Kendal Power Station).

The water used in this system is demineralised and contains free oxygen. The water is treated with hydrazine which reacts with any free oxygen to produce water and free nitrogen, thus inhibiting corrosion.

If the dissolved oxygen in the cooling water is not reduced, it promotes oxide formation. The hydrazine reacts with the ferrous oxide if present to form magnetite which is very stable and protects the steel.

Since the volume of the water in the cooling circuit changes with changes in temperature it is not possible to achieve a completely closed system. To minimise the ingress of oxygen as much as possible, a nitrogen blanketing system is used. This supplies nitrogen at a pressure of 2 kPa to the free surface of the water in the head tank and storage tanks as well as to the headers of the cooling bundles.

2.4   DIRECT DRY COOLING SYSTEMS

Matimba power station utilises direct dry cooling. In this case cooling towers are not used. Exhaust steam from the turbine is passed to the heat exchanger. Air is driven through the exchanger by forced draught fans to remove the heat. The cooled water is then pumped back to the boiler (Anon, Chemistry Standards and Procedures for the Closed Cooling Systems at Kendal Power Station).

2.5   THE COOLING WATER SYSTEM AT MATLA POWER STATION

The cooling water circuit is operated according to Eskom's chemistry guidelines for cooling water (GGG 0518 rev. 1). This document lays down the chemical limits, inter-related limits and control ranges. The guidelines are of a general nature and therefore are not specific to any particular plant.

Since this investigation was carried out at the Matla power station, a detailed description of that cooling water system is given. It must be noted, however that during this investigation the cooling water circuit underwent several changes, resulting in the research work having to adapt to these changes.

At the beginning of this investigation and for most of its duration, the raw water supplied to Matla power station came from the Usutu-Vaal river system. During 1994 work commenced on the additional supply of Usutu water to the power station with the switch over occurring towards the end of 1994. Preparatory work on the best ratio of Usutu-Vaal to Usutu water to use for the raw water supply was required. A portion of this work included chemical speciation modelling of the two water supplies. Generally, using MINTEQA2, the lower the concentration of contaminants in the water the better it is as there is less chance of precipitation. However, several other aspects had to be considered, one of the most important being the ease of flocculation of the raw water. Normally the more contaminated the raw water is the easier it is to flocculate.

The southern cooling water circuit consists of three 45 m diameter clarifiers, the first, (RAW CLAR) treats raw water for make-up to the cooling towers and for raw water production. The second, (RW/CCW), is a dual purpose clarifier which treats raw or cooling water depending on station conditions. The third clarifier, (CCW), treats a cooling water side stream, removing turbidity, alkalinity and hardness ions. The cooling water treatment plant of Matla power station is represented schematically in **Fig 2.3**.

Fig 2.3 : Schematic diagram of the cooling water treatment plant
at Matla power station

1 - 6	Cooling towers	10	CCW
7	Re-carbonisation units	11	Southern cooling water pumphouse
8	RAW CLAR	12	Northern cooling water pumphouse
9	RW/ CCW		
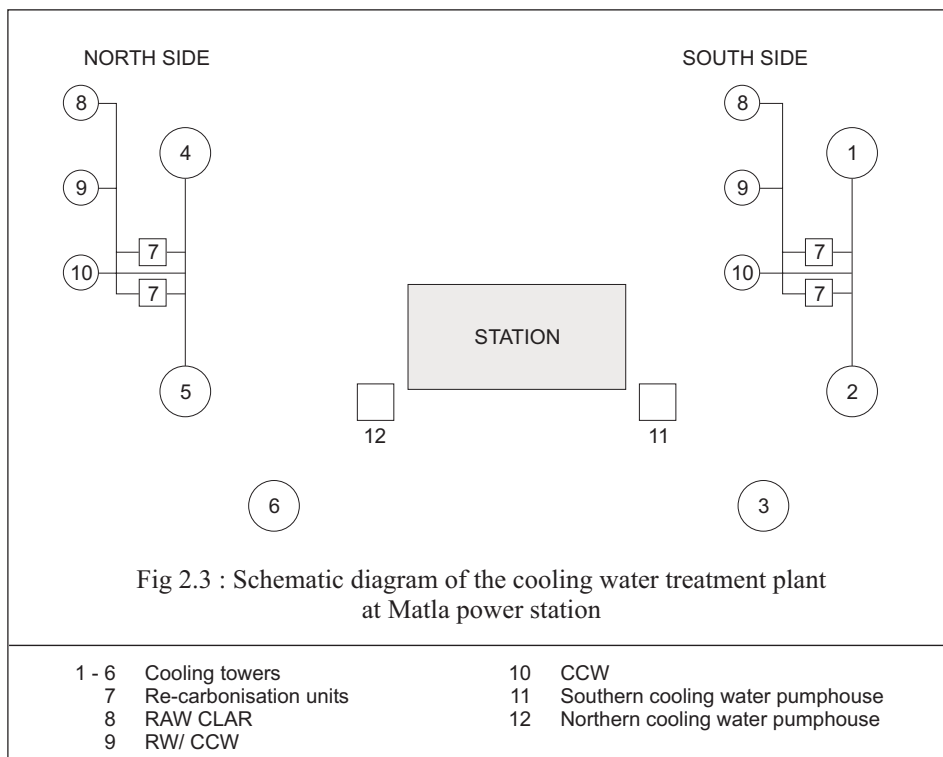
The cooling water is blown down to maintain the concentration of cations and anions, which are not removed during the clarification process, within specification.

The overflows from the clarifiers are combined, and at the beginning of the investigation were routed through the recarbonisation unit, where flue gas was bubbled through the water. The purpose of the recarbonisation unit is to add carbon dioxide to the cooling water for pH and alkalinity control. Flue gas contains 14 % carbon dioxide, 5 % oxygen, 6 % water vapour, 800 mg/m^3 sulphur dioxide and 500 mg/m^3 mixed nitrous oxides. The remainder of the flue gas is nitrogen gas. At the end of 1993 the recarbonisation unit was taken out of the circuit as it was not resulting in a decrease in scaling of the cooling water circuit. The combined water then flows into the basins of the cooling towers. The cooling water from the towers is then pumped into the power station where it passes through the condensers. The cooling water then passes through a series of ducts, 5 to 10 % is bled off to the clarifiers and the remainder flows back to the cooling towers.

At the time of this investigation, it was reported that the average amount of raw water used for make-up purposes was 26.3 Ml/day and approximately 1.55 Ml of cooling water was evaporated per day (Wessels, 1996).

For the on-line, day-to-day physical cleaning of the condenser tubes, abrasive balls are injected into the inlet of the condenser. These balls are caught at the outlet of the condenser in a basket and are then recirculated. The balls, which are compressible, start off with a larger diameter than the tubes and once they become smaller they are discarded. A blockage of the tubes is indicated by either an increase in the condenser back-pressure or inadequate steam heat transfer. Another indicator of tube blockage is when the number of abrasive balls retrieved is lower than the amount injected. When the degree of tube blockages has reached an unacceptable level, the condenser tubes are

cleaned off-line under high pressure, either by hydrochloric acid or water.

2.5.1 RAW WATER TREATMENT

The raw water is prechlorinated prior to entering the clarifiers. Polyaluminium chloride and polyelectrolyte are generally used as flocculants although alum and a polyelectrolyte are sometimes used.

2.5.2 GENERAL OVERHAUL OF THE SOUTH SIDE OF THE PLANT

The south side of the plant underwent a complete overhaul in January 1994 and was back on line at the end of March 1994. This resulted in the opportunity to study the cooling water as the concentration of contaminants increased.

2.5.3 ANTISCALANT DOSING

At the Matla power station fresh ash is conditioned by adding water to form ash water which can then be transported by a conveyer. The ash water is strongly alkaline and many trace metals are immobilised as hydroxides (British Electricity International, 1992). Due to the alkaline properties of the ash water it can be returned to the clarifiers for cooling water treatment purposes.

Due to the scaling problems experienced at Matla power station during 1993, it was decided that all raw water used for cooling purposes should be treated with an antiscalant before entering the cooling water system. On the north side of the plant the descaling chemical used was a mixture of polymaleic anhydride and polymaleic acid at a dosing rate of 6.5 mg/l, the active ingredient being the COOH groups which release H^+ and hence have an affinity for all cations. In the short term the use of this antiscalant had been useful in the removal of existing scale and the dosage was reduced when sufficient scale had been removed. The whole system is further complicated by the use of biologically active ingredients such as biodispersants.

By the end of September 1994 the antiscalants were continuing to prove effective against scale build-up. During an outage in September 1994, tower 3 was inspected and there was no evidence of organic fouling or scale deposit.

2.6 LITERATURE REVIEW OF ANTISCALANTS

In a report by Venter (1984), various calcium carbonate inhibiting chemicals were tested to

establish an economical method of preventing the scaling of ash water return systems. The influence of these chemicals on the flocculation processes and on the building of ash dams was also investigated.

It was found that the scale build-up in an untreated cooling water system was approximately 60 times greater than in a treated system. None of the chemicals tested had a negative effect on the flocculation process. It was also assumed that the chemicals would not influence the building of ash dams as they only influence the calcium carbonate crystal structure.

It was recommended that scale inhibiting materials be used at power stations experiencing the problem of calcium carbonate scale in ash water return systems.

The presence of a scale inhibitor results in an oversaturated solution of calcium carbonate being dispersed. The inhibitors are polymers which increase the surface charge of particles, keeping the particles in suspension so that crystal growth is inhibited. Without a scale inhibitor, crystal growth takes place spontaneously due to the availability of suitable growth nuclei. These nuclei are present as suspended solids and deposit on rough surfaces in the pipe, especially if crystal growth is already present at these sites.

Pressly (1989), conducted tests to evaluate antiscalant formulations available on the South African market. The organophosphorus compounds were found to be good crystal modifiers and hence strong stabilising agents, however they are usually poor dispersants. Conversely, polyacrylates and related compounds are strong dispersants and since they operate by a charge repulsion mechanism, are relatively poor calcium carbonate stabilisation agents. Hence, the most effective dispersants are combination products as they take advantage of the two distinct mechanisms.

According to Dernat et al. (1985), an attractive analytical method for the study of scale inhibitors in cooling water, is the use of a glow discharge lamp (GDL). The lamp is used to produce a discharge which occurs under low pressure conditions and the region of interest appears to glow with considerable intensity. Electrons are excited and consequently emit light (Parker, 1992). Their aim in using GDL was to understand the complex phenomena that occur in cooling water systems clearer. They identified three main mechanisms of protection :

- using chromate or phosphate treatments, a chemical reaction occurs between the inhibitor and the metal ion,

- at a basic pH the growth of an unreactive protective layer is limited by antiscale treatment, and

- zinc always remains on the outside of the protective layer.

  In a report issued by Martynova et al. (1991), several aspects of antiscale dosing were investigated, including, the surface energy changes of calcium carbonate and magnesium hydroxide nuclei, and the dependence of mass transfer coefficients on antiscalant dosages. It was found that, in the presence of antiscalants, there was a relationship between nuclei formation moderation and the increase in the crystal specific energy. The Gibbs-Folmer model was used as a basis for the calculations.

  The effect of treatment chemicals on both scaling and corrosion was investigated by Ohler and Hollingshad, (1985). The investigation centred around phosphorous-containing compounds both alone and in combination with dispersant / inhibitor polymers. In their case they found that a sulphonic acid / acrylic acid coploymer gave the best results. Advantages of this system were the effective control of zinc corrosion and the superior dispersion of silt and metal oxides. Using this system there was a substantial improvement in corrosion inhibition.

2.7   CONCLUSION

Cooling water systems have been identified as having a complex chemistry. When considering cooling water treatment, the most important factors to consider are scaling, corrosion and fouling. Different types of cooling systems have been discussed and the focus was on open recirculating systems as this was the type of system in operation at the Matla power station at the time of this investigation.

The cooling water system at the Matla power station has been discussed, together with a major change in its treatment, the addition of antiscalants, which occured during the investigation.

Chapter 3
EQUILIBRIUM CHEMICAL SPECIATION

MODELLING

The aim of this chapter is to give a detailed account of computer based chemical speciation modelling. The theory behind the models and the models available at the time of this investigation will be critically discussed. The only available models at the time were based on thermodynamics which assume that the water system in question is in equilibrium. The problems associated with this type of modelling are that not all water systems are in equilibrium, and kinetics (speed of reaction) are not taken into account. Since MINTEQA2 was the model chosen to carry out the investigation, the reasons for the choice and a complete description of MINTEQA2 is given. This **Chapter** also includes a discussion on the advantages and disadvantages of MINTEQA2 and suggestions on ways in which the program can be improved.

3.1   AVAILABLE CHEMICAL SPECIATION MODELS

Stasoft is a program developed by Loewenthal et al.,1988, which addresses pH and calcium carbonate precipitation potential and is limited to low salinity waters, with total dissolved solids content (TDS) of less than 1 000 mg/l. One of the outputs of the work of Friend, 1990, which extended Stasoft so that it could be applied to waters with TDS values up to 15 000 mg/l by including ion pairing effects between the major cation and anion species, was the development of the program, STASOFT Ver 3. This program is user-friendly, and provides information on the total concentration of selected dissolved species present: final pH and temperature, total dissolved solids, conductivity and ionic strength values, bicarbonate alkalinity, carbonate acidity and calcium carbonate precipitation potential. The strengths of the program are that it can predict the quantity of chemicals required to achieve a desired task, and that the data input is quick and easy. The disadvantages are that it does not include data for transition metals, and does not include calculations on the precipitation potential of compounds other than calcium carbonate (calcite) and magnesium hydroxide (brucite). The program is therefore applicable to aqueous solutions where the carbonate system dominates all other reactions, but cannot be used to solve general speciation applications. This database cannot be expanded as it is fixed.

PHRQPITZ is a FORTRAN computer program which is capable of making geochemical calculations in brines and other highly concentrated electrolyte solutions using the Pitzer virial-coefficient approach for activity coefficient corrections. *Reaction modelling capabilities include calculation of (1) aqueous speciation and mineral-saturation index, (2) mineral solubility, (3) mixing and titration of aqueous solutions, (4) irreversible reactions and mineral-water mass transfer, and (5) reaction path.* Two advantages of this program are its ability to address high concentration equilibria (which is particularly relevant to cooling water) and its mixing and titration capabilities. A disadvantage of the program is that it is not user-friendly and that source codes are required as input data. PHREEQE was the predecessor of this model, which works on the same principles, but is used for solutions of lower concentration. PHREEQE is capable of following one or more phase boundaries and calculating the pH, pe, mass transfer and aqueous phase speciation as dependant variables in the calculations. PHREEQE has the same disadvantages as PHRQPITZ. Both computer programs are user modifiable and the programs could be used to advantage when considering the mixing of different sample streams. (Lujan and Peck).

MINTEQA2 is a geochemical speciation model for dilute aqueous solutions, in which particular attention is paid to the transport and speciation of metals. The program was developed for the United States Environmental Protection Agency (US-EPA) as a tool for environmental risk assessment and hazard evaluation. MINTEQA2 was developed from MINTEQ (Felmy et al, 1984). MINTEQ combined the fundamental mathematical structure of MINEQL (Westall,1986) with the thermodynamic database of the WATEQ3 model (Ball et al, 1981). MINTEQA2 is an improvement on MINTEQ as it contains PRODEFA2, an interactive program used to create input files for the main speciation program. The way in which calculations are implemented and the features and options also differ. A broad outline of the program's capabilities is that it can compute equilibria among the dissolved, adsorbed, solid and gas phases in solution. This program is capable of satisfying most of the aims of the project, and because of its user-friendliness was chosen as the best option for investigating occurences in cooling water.

In the literature MINTEQA2 has been used extensively for chemical modelling purposes (Lumsdon and Evans,1996). In some cases the model has been added to or modified in order to obtain more specific outputs. For example the model has been used to simulate changes in concentration of aqueous

constituents along a flow path in an aquifer in Arizona (Stollenwerk, 1994). Here a geochemical model was developed and used in MINTEQA2. In another application, SOLTEQ, which was developed from MINTEQA2 was used to calculate concentrations of contaminants in both mobile and immobile phases and to provide mechanisms to integrate chemical information from a variety of systems, including cementitious-pozzolanic systems such as soils or wastes by stabilization / solidification (Merritt, 1993).

The data required to predict the equilibrium composition consist of a chemical analysis of the sample to be modelled, giving total dissolved concentrations for the components of interest, and any other measurements e.g. pH or the partial pressure of one or more gases. Also, a mineral may be specified as possibly present at equilibrium, but subject to dissolution if equilibrium conditions warrant, or definitely present at equilibrium and not subject to complete dissolution.

3.2 CHEMICAL AND MATHEMATICAL CONCEPTS USED IN MINTEQA2

Two approaches are presently used in different speciation programs to formulate and solve multi-component chemical equilibrium problems. The one minimises the system free energy under mass balance constraints and the other, which is used by MINTEQA2, simultaneously solves the non-linear mass action expressions and linear mass balance relationships. The non-linear equations are solved iteratively.

After equilibrating the aqueous phase MINTEQA2 computes the saturation index (SI) for each possible solid with respect to the solution. The solid with the most positive SI is allowed to precipitate by depleting the dissolved concentrations of those components which comprise the solid. The reverse process is carried out if the solid is undersaturated with respect to the solution. The aqueous solution will then be re-equilibrated. Thus the aqueous solution is re-equilibrated just as before except with one less degree of freedom if precipitation has occurred or one more if dissolution has occured. The number of degrees of freedom of the system is the number of independent variables. These would normally include temperature and partial pressure of relevant components (e.g. CO_2), but since they are both specified as invariant by the user, MINTEQA2 modifies the "phase rule" as follows :

$$f = C - P$$

where   f = the number of degrees of freedom,

          C = the number of components, and

          P = the number of species with fixed activity and the number of finite solid species.

The use of the term "phase rule" is not correct, the use of the term "degrees of freedom" being more appropriate, related to the system of equations used by MINTEQA2, which does not include all the relationships which govern chemical and phase equilibrium. In particular, it does not consider the effect of total pressure.

If f is greater than zero MINTEQA2 will proceed with the calculations. If not a "phase rule" violation will occur. The manual (Allison et. al., 1990) provides the user with reasons for "phase rule" violations and how to overcome them. These violations can occur when only a few determinands are entered into MINTEQA2, especially when the solids option is allowed. These violations can be avoided by entering extra components (e.g. sodium, potassium, nitrate, etc.) which are not strong complex formers and hence do not effect overall precipitation potentials. Another reason for "phase rule" violations occuring is when too much data is entered in one run, which can be avoided by simplifying the problem and taking one step at a time (Kerr, 1994).

Redox reactions and adsorption models are available in MINTEQA2. Redox reactions have not been used in this thesis, however adsorption models have been used to a limited extent and so will be described briefly. Seven adsorption models are available in MINTEQA2 for modelling surface reactions. These include the activity K_d model, the activity Langmuir model, the activity Freundlich model, the ion exchange model, the constant capacitance model and the diffuse-layer model (Loux et al., 1990). As the thermodynamic database files of surface reactions are not provided for these models, it is up to the user to provide the set of surface reactions and their equilibrium constants. Mathematical formalisms and input data requirements of the individual adsorption models are thoroughly discussed in the users manual.

3.3   EXPERIMENTATION WITH THE PROGRAM

The application of the equilibrium model to a water problem involves the following four steps :

- formulate one or more precise and relevant chemical questions that can be answered if one knows the equilibrium composition of the system,

- formulate the questions in terms of the structure and coventions of the program,

- use the computer to solve the mathematical problem, and

- interpret the output from the model in terms of the original chemical problem.

Step 1 is the most difficult part of the process, as the chemical question must be correctly formulated, taking degrees of freedom into consideration. An example of a question that was put to the system was *After analysing for the dissolved content of cooling water at 25 $^{\circ}$C, compute how the dissolved content of that water will change with every 5 C$^{\circ}$ increase in temperature.*

For **step 2** the full chemical analysis of a cooling water analysed at 25 $^{\circ}$C was transformed to independent species as defined in MINTEQA2, and the multi-problem generator was used to enter the same set of results from 5 $^{\circ}$C to 95 $^{\circ}$C.

Step 3 is carried out entirely by the computer program after entering a series of commands.

The outputs of the model are complex, but major points of interest are the quantity and composition of precipitating solids, the equilibrium distribution of species in solution, pH value and if the program has been allowed to compute it, quantity and composition of adsorbed species, etc.

3.4 PROCEDURE FOR SPECIATING RAW, COOLING AND CLARIFIED COOLING WATER

3.4.1 INITIAL PROGRAM INPUTS

- The temperature was set at 25 $^{\circ}$C as this was the temperature at which the analytical results were obtained.
- Units of concentration option (**mg/l**) was chosen as these were the units of analysis.
- Inorganic carbon was entered as total alkalinity with the unit chosen being mg/l $CaCO_3$.
- The maximum number of iterations was increased from 40 to 200 to prevent the premature termination of the program for complicated solutions.
- The measured pH was entered.
- Finally in this initial simulation each individual anion and cation was entered.

3.4.2 CONVERSION OF ALKALINITY AND pH TO CONSERVED SPECIES

After the initial simulation was undertaken, the output contained conversions of alkalinity and pH values into conserved species such as carbonate and total proton concentrations. These values were necessary for further simulations to establish precipitation potentials and the effect of changing the chemistry of the system. In order to undertake this run it was necessary to specify the *no solids* option. This option does not allow solids to precipitate.

3.4.3   SPECIATION

The second simulation was undertaken using the carbonate and proton concentration outputs. Prior to entering these results the units of concentration were converted to molar as all MINTEQA2 outputs are in molar form. The simulation was then carried out using the *solids precipitation* option. The output indicates the amount and nature of the precipitates (if formed) and the composition of the remaining solution.

3.4.4   CONTACT WITH THE ATMOSPHERE

The output from **Section 3.4.3**, including the solids, if present, is then speciated with carbon dioxide at standard partial pressure (i.e. $10^{-3.5}$ atm). Simulations can be undertaken to evaluate the effect of changes in carbon dioxide partial pressure.

3.4.5   DISSOLVED ORGANIC MATTER

The presence of dissolved organic matter, DOM, will effect the speciation of inorganic species. MINTEQA2 has a DOM sub-model (Centre for Exposure Assessment Modelling, 1991) based on the work of Susetyo et al. (1991) which computes the complexation of various metals with dissolved organic matter. This model treats dissolved organic matter as a complex material consisting of many different types of monoprotic sites (Dobbs et al., 1989). This simplistic approach has been taken due to the analytical difficulties in identifying all of the organic compounds present and is known as the composite ligand approach in which the binding affinities are considered as a continuous spectrum. Runs can be undertaken to assess the effect of including total organic carbon on the system.

3.4.6   FURTHER INPUTS

Once the above four steps have been carried out, a *seed file* for any further manipulations will have been created. Further work will involve the use of other menu options which will vary according to the type of outputs required.

3.4.7   SURFACE ADSORPTION

The effects of surface adsorption can be modelled by assuming that the properties of adsorption surface, regardless of its original state, will be controlled by a surface layer of amorphous ferric hydroxide (Kerr, 1994). Support for this assumption can be found in the

literature (Loux et al., 1990), (Dzombak and Morel, 1990) . In MINTEQA2, a separate database file called FEO-DLM.DBS is provided. This database contains surface reactions which are applicable to the Diffuse Layer Model for adsorption of some metals and ligands onto an amorphous iron oxide surface. The EPA have calculated the values required for this model based on average porosity, dry density and amorphous iron concentrations of some aquifer materials.

3.4.8   PREDICTION OF CONDUCTIVITY USING MINTEQA2 OUTPUTS

In a poster by Brouckaert et al., 1996, a method for predicting conductivity using MINTEQA2 outputs was given. The equilibrium speciation was used to obtain the distribution of ions present in solution. Other values that were required for the calculation were a limiting specific solution conductivity at 20 $^{\circ}$C calculated from the distribution of ions and the limiting equivalent conductivities of the original ions, a correction for concentration of similar form to the Kolrausch law and a correction for temperature. These calculations are included in tables of results found in **Appendix 2**, together with the calculated cation/anion balances.

3.5   FLEXIBILITY OF THE PROGRAM

The database comprises of about 1 400 species, however the program allows users to add their own species, reactions, etc. to the database, provided that the user has the relevant thermodynamic information. For example, to add a new species to the database the enthalpy, logK, and formula of the reaction product species is required. A series of commands have to be carried out during this process, however this is well documented and easy to follow. Important aspects of these commands are:

- make a backup copy of the file to be modified,
- modify the required databases e.g. a new aqueous species need only be entered in THERMO.DBS, whereas a new solid must be entered in THERMO.DBS and TYPE6.DBS, and
- ensure that the codes and thermodynamic values are entered in the correct positions (Allison et. al., 1990).

The program has many user friendly features e.g. it is capable of interconverting units of concentration which can be entered as molal, mg/l, ppm or meq/ml. Hence, since the program converts all the units

to molal, it is not necessary for the user to carry out this computation and the more usual unit of mg/l can be entered.

3.6   LIMITATIONS OF THE PROGRAM

- Water is presumed to exist at constant activity. This is a good assumption for all dilute solutions because the mass of water present is several orders of magnitude greater than the other components. This factor must be borne in mind for the more concentrated solutions.

- Caution should be used in attempting to apply MINTEQA2 to high temperature systems, as MINTEQA2 was not designed to handle high temperatures. The van't Hoff equation, which corrects the equilibrium constant for temperature variations from 25 $^\circ$C, implicitly assumes the enthalpies of reaction to be independent of temperature, therefore significant errors can result at temperatures above 25 $^\circ$C. Only a single $\log(-\vert G^0/298*R)$ value is entered into the database which does not allow for the maximum and minimum solubilities which occur with many species.

- The model is an equilibrium model which does not take kinetics into consideration. Hence, the model may perfectly validly predict that a particular solid may precipitate, but the precipitation process may be such a lengthy one that such a precipitation will be of insignificance in a real water system.

- The model is not equipped to work out final equilibrium conditions for a mixture of one or more water streams. The user has to sum the conserved parameters before undertaking the entering of the chemical parameters into MINTEQA2.

- Errors have been found by Serkiz et al., (1996) in the equilibrium formation constants between metals and organic ligands e.g. EDTA and citrate, contained in the MINTEQA2 database. Inorganic complexes do not appear to be affected by this problem. Two classes of errors have been defined, namely those that occur because the reaction is not properly expressed in terms of MINTEQA2 components, and those that arise due to the reaction log K value not being referenced to zero ionic strength and 25 $^\circ$C. These errors can be corrected if an understanding of the database and how it works exists. The log K and standard enthalpy of reaction, $\vert H^0$ is normally reported in the literature as a solubility product constant which

is opposite in sign to that required by MINTEQA2. Also, all reactions must be reformulated in terms of MINTEQA2 components the convention being that reactions must be written as formation reactions using only MINTEQA2 components on the left hand side and one and only one product on the right hand side. The product cannot be a MINTEQA2 component (Serkiz, et al).

3.7   IMPROVEMENTS THAT WOULD ENHANCE THE PROGRAM

● Automatic transfer of results to Windows based programs, i.e. spreadsheets and graphical packages.

● Expansion of the database to contain $\log(-\lvert G^0/298*R)$ values at different temperatures.

● The ability to enter several water streams with their concentrations and percentages of each stream and obtain final concentrations of the mixture.

● As most computer users are more comfortable using Windows based programs the program would find a wider market if a front end was developed using Windows.

3.8   CONCLUSION

There is a potential for the use of personal computer based chemical speciation modelling as a tool for a better understanding of cooling water circuits. The model chosen for evaluation, mainly because of its user-friendliness and the size and flexibility of its database, compared to other models available at the time was MINTEQA2. Using the model, a procedure was developed for speciating raw, cooling and clarified cooling water, the different types of water all forming an integral part of the cooling water circuit.

The advantages and limitations of MINTEQA2 have been assessed and bearing them in mind it was decided to investigate the model's use on an Eskom power station cooling water circuit.

Chapter 4
EXPERIMENTAL TECHNIQUES

This **chapter** describes the experimental methodology used by the analytical laboratory at Eskom's Technology, Research and Investigations (T-R-I) Division during the investigation. A brief summary of the experimental techniques is given, with a more detailed discussion in **Appendix A1**. Since results produced by the Matla power station are included in **Appendix A2** and in **Results and Discussion**, the experimental techniques used by the power station are described briefly in **Appendix A2** and the differences between the techniques used in the two laboratories are highlighted in this **chapter**. The methodology for raw water analysis and obtaining a cooling water speciation profile is outlined. The **chapter** concludes with sections on the effect of iron and other species in solution.

4.1   DESCRIPTION OF ANALYTICAL TECHNIQUES

The analytical laboratory, (T-R-I) was accredited according to SABS 0259 in 1996. Although all analyses were done prior to accreditation, procedures and methods which have subsequently been accepted were followed. Eskom Standard Methods were used in all cases and were derived from ASTM and STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER. The analytical determinations were carried out by laboratory personnel after the methods had been setup and validated by the author.

Samples were taken on site, filtered and preserved with nitric acid for samples taken for trace metal analyses. The sample temperature was reduced to approximately 4 $^{\circ}$C, and the samples were transported to Eskom's central laboratories in Cleveland, Johannesburg for analysis. For all sample and standard preparation, purified water with a resistance of 10 megohms was used. The water was treated using a Milli-Q reagent water system.

The samples were taken in plastic Kartell sample bottles which were prepared as follows:
- overnight soaking in 100 ml/l Decon cleaning solution,
- thorough rinsing with deionised water,
- overnight soaking in dilute nitric acid solution,
- thorough rinsing in deionised water, and
- rinsing with the sample solution.

All standards used were purchased from approved chemical suppliers and a quality control standard was analysed to confirm the accuracy of calibration. At least one sample in every batch of 10 samples was analysed in duplicate to confirm the precision of analysis.

4.1.1   ION CHROMATOGRAPHY

The anions (chloride, sulphate, nitrate and nitrite) were analysed by means of ion chromatography (IC). The equipment used in this investigation was a Dionex IC 2120i equipped with a Dionex HPIC AS4A separation column.

Ion chromatography is a specialised form of liquid chromatography which uses conductivity detection. The mobile phase that was used for the determination of anionic species in solution was a mixture of 0.75 millimolar sodium bicarbonate and 2.0 millimolar sodium carbonate and the stationary phase was the ion exchange resin column referred to above. Because the high conductivity of the mobile phase can mask the conductivity of the sample ions, chemical suppression was used to increase the sensitivity of the technique. Details of the technique can be found in **Appendix A1.**

All samples were kept chilled at 4 °C for storage purposes as the major anions and cations are stable at this temperature. All samples were warmed up to 25 °C, filtered through a 0.45 Fm Millipore filter and injected and hence analysis results refer to dissolved constituents only. However, since the anions determined by this technique are highly soluble, the analyses give a true reflection of the composition of the water. No sample preservation was required for these anions as they are stable in solution. Working standards were prepared by weighing out the correct quantity of the appropriate salt purchased from Merck and dissolving in MilliQ water.

4.1.2   INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

The cations (sodium, potassium, calcium, magnesium, zinc, barium, copper, iron and manganese), and silica were determined by inductively coupled plasma optical emission spectrometry, (ICPOES). The analyses were performed on a Varian Liberty 100 ICPOES, using a Babington type *v-groove* nebuliser. Riedel de Haen and Clinical Sciences Diagnostics 1 000 mg/l standards were used to prepare the working standards for elements measured.

Each element was determined at its most sensitive spectral line provided that this line was free from interference by other elements in the sample. The sample was compared directly with calibration standards.

As for the ion chromatographic analyses, all samples were kept chilled at 4 °C, warmed up

to 25 ℃ and filtered prior to analysis. Sample preservation was undertaken for the samples in which the trace metals (zinc, barium, copper, iron and manganese) were determined, in order to ensure that these metals remained in solution. If the samples were not preserved the metals would have adsorbed onto the inner surfaces of the sample containers, resulting in the analytical values obtained being lower than the true values. Sample preservation involved filtering of fresh samples on site through a 0.45 Fm Millipore filter, and then adding 1 ml of concentrated Analytical Reagent (AR) grade nitric acid per litre of sample.

4.1.3 CONDUCTIVITY

All conductivity measurements were carried out on a Radiometer CDM 83 conductivity meter. The conductivity meter is calibrated using 0.001 molar sodium chloride and then following the auto-calibration procedure in the Radiometer Users Manual. The conductivity is temperature dependent and hence all analyses were carried out at 25 ℃. Apart from the temperature, the conductivity measurement depends on the speciation, mobility, valence and total concentration of ions.

Samples were not filtered prior to conductivity measurements, as exposing them to the atmosphere results in inaccuracies (STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER). Conductivity measurements were carried out in the laboratory.

4.1.4 TOTAL ALKALINITY AND pH

Both alkalinity and pH measurements were carried out on a Metrohm 702SM Titrino autotitrator. The pH meter and associated electrodes were standardised against two reference buffer solutions which were closest to the anticipated sample pH. The pH measurement of the sample was made under controlled conditions and prescribed techniques. (ASTM)

Samples were not filtered prior to measurement, as exposing them to the atmosphere results in inaccuracies. Dissolved gases contributing to alkalinity e.g. carbon dioxide, can be lost or gained at any time from sampling to titration. To minimise this effect sample bottles were filled to overflowing, titration to the endpoint was carried out promptly after opening the sample container and vigorous shaking or mixing was avoided. No

precipitation was observed in the samples, however if a small amount of calcite had precipitated this would have resulted in lower readings than those obtained on site being recorded.

4.1.5   FLUORIDE DETERMINATION

The fluoride concentration was determined potentiometrically using an ion selective fluoride electrode in conjunction with a standard single junction, sleeve-type reference electrode and a pH meter having an expanded millivolt scale. Samples were filtered before analysis.

4.1.6   X-RAY DIFFRACTION

X-Ray diffraction (XRD) was used in this investigation to determine the composition of mineral species where appropriate. This technique is based on the measurement of diffraction of electromagnetic radiation. X-Ray diffraction instruments are equipped with extensive libraries, which are capable of matching spectra with the most likely mineral species. This application is based upon the fact that an XRD pattern is unique for each crystalline substance. If the sample contains two or more crystal compounds, identification becomes more complex. In this case various combinations of the more intense lines are used until a match can be found.

The water sample containing the deposit was filtered through a 25 mm diameter 0.8 Fm Millipore filter. The volume of water passed through the filter was dependent on the amount of deposit. The mass of deposit on the filter paper must be greater than 0.5 mg and must not exceed 10 mg. The filter paper containing the deposit was then air-dried. Oven drying was not used because of the volatility of certain mineral species. The filter paper was then placed on a glass or aluminium disk and submitted to the XRD for analysis. The aluminium disk is preferable, due to aluminium having a lower background reading, but was not used if aluminium was suspected in the sample.

4.1.7   SCANNING ELECTRON MICROSCOPE COUPLED TO ENERGY DISPERSIVE ANALYSIS OF X-RAYS

The XRD cannot detect a solid which is amorphous, and in this case scanning electron microscopy (SEM) coupled to energy dispersive analysis of X-Rays (EDAX) was used to determine the relative concentration of elements present in the solid material. It was also

proven to be an extremely useful backup technique when interpretation of XRD diffraction patterns were ambiguous.

The sample was prepared by mixing the sample obtained after XRD analysis with a carbon paste and submitting it to the instrument.

4.1.8 DIFFERENCES IN THE ANALYTICAL TECHNIQUES USED BY THE TWO LABORATORIES

The samples taken for analysis at the Matla power station did not require any sample pretreatment as they were analysed immediately. Trace metal analyses were not carried out on these samples as they are not required for the day to day running of the plant. The conductivity, pH and total alkalinity were the only analyses carried out by the same techniques as were used at T-R-I. Sodium and potassium were analysed by atomic absorption rather than atomic emission. Calcium results were obtained by hardness titration and the magnesium results were obtained by the difference between a total hardness titration and the calcium hardness titration. Chloride, sulphate and chemical oxygen demand were analysed for by titration and nitrate, phosphate and silica were analysed spectrometrically. All of the techniques used by the Matla power station laboratory are either recognised standard methods or have been validated over the many years of their use. The only difference between the techniques used by the two different laboratories is that some of the techniques used by T-R-I are more sensitive than those used by the Matla power station e.g. ion chromatography is a more sensitive technique than titration. However, since the water samples being analysed contained determinands of high concentration, the difference in sensitivity between techniques was insignificant.

4.2   RAW WATER ANALYSIS

The first step in characterising the chemistry of a cooling water circuit is to examine the raw water quality at the inlet to the power station prior to any chemical treatment. The raw water quality dictates the type of treatment and also the quantity of treatment chemicals required to achieve the desired water quality. The resultant treated water can also vary in quality with variations in raw water composition and the dosage of treatment chemicals.

Raw water samples were taken of both Usutu river and Usutu-Vaal river waters at the Kriel and Matla power station raw water sampling points. At this stage of the investigation the Kriel power

station was using Usutu river water and the Matla power station was using Usutu-Vaal river water. A full chemical analysis was carried out on three samples of each water type and the individual results were speciated using MINTEQA2. Results were assessed against a cation anion/balance prior to entering into MINTEQA2.

4.3 COOLING WATER SPECIATION PROFILE

In order to establish a speciation profile of cooling water as the concentration of contaminants increased, samples of raw water, clarified cooling water and cooling water from the recommissioned south side of the Matla power station were taken on a regular basis until the basic constituents approached a steady state (19 d) and then intermittently for two months thereafter. Each sample was analysed for conductivity, pH, total alkalinity, sodium, potassium, calcium, magnesium, zinc, barium, copper, iron, manganese, silica, chloride, nitrite and nitrate, sulphate, and fluoride (**Appendix A2**). These results were entered into MINTEQA2 and predictions studied.

4.4 THE EFFECT OF IRON IN A SOLUTION

In order to investigate the rate at which iron in solution with a neutral pH will precipitate, a ferric chloride solution was made up in raw water to contain 9.21 mg/l Fe^{3+}. Samples of the solution were filtered and then analysed for Fe^{3+} immediately and then at regular intervals using ion chromatography with post-column derivitisation and UV-visible detection. Post-column derivitisation is used because the solutes eluting from the analytical column are not detectable in their present forms by any spectrophotometric technique. A post-column reagent is added to form a derivative which is detectable. The iron concentration decreased rapidly, and the precipitate formed was analysed by XRD and EDAX.

In order to determine the amount of iron in a cooling water system, a cooling water sample was filtered, the filtrate was dissolved in nitric acid and the resulting solution was analysed for iron content using ICPOES. MINTEQA2 outputs of the cooling water solution containing the iron were then compared to those outputs where iron was not included.

4.5 THE EFFECT OF OTHER DETERMINANDS ON SOLUTION CHEMISTRY

In order to study the effect of dissolved organic matter (DOM) and phosphate the chemical analyses of cooling water south and north obtained from Matla power station were speciated

without and with these two determinands, in order to compare the results. The effect of surface adsorption modelling was studied using the diffuse layer model and iron hydroxide as the adsorption medium.

4.6   SUMMARY

Two laboratories were used to produce analytical data, one on site and one at Eskom's central laboratory, T-R-I. Although different techniques were used by the two laboratories they were all recognised analytical techniques and hence results were expected to be comparable.

The effect that different determinands were predicted to have on solution chemistry was investigated.

The knowledge gained using the analytical and speciated results was used to evaluate how MINTEQA2 could be used as a predictive tool.

Chapter 5
RESULTS AND DISCUSSION

This **chapter** commences with an experimental programme carried out in order to validate the MINTEQA2 model. This is followed by a discussion on the possibility of minerals forming. All results produced by the analytical techniques described in **Chapter 4** and in **Appendix A1** are detailed in this chapter, followed by a discussion of each set of results. All results are listed in tables in **Appendix A2**, followed by relevant speciation modelling results on each set of samples, namely the percentage distribution of components among species and the saturation indices of all minerals. For comparison purposes, all speciation modelling results reported in **Appendix A2** are based on a closed system (one from which carbon dioxide is excluded), with a fixed pH, prior to allowing precipitation. Analytical results produced by the Matla power station over the same time period and the speciation thereof are also included in **Appendix A2**, for comparison purposes. Speciation modelling results are discussed and where possible related to system chemistry. The use of MINTEQA2 as a predictive modelling tool is investigated briefly. The period over which detailed study of the south side of the plant was carried out was 28 March to 16 June 1994.

5.1   VALIDATION OF MINTEQA2

In order to use MINTEQA2 as a tool it was necessary to establish whether predicted precipitations could be simulated in the laboratory. The following experiment was carried out. A basic synthetic water sample was prepared to resemble the cooling water at Matla power station as closely as possible with respect to the major anions and cations (**Synthetic sample 1 (SS1)**). However, the sample was made up to have low alkalinity and pH values to avoid the possibility of calcite precipitation. The sample was made up by weighing out the following chemicals and dissolving them in a 2 l volumetric flask;

- 226.7 mg $CaCl_2$
- 662.3 mg $MgSO_4.6H_2O$
- 492.2 mg Na_2SO_4
- 72.2 mg KCl

The sample was then analysed for calcium, magnesium, sodium, potassium, chloride, sulphate, pH and total alkalinity. The analytically obtained values for **SS 1** were entered into MINTEQA2 rather than the calculated values (using the quantities of chemicals added to the demineralised water). The relationship between the calculated values and the analytically obtained values is given in **Table 5.1**.

TABLE 5.1
Relationship between calculated values and analytically obtained values for Synthetic Sample 1

Determinand	Calculated Value	Analytical Value
Calcium (mg/l Ca)	40.8	36.9
Magnesium (mg/l Mg)	35.3	37.8
Sodium (mg/l Ca)	79.7	74.1
Potassium (mg/l K)	17.8	19.7
Chloride (mg/l Cl)	89.7	92.0
Sulphate (mg/l SO$_4$)	306	305
pH	7.0	6.9
Total Alkalinity (mg/l CaCO$_3$)	0	<1.0

Using MINTEQA2, no precipitation was predicted to occur with this sample as no carbonate or bicarbonate salts were added. This was validated in the laboratory as no precipitation had occurred after a six month standing period. In order to try and produce a small amount of calcite precipitate from solution, a 10 liter solution was made up according to the following formulation:

- 1.7602 g CaCl$_2$.2H$_2$O
- 3.3115 g MgSO$_4$.6H$_2$O
- 2.4614 g Na$_2$SO$_4$
- 0.3615 g KCl
- 0.9333 g Na$_2$CO$_3$

The sodium carbonate was added to the solution last and no immediate precipitation was observed. An aliquot of the solution was analysed immediately for calcium, magnesium, total alkalinity, pH and conductivity. The remainder of the solution was distributed into twelve airtight 500 ml sample bottles which were filled to overflowing before being capped. Two series of sample bottles were prepared. The first series of six bottles were left alone (**Synthetic sample 2 (SS2)**) having been made up to contain an alkalinity of 88 mg/l as CaCO$_3$. The second series of six bottles had approximately 0.017 g of sodium carbonate (exact weights were recorded for each bottle) added to them (**Synthetic sample 3 (SS3)**).

One solution of each type was monitored on a daily basis by carrying out calcium, magnesium, total alkalinity, pH and conductivity analyses. Once the analyses were carried out the samples were discarded, as an ingress of air can cause a change in the values of interest. The precipitates which formed as well as the remaining dissolved concentrations of species were analysed and results were compared to MINTEQA2 predictions. In addition, the MINTEQA2 runs were carried out for a closed system.

5.1.1   SYNTHETIC SAMPLE 2

MINTEQA2 predicts that **SS2** will precipitate 75.34 mg/l calcite and 16.55 mg/l magnesite, with the

following percentages of each element precipitating;
Ca: 63 %
Mg: 14 %
CO_3: 89.9 %
The predicted MINTEQA2 values (PMV) are given in **Table 5.2**. The PMV's given in brackets were those

obtained when magnesite was excluded from the MINTEQA2 run.

TABLE 5.2
Analytical results obtained for synthetic sample 2

Day	pH	Conductivity (FS/cm)	Calcium (mg/l Ca)	Magnesium (mg/l Mg)	Total Alkalinity (mg/l $CaCO_3$)
1	10.2	1062	47.9	33	88.0
2	10.2	1035	43.0	34	75.1
3	9.9	1029	40.0	31	68.0
4	10.0	1024	36.0	34	59.8
8	9.7	995	20.9	32	20.0
14	9.7	986	16	31	12.5
PMV	9.7		17.7 (11.4)	28.4	8.9 (12.1)

As there was no marked change in the magnesium value, a further MINTEQA2 run was carried out with magnesite

excluded as a precipitate and then there was an increase in the amount of calcite predicted to precipitate with the

following percentages of each element precipitating;
Ca: 76.2 %
CO_3: 86.3 %
These predictions compared well with the actual results where the following percentages of each element

precipitated;
Ca: 66 %
CO_3: 85.8 %

5.1.2   SYNTHETIC SAMPLE 3

In order to try and speed up the precipitation process, an additional 0.017 g Na_2CO_3 was added to six 500 ml bottles

containing **SS2**, (**SS3**). MINTEQA2 predicts that 79.47 mg/l calcite and 26.1 mg/l magnesite will precipitate, with

the following percentages of each element precipitating;
Ca : 66.5 %
CO_3 : 90.8 %
Mg : 22.0 %
The PMV's are given in **Table 5.3**.

TABLE 5.3
Analytical results obtained for synthetic sample 3

Day	pH	Conductivity (FS/cm)	Calcium (mg/l Ca)	Magnesium (mg/l Mg)	Total Alkalinity (mg/l CaCO₃)
1	10.1	1103	47.7	33.4	118.3
2	9.9	994	18.0	33.9	45.8
3	9.7	980	16.0	33.9	41.0
7	9.8	952	7.9	34.0	21.0
9	9.7	950	7.4	33.8	20.2
10	9.8	950	7.4	33.6	20.0
PMV	9.7		16.0 (7.2)	26 (34)	11.0 (19.8)

As for **SS2,** there were no marked change in the magnesium value, and a further MINTEQA2 run, with magnesite excluded as a precipitate, increased the amount of calcite predicted to precipitate with the following percentages of each element precipitating;

Ca: 84.9 %
CO₃: 83.3 %

These predictions compared extremely well with the actual results where the following percentages of each element precipitated;

Ca: 84.5 %
CO₃: 83.1 %

The results for **SS3** are closer to the MINTEQA2 predicted results than those for **SS2**. The most likely reason for this is that the rate of reaction was much more rapid for **SS3** than **SS2**, and the time period over which the analyses were carried out was sufficient for **SS3** to come to equilibrium, whereas **SS2** was still equilibrating at the end of the study.

5.1.3   THE EFFECT OF ANTISCALANTS IN THE WATER

Synthetic Sample 4 (SS4) had 5 mg/l of an antiscalant supplied by Anichem added to **SS2**. **Synthetic Sample 5 (SS5)** had 5 mg/l of an antiscalant supplied by Buckman added to **SS2**. The results obtained for calcium, magnesium and total alkalinity analyses on **SS4** and **SS5** can be found in **Table 5.4**

TABLE 5.4
Calcium, magnesium and total alkalinity results obtained for synthetic samples 4 and 5

	Calcium (mg/l Ca)		Magnesium (mg/l Mg)		Total Alkalinity (mg/l CaCO$_3$)	
DAY	SS 4	SS 5	SS 4	SS 5	SS 4	SS 5
0	176.6	190.6	18.05	16.5	38.0	38.8
1	178.4	180.4	17.79	15.72	38.1	36.0
4	179.4	190.6	16.32	17.39	36.5	36.4
5	172.3	170.3	18.48	17.25	36.2	36.2
8	170.3	174.4	18.79	16.79	37.2	37.1
11	174.4	172.3	18.17	16.02	43.1	39.0

The synthetic samples, **SS4** and **SS5** remained fairly constant over the 11 day period showing the stabilising effect of the antiscalants.

5.2 MINERALOGY

A detailed discussion on each mineral predicted to precipitate and each mineral with a positive saturation index, obtained using MINTEQA2 is given in **Appendix A4**. At the end of each mineral discussion, the information has been used to decide whether the mineral is likely to precipitate and therefore be included or excluded in MINTEQA2. This section summarises this information on predicted precipitates only and includes a tabulated summary on the likelihood of the formation of each of the minerals under conditions prevailing in the cooling circuit.

TABLE 5.5
Summary of the likelihood of formation of each of the MINTEQA2 predicted minerals

Mineral	Likelihood of formation in the cooling circuit
Barite	yes
Calcite	yes
Ca - Nontronite	no
Diaspore	no
Hematite	yes
Leonhardite	no
Magnesite	no
Quartz	no
Tenorite	yes
Tremolite	no
Zinc Silicate	no

The presence of silica complicates matters, and when silica is entered into MINTEQA2, several silica containing species are predicted to precipitate, namely zinc silicate, tremolite, quartz and Ca-nontronite. It has been found in practise that an amorphous silica precipitate is formed, rather than these crystalline species. Diaspore is considered unlikely to form as it requires heat and pressure to crystallise.

5.3   DISCUSSION OF ANALYTICAL RESULTS

5.3.1   COMPARISON BETWEEN RESULTS OBTAINED AT MATLA POWER STATION AND AT T-R-I

Analytical results obtained at T-R-I were compared to those obtained at Matla power station over the intense period of study in order to validate results. The samples were taken at different times of the day and by different samplers. The comparison was not possible in the case of all determinands, as the two laboratories carry out different types of analyses on different days. The T-R-I results for the clarified cooling water could not be compared to Matla's as these analyses were not available. **Table 5.19** in **Appendix A2** compares results obtained by the two laboratories on day 8.

The results compare very well with the exception of pH and total alkalinity. It can be expected that the results obtained at Matla power station are more accurate than those obtained at T-R-I for these analyses, as pH and alkalinity can change during transportation.

5.3.2   COMPARISON BETWEEN MEASURED AND CALCULATED CONDUCTIVITIES

In **Appendix A2** all measured and calculated conductivities have been listed. The two results were compared using the following equation:

$$\text{Percentage difference (\%)} = \frac{\text{measured conductivity - calculated conductivity}}{\text{measured conductivity}} * 100$$

Out of the 48 sets of conductivity values compared, 44 sets of results of the above equation ranged between -0.6 % and -20.8 %, indicating that the majority of calculated conductivities were higher than the measured conductivities. Three of the results yielded positive values and were within 13 %. There was only one large discrepancy, the conductivity comparison for CCW on day 19. The measured conductivity was 840 ΓS/cm and the calculated conductivity was 1 491 ΓS/cm. In this case the calculated conductivity has exposed an analytical error. When cations and anions are converted to calcium carbonate equivalents, (i.e. sodium expressed as calcium carbonate = Na (mg/l) * 2.17), then the sum of the cations plus the sum of the anions gives a close estimation of what the conductivity should be. When this calculation was carried out for CCW, day 19, the result obtained was 1 328 ΓS/cm, showing a much closer correlation to the calculated conductivity.

5.3.3 COMPARISON BETWEEN SPECIATED MINTEQA2 BALANCES AND NON-SPECIATED CALCULATED BALANCES

The non-speciated calculated balances that were carried out did not include trace elements, as their contribution to the balance was insignificant and also did not account for pH contribution. However, in the majority of cases the balances compared very well to those calculated by MINTEQA2. Discrepancies only occurred with cooling water analyses obtained from Matla power station, probably due to the high pH values for these samples.

5.4   RAW WATER

Appendix A2 details and **Table 5.6** summarises the results obtained for raw water analyses over the period 28 March to 16 June 1994 for Usutu-Vaal river water, which was the supply over this time period. In accordance with the conductivity, the major elements only fluctuated slightly. The pH varied significantly between 6.54 and 8.01. With the exception of copper and zinc (which were both close to the detection limits, 0.01 mg/l for each element, of the technique) and strontium (which remained between 0.10 and 0.12 mg/l with one outlier), the trace elements varied markedly and no trends were observed.

TABLE 5.6
Summary of raw water results obtained over the detailed period of study (28 Mar - 16 Jun 1994) and subsequent years

Determinand	Period of	intense	study	Subsequent	years*
	Max	**Min**	**Mean**	**1995**	**1996**
Conductivity @ 25 ℃ (μS/cm)	255	223	236	185	256
pH @ 25 ℃	8.01	6.54	7.08	8.01	8.11
Total Alkalinity (mg/l $CaCO_3$)	87.3	73.1	77.8	67.5	60.0
Sodium (mg/l Na)	16.7	10.0	13.4	12.8	23.0
Potassium (mg/l K)	3.8	2.1	2.9	8.4	9.0
Magnesium (mg/l Mg)	13.4	12.3	12.8	7.3	4.9
Calcium (mg/l Ca)	20.4	17.1	18.6	24.8	20.8
Chloride (mg/l Cl)	10.5	9.8	10.2	13.2	8.0
Nitrate (mg/l NO_3)	1.24	<0.10	0.91	N/A	N/A
Sulphate (mg/l SO_4)	22.2	19.1	20.7	9.31	28.7
Fluoride (mg/l F)	1.10	0.16	0.39	N/A	N/A

NOTES**:**
- Since values given in this table are means, maximums and minimums cation/anion balances do not apply and therefore results cannot be speciated.
- * Results obtained from Matla Chemical Services department.
- N/A = Results not available.

The results of the analysis of raw water samples from the Usutu-Vaal and Usutu river systems **(Appendix A2)** showed that for all determinands tested, with the exception of copper, Usutu water contained lower values than Usutu-Vaal water. Speciation results of both raw waters **(Table 5.7)**, predict that only hematite, (Fe_2O_3) would precipitate from both waters, but that 50 % more hematite by mass would precipitate from Usutu-Vaal water than from Usutu water. In addition to the hematite, $ZnSiO_3$ was predicted to precipitate from the Usutu-Vaal water. Since zinc was not detected in the Usutu water, no precipitation was predicted.

TABLE 5.7
Summary of speciation results obtained on Usutu-Vaal and Usutu river waters

	Usutu-Vaal River Water				Usutu River Water			
Molar conc. of hematite precip.	2.588 E-6				1.226 E-6			
Molar conc. of $ZnSiO_3$ precip.	2.945 E-7				0			
Equilibrated mass distribution	**Dissolved**		**Precipitated**		**Dissolved**		**Precipitated**	
	Mol/kg	**%**	**Mol/kg**	**%**	**Mol/kg**	**%**	**Mol/kg**	**%**
Zn	1.042 E-8	3.4	2.945 E-7	97	0	0	0	0
H_4SiO_4	7.619 E-5	99.9	2.945 E-7	0.4	0	0	0	0
Fe	8.119 E-16	0.0	5.176 E-6	100	1.618 E-15	0	2.453 E-6	100

5.5   COOLING CIRCUIT DURING CONCENTRATION - SOUTH SIDE

During start-up, the cooling water system is more difficult to control than a system in which the concentration of contaminants are being kept at a steady state. This is due to the prevalence of mechanical and electrical problems on start-up. The paint used to protect the pipework was also found to leach into the water during the first two weeks.

5.5.1   COOLING WATER

Over the period studied, the conductivity of the cooling water increased from 278 FS/cm to a steady conductivity ranging between 1 660 and 2 030 FS/cm. **Appendix A 7, Table A 7.1** shows how the concentration of individual determinands is expected to increase. The calculations are based on the following assumptions and figures:

The power produced per day in Mwh was obtained from Matla power station and entered into a

spreadsheet (**Appendix A 7, Table A 7.1**). This value ranged from 11 859 to 36 344 Mwh with an average

of 25 805 Mwh and a relative standard deviation of 17.1 %. These statistics have been included to show

the large variation in power output over the period studied.The evaporation per day could then be

calculated as it has been determined that at Matla power station the evaporation rate is 1.55 kl/Mwh

(Hanekom, 1997). The evaporation volume per day ranged from 18.4 Ml to 56.3 Ml. During the first 5

days the system was not blown down and ferric chloride was not dosed into the system, hence the raw

water make-up was equivalent to the evaporation. The volume of the system was then calculated using the

analytical results for sodium (Na) and chloride (Cl) over the first 5 days. For all calculations in this section

the following abbreviations are used:
- V_s = Total volume of system in Ml
- V_r = Volume of raw water make-up in Ml
- V_{bd} = Volume of blowdown in Ml

Note: All analytical values used are in units of kg/Ml.

(The units used in the spreadsheet were kl and g/kl, but these values have been converted to Ml in the text

for convenience.)

The calculation used was:

V_s = (V_r* Na or Cl (in raw water) / ((Na or Cl result (day n + 1) - Na or K (day n)).

Using this calculation the total volume of the system was calculated at 55 Ml.

Once blowdown commenced on day 6, the raw water make-up was calculated as the sum of the volume

of water evaporated and water blown down.

The blowdown volume was calculated using the Na results as ferric chloride dosing resulted in chlorides

being higher than predicted. The calculation used was:

V_{bd} = (V_r * Na (in raw water) - ((Na (day n + 1))- Na (day n) * V_s))/Na (day n).

Using these calculations the raw water make-up ranged from 19.3 Ml to 61.8 Ml per day, with the blow

down volume ranging from 0.9 to 11 Ml per day. It was difficult to explain what happened in the cooling

water system from day 63 to day 68, where the sodium value increased from 123 to 292 kg/Ml. There was

also a marked increase in chloride, from 136 to 225 kg/Ml and sulphate, from 284 to 465 kg/Ml. There are

two possible explanations for this large increase. Firstly, the make-up water could have changed and would

have contained approximately 43 kg/Ml of sodium and also higher concentrations of the other

determinands. Since the highest value for sodium in the raw water was 22 kg/Ml, a different source of

water would have been used. A second, and more likely explanation, is that a poor sample was taken

resulting in an invalid set of results.

The results for the other species were then predicted using the calculation:

salt Conc. (day n) = Salt conc (day n - 1) + ((V_r * raw water salt content - V_b * salt conc (day n - 1)) / V_s

The determinands which were considered were chloride, sulphate, potassium, calcium, magnesium, DOM,

nitrate and total alkalinity. The correlation between predicted and actual results for potassium is depicted

in **Fig 5.1a**.and for nitrate in **fig 5.1b**.
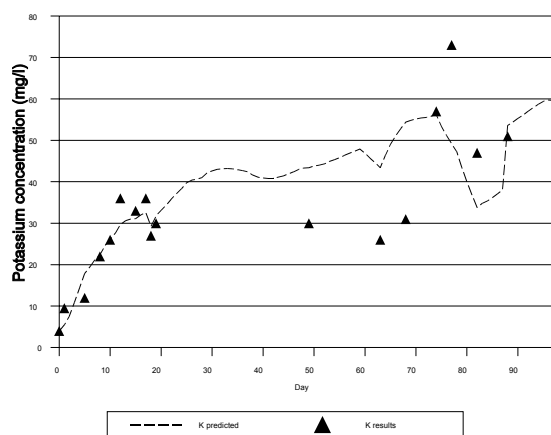
Fig 5.1a: Comparison between predicted and actual potassium results for Matla cooling water over a one hundred day period

The potassium results compare fairly well to the predicted results over the first 20 day period and the last 10 day period. Between days 49 and 68 the results obtained are lower than those predicted, however this was identified as a problem area when the sodium results were investigated. On day 74 the predicted and actual results corresponded well and on days 77 and 82 results were higher than predicted. Hence, all MINTEQA2 runs were carried out within the first 20 days.
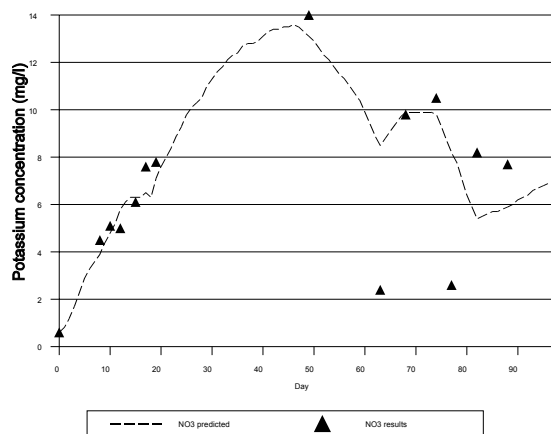
Fig 5.1b: Comparison between predicted and actual nitrate results for Matla cooling water over a one hundred day period

The predicted results for nitrate compare well with the actual results, with 3 outliers on days 63, 77 and 98.

The correlation between predicted and actual results for chloride is depicted in **Fig 5.1c**. The cooling water is treated with ferric chloride and hence the chloride concentration is expected to be higher than predicted. In order to calculate how much chloride was dosed, the analytical results were entered into the spreadsheet

on the days on which the results were known. The difference between the predicted result and the analytical result was attributed to the addition of ferric chloride. The amount of ferric chloride dosed between each set of analytical results could then be predicted. These results are represented on the graph as Cl (corr). The amount of chloride dosed ranged from 0 to 17 kg/Ml, therefore the amount of ferric chloride dosed ranged from 0 to 25.9 kg/Ml.
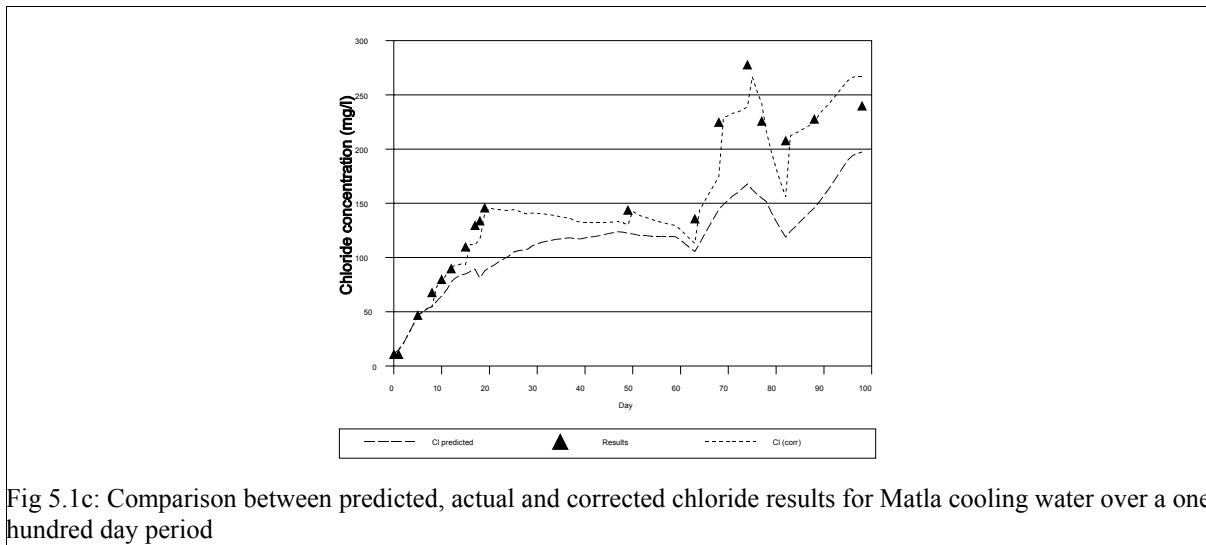
Fig 5.1c: Comparison between predicted, actual and corrected chloride results for Matla cooling water over a one hundred day period

The correlation between predicted and actual results for sulphate is depicted in **Fig 5.1d**. The cooling water is treated periodically with sulphuric acid for alkalinity and pH control and hence is expected to be higher than predicted. In order to calculate how much sulphate was dosed, the analytical results were entered into the spreadsheet on the days on which the results were known. The difference between the predicted result and the analytical result was attributed to the addition of sulphuric acid. The amount of sulphuric acid dosed between each set of analytical results could then be predicted. These results are represented on the graph as SO_4 (corr). The amount of sulphate added ranged from 2.3 to 39 kg/Ml, therefore the amount of sulpuric acid dosed ranged from 2.35 to 39.8 kg/Ml.
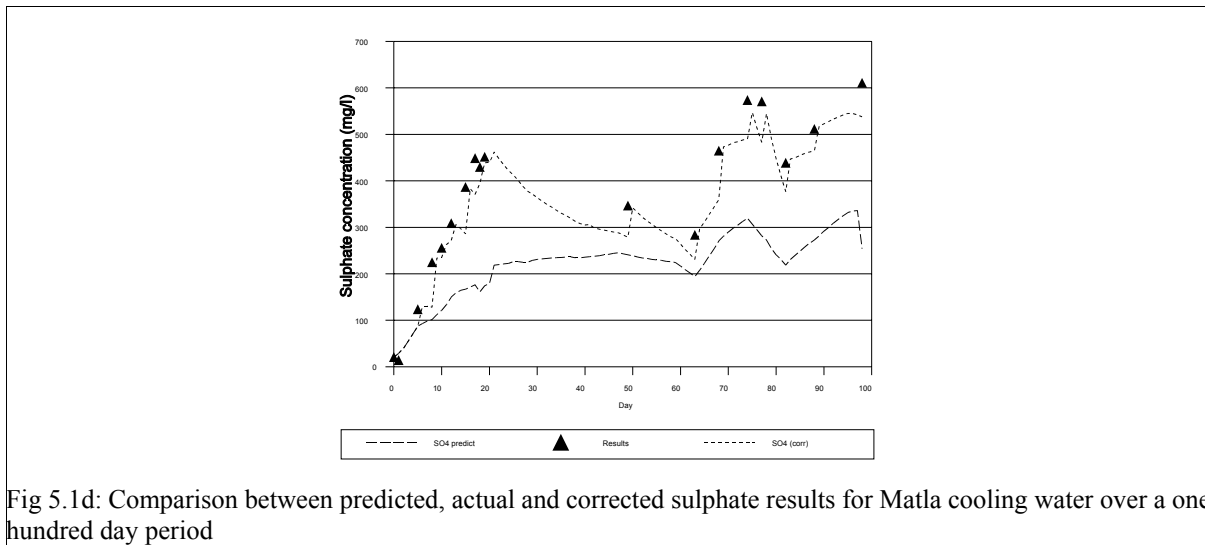
Fig 5.1d: Comparison between predicted, actual and corrected sulphate results for Matla cooling water over a one hundred day period

MINTEQA2 was then used to predict occurrences in the clarifier, including the effect of DOM (**Section 5.7.6**) and surface adsorption modelling (**Section 5.10**). Since the total alkalinity results obtained by the T-R-I laboratory for cooling water were approximately 1.1 times lower than those obtained by the Matla power station laboratory the total alkalinity results were multiplied by this factor. The total alkalinity results obtained by the T-R-I laboratory for raw water were approximately 1.2 times lower than those obtained by the Matla laboratory and hence were multiplied by this factor. The total alkalinity values were assumed to increase or decrease linearly on the days between which actual results were obtained i.e. for the cooling water, the total alkalinity on day 10 was 124 kg/Ml, on day 12 it was 106 kg/Ml and hence it was assumed to be 115 kg/Ml on day 11. The pH values obtained by the T-R-I laboratory were also questionable and hence MINTEQA2 was used to calculate the pH values.

Using all of the calculated figures above, the total alkalinity at the end of day 1 was predicted to be 144 kg/Ml. Before entering results into MINTEQA2, the reduction in total alkalinity due to sulphuric acid and ferric chloride dosing was calculated. This was found to be 135 kg/Ml on day 1. The clarification (clar) process at Matla power station was run in such a way as to reduce the total alkalinity down to approximately 50 kg/Ml in the clarifier. Using MINTEQA2 it was found that the amount of portlandite required to accomplish this task was 91.2 kg/Ml. (This is assuming a 100 % purity of portlandite. Hence, if the portlandite was analysed and found to be 70 % pure, this value would have to be multiplied by 1.43). The resultant calcium and magnesium values predicted by MINTEQA2 were noted. The following

calculations were then carried out:
- Total Alkalinity removed = 135 kg/Ml - 49.4 kg/Ml = 85.6 kg/Ml
- Total alkalinity of the system = 135 kg/Ml * 55 Ml = 7 425 kg
- Desirable total alkalinity of the cooling water = 120 kg/Ml.
- Desirable total alkalinity of the system = 120 kg/Ml * 55 Ml = 6 600 kg
- Hence the mass of total alkalinity which requires removing is 7 425 kg - 6 600 kg = 825 kg
- Therefore the amount of water which requires treatment is 825 kg / 85.6 kg/Ml = 9.6 Ml
- Using the volume of water treated, the reduction in calcium and magnesium could also be calculated.

These results were then entered into the spreadsheet.
This procedure was carried out from day 0 to day 12 and comparison with the actual results is shown in

Table 5.8. Actual values are given in italics.

TABLE 5.8
Comparison between actual and predicted results for calcium, magnesium and total alkalinity

Day	Calcium (kg/Ml Ca) (before clar)	Calcium (kg/Ml Ca) (after clar)	Magnesium (kg/Ml Mg) (before clar)	Magnesium (kg/Ml Mg) (after clar)	Total Alkalinity (kg/Ml CaCO$_3$) (before clar	Total Alkalinity (kg/Ml CaCO$_3$) (after clar)
0	24	-	12	-	105	-
1	33.0	28	16.5	14.0	135	120
1	-	*30.4*	-	*9.7*	-	*105*
2	40.5	30	20.3	15.0	166	130
3	48.4	31.8	24.2	15.0	202	140
4	49.8	34.8	24.4	15.6	213	150
5	52.8	39.2	25.0	16.4	224	160
5	-	*32*	-	*32*	-	*160*
6	52.6	41.1	23.7	16.9	191	145
7	53.8	41.5	24.5	16.9	178	130
8	52.5	38.3	23.6	14.8	158	105
8	-	*67*	-	*32*	-	*105*
9	52.7	38.7	23.8	13.9	170	114
10	53.2	42.7	22.8	15.3	170	124
10	-	*82*	-	*26*	-	*124*
11	56.7	37.6	25.7	10.3	182	115
12	55.9	37.6	23.1	10.3	193	106
12	-	*104*	-	*39*	-	*106*

It can be seen that, with a few exceptions, MINTEQA2 predicted a greater removal of calcium and magnesium than what had actually occurred. If portlandite was overdosed, the amount of calcium in the system would have increased and since total alkalinity would have been reduced below 50 kg/Ml, less water would have been treated and hence the resultant concentrations of the calcium and magnesium in the cooling water would have increased. Magnesium and calcium removal does occur but to a lesser extent than that predicted by MINTEQA2 e.g. on day 8:

Magnesium content using portlandite addition in MINTEQA2 : 14.8 kg/Ml
Magnesium content if no reduction occurs : 59.7 kg/Ml
Analytical result for magnesium: 32.0 kg/Ml
Calcium content using portlandite addition in MINTEQA2 : 38.3 kg/Ml
Calcium content if no reduction occurs : 116 kg/Ml
Analytical result for calcium: 67 kg/Ml

Another reason for the discrepancy between predicted and actual results could be that the amount of sulphuric acid and ferric chloride dosed was greater than that which was predicted, as this would have lowered the total alkalinity further, prior to portlandite dosing. Again, this would have led to a lower volume of cooling water being treated and hence a higher resultant calcium and magnesium concentration in the cooling water.

A further reason for the discrepancy between results could be that the total alkalinity values were assumed to increase or decrease linearly on the days between which actual results were obtained. If these total alkalinity results were substantially different, the results predicted for calcium and magnesium would have differed.

Days 17 and 18 were investigated using MINTEQA2, since analytical results were available for the cooling water on both days and analyses were available for the raw water and clarified cooling water on day 18. The results on day 17 were entered into the spreadsheet to obtain the increase in calcium, magnesium and total alkalinity due to the addition of raw water and their decrease due to blowdown.

The actual results obtained for the clarified cooling water were then used to calculate whether the cooling water results from day 18 could be obtained:

- Total alkalinity predicted using raw water added: 176 kg/l
- Therefore total alkalinity present in the system = 176 kg/Ml * 55Ml = 9 680 kg
- Total alkalinity of the system after clarification = 101 kg/Ml * 55Ml = 5 555 kg
- Total alkalinity removed by the clarifier = 9680 kg - 5555 kg = 4125 kg
- Reduction in total alkalinity = 176 kg/Ml - 38 kg/Ml = 138 kg/Ml
- Ml of cooling water treated = 4125 kg / 138 kg/Ml = 29.9 Ml
- Calcium reduced / Ml = 105 kg/Ml - 89.4 kg/Ml = 15.6 kg / Ml
- Therefore total reduction in calcium = 15.6 kg /Ml * 29.9 Ml = 466 kg
- Total calcium in the cooling water system = ((55 Ml * 105 kg/Ml) - 466 kg) / 55Ml = 96.5 kg/Ml
- Analytical result for calcium on day 18 = 104 kg/Ml
- Magnesium reduced / Ml = 54 - 23.9 = 30.1 kg / Ml
- Therefore total reduction in magnesium = 30.1 kg /Ml * 29.9 Ml = 900 kg
- Total magnesium in the cooling water system = ((55 Ml * 54 kg/Ml) - 900 kg) / 55Ml = 37.6 kg/Ml
- Analytical result for magnesium on day 18 = 41 kg/Ml

These results are within 8.3 % of the analytical results obtained. It was then claculated that if sulphuric acid and ferric chloride had been dosed to reduce the total alkalinity from 176 kg/Ml to 150 kg/Ml and the above figures recalculated, then the total calcium in the cooling system would be 98.2 kg/Ml and the total magnesium in the cooling water system would be 41 kg/Ml, which is a much better correlation with the actual results.

All results were then entered into MINTEQA2 and in order to obtain an alkalinity of 38 kg/Ml as $CaCO_3$, the amount of portlandite required was 57 kg/Ml, which resulted in the values obtained for calcium and magnesium which are given in **table 5.9**.

TABLE 5.9
Comparison between actual and predicted results for calcium, magnesium and total alkalinity in the

clarified cooling water (CCW) sample on day 18

	CCW (MINTEQA2)	CCW (Actual Results)
Calcium (kg/Ml Ca)	47.4	89.4
Magnesium (kg/Ml Mg)	22.1	23.9
Total Alkalinity (kg/Ml $CaCO_3$)	38	38

When the calculations used above were carried out using the MINTEQA2 predicted results, the following

values were obtained:
- Total calcium in the cooling water system = 80.0 kg/Ml
- Total magnesium in the cooling water system = 40 kg/Ml

Hence, in this simulation a good correlation was obtained between total alkalinity and magnesium, but the

predicted calcium value was lower than the analytical result. Since DOM plays a large part in the

simulation (**section 5.7.6**), a more accurate model with greater adsorptive properties, would have resulted

in the actual and predicted results having a better correlation.

Using the analytical results, the following patterns emerged. Calcium and magnesium showed an

increasing trend. The pH remained fairly constant over the period studied. The total alkalinity went to high

values in the first few days and then was brought down to controlled levels (**Fig 5.2a**). The results obtained

for zinc, fluoride, aluminium, barium, copper, iron, and strontium were erratic (**Fig 5.2b**) and did not

show any particular trends. All results can be found in **Appendix A2.**
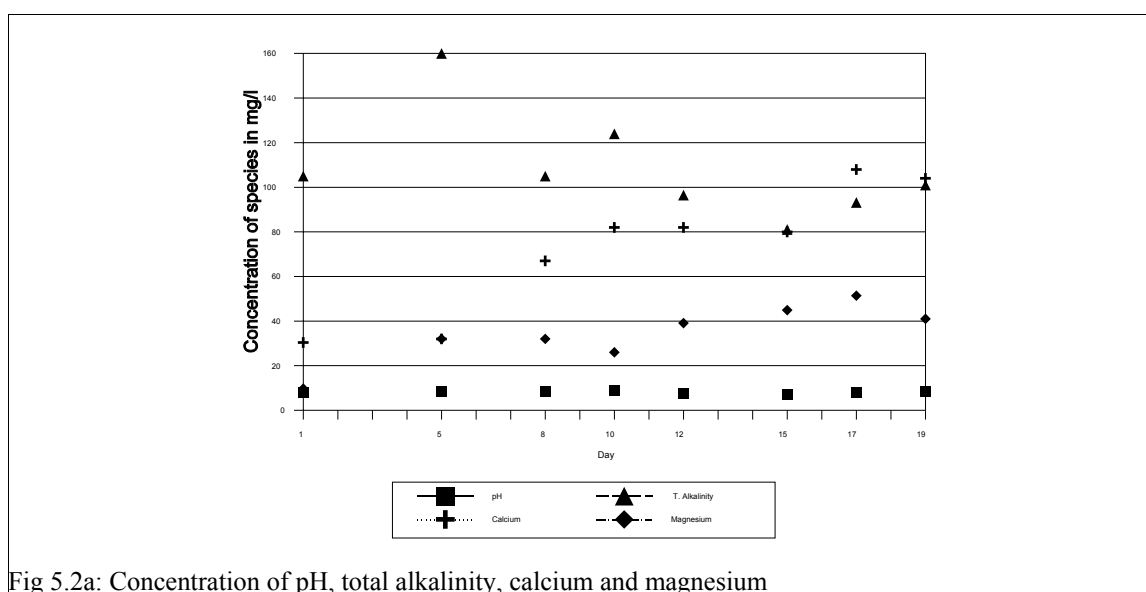
Fig 5.2a: Concentration of pH, total alkalinity, calcium and magnesium

All cooling water analyses were speciated (initially as closed systems and then as open systems (a system in which
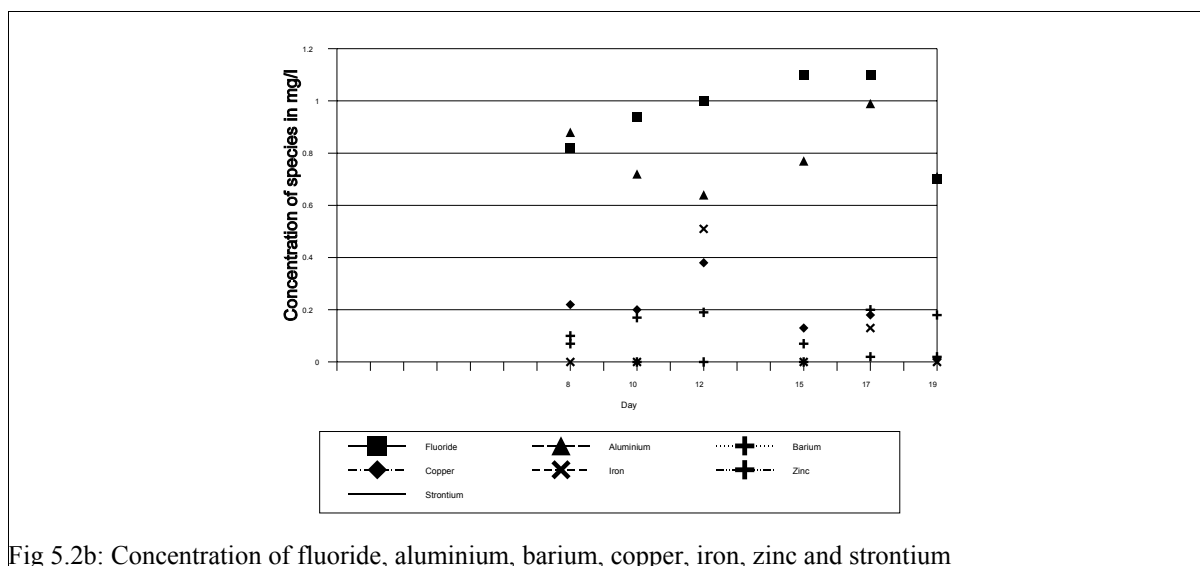
Fig 5.2b: Concentration of fluoride, aluminium, barium, copper, iron, zinc and strontium

carbon dioxide is allowed to equilibrate)). In all cases calcite, barite and leonhardite were predicted to precipitate.

Where zinc was found present in solution, it was predicted to precipitate as zinc silicate. Tenorite was predicted

to precipitate from all solutions containing more than 0.09 mg/l Cu. Other silica - containing compounds predicted

to precipitate in some of the cooling waters were tremolite, quartz and Ca-nontronite. The entry of silica into the

program complicates matters, but the values of silica are generally low and hence the quantity precipitated per Ml

is very low.

5.5.2   CLARIFIED COOLING WATER

Over the same period the conductivity of the clarified cooling water ranged between 860 and 1 950

FS/cm. The conductivity showed a general increasing trend, however there was a marked decrease on day

19. Again analytes which showed a steady increase were sodium, chloride, nitrate and sulphate. All results

can be found in **Appendix A2.**

The clarified cooling water samples were also speciated (as closed systems). In all cases barite and calcite

were predicted to precipitate, with fewer silica - containing species predicted to precipitate than in the

cooling water.

5.5.3   RELATIONSHIP BETWEEN COOLING WATER AND RAW WATER

Figs 5.3 a and **b** represent the ratio of cooling water constituents to those of the average raw water. From

these graphs it can be clearly seen that the species which concentrate up the most are sodium, potassium,

chloride and sulphate.

Fig 5.3a: Ratio of cooling water constituents, conductivity, sodium, potassium, chloride and sulphate, to those of average raw water

Fig 5.3b: Ratio of cooling water costituents, pH, total alkalinity, magnesium and calcium to those of average raw water
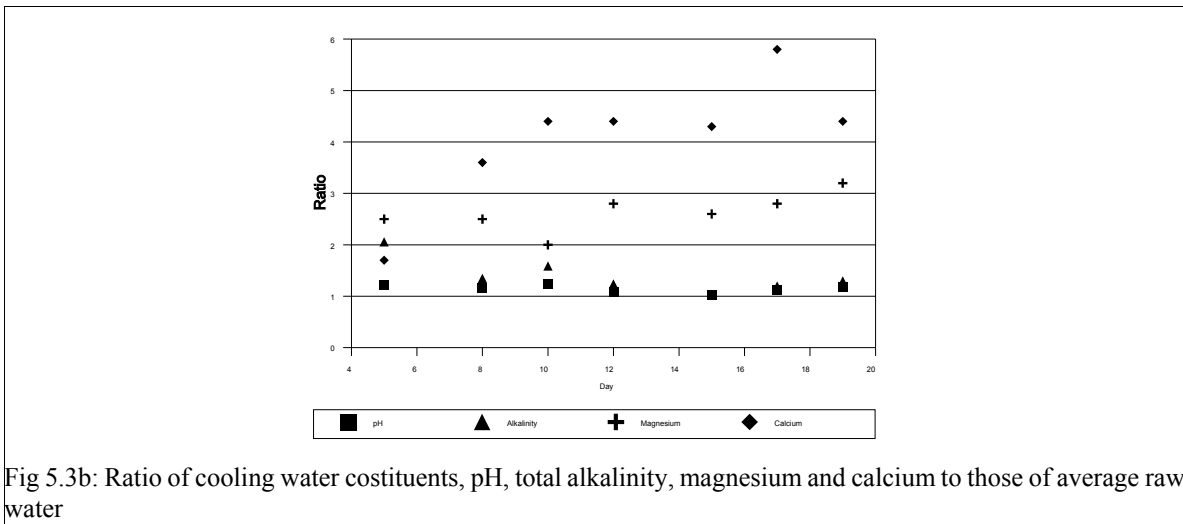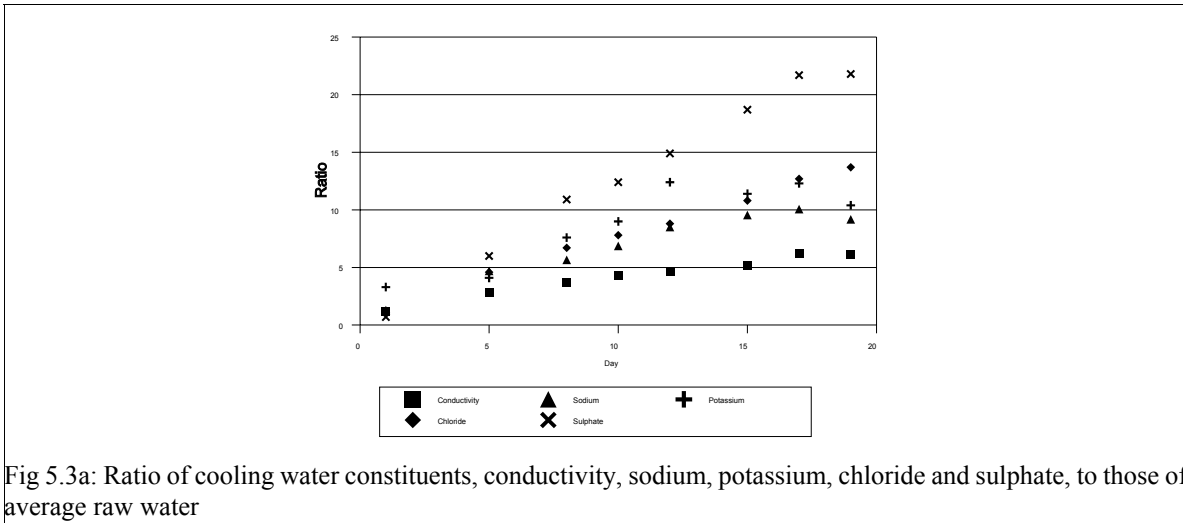
Fig 5.4 shows the amount of calcite predicted to precipitate on a daily basis as the concentration of contaminants increased. The **fig.** clearly shows that the calcite predicted to precipitate was higher at the beginning of the concentration period (except on day 1) than after about 10 days when the total alkalinity was under better control.
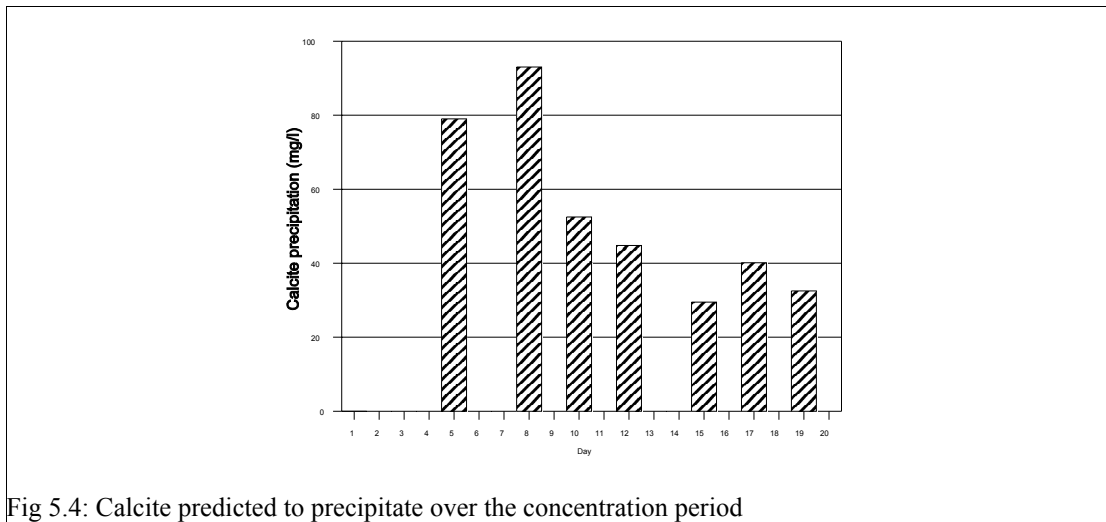
Fig 5.4: Calcite predicted to precipitate over the concentration period

5.6 STUDY OF COOLING WATER ANALYSES ON THE NORTH SIDE

While the southern plant was undergoing a complete overhaul, the northern part of the plant was studied. **Table 5.10** shows results obtained of samples taken from the northern cooling water system (NCW) and the two northern clarifiers (NCCW) and (R/CCW) on 10 February 1994. These are compared with results obtained from the southern cooling water system (SCW) and the southern clarifier (SCCW) after the overhaul on the southern side of the plant and once the components had reached steady state.

TABLE 5.10
Results obtained for cooling water and its clarifiers on the northern side of the plant compared to

southern plant results

ANALYTE	NCW	SCW	NCCW	SCCW	R/CCW
Conductivity @ 25℃ (FS/cm)	2 310	2 030	2 220	1 950	2 270
Conductivity (calculated)	2 780	2 428	2 627	1 806	2 774
pH @ 25℃	8.59	6.9	9.2	9.53	8.73
Total Alkalinity (mg/l $CaCO_3$)	114	98.2	53.2	31.6	95.8
Sodium (mg/l Na)	269	302	268	193	387
Potassium (mg/l K)	89.5	57.3	89.3	31.2	102
Calcium (mg/l Ca)	182	103	146	88	109
Magnesium (mg/l Mg)	36	32	27	23	30
Chloride (mg/l Cl)	306	278	330	295	309
Sulphate (mg/l SO_4)	614	574	603	571	595
Nitrate and Nitrite (mg/l N)	10.2	2.4	10.4	2.3	10.1
Zinc (mg/l Zn)	0.02	0.02	0.02	<0.01	0.02
Fluoride (mg/l F)	0.72	1.1	0.68	0.8	0.76
Barium (mg/l Ba)	0.139	0.17	0.103	0.11	0.125
Copper (mg/l Cu)	0.232	0.02	0.09	0.06	0.104
Iron (mg/l Fe)	0.14	0.01	0.045	0.01	0.048
Manganese (mg/l Mn)	0.004	N/A	0.006	N/A	0.025
Silica (mg/l Si)	5.05	1.08	3.87	0.76	4.63
Speciated Balance (%)	3.5	1.0	0.6	4.8	7.6
Calculated Balance (%)	3.2	1.0	0.5	4.3	7.0
Calculated TDS (mg/l)	1 733	1 523	1 665	1 463	1 703

N/A = Results not available for this sample.

There is very little difference between the major components of the two systems. Components which have come down significantly and which are of benefit to the southern cooling system are total alkalinity, calcium, nitrate and nitrite, copper, iron and silica. The results also indicate that the clarifiers on the south side were operating more efficiently in terms of alkalinity removal, the percentage removal being 67.8 compared to 53 on the north side.

5.7   CALCITE FORMATION POTENTIAL

As mentioned in **Chapter 4**, the predominant species predicted to precipitate from many areas in the circuit, was

calcite. This prediction was verified by a mineralogical analysis on a sample of scale taken from a condenser high

pressure (HP) outlet tube where calcite, of a very high purity (99.9 %) was the only phase identified by XRD. In

trying to reduce the precipitation potential of calcite the following aspects were investigated:

- effect of carbonate concentration,
- effect of temperature,
- effect of calcium concentration,
- effect of pH,
- effect of carbon dioxide,
- effect of organic matter, and
- effect of other species.

5.7.1   EFFECT OF CARBONATE CONCENTRATION ON CALCITE PRECIPITATION

As is to be expected this precipitation is dependent on the carbonate concentration, the higher the

carbonate content the greater the amount of precipitation. For a raw water sample containing 16.9 mg/l

calcium and an average composition of the other determinands, (with the exception of potassium which

was increased to maintain the electroneutrality of the solution and which did not affect calcite

precipitation) the relationship between carbonate concentration and calcite precipitation at 25 °C, can be

found in **Fig. 5.5.**
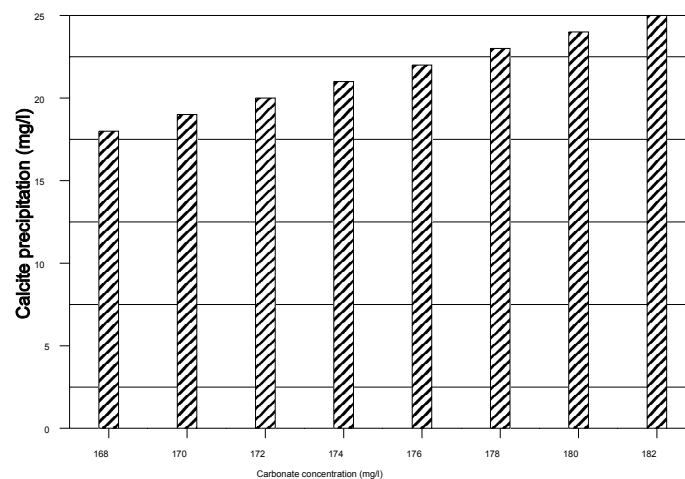
Fig 5.5: Effect of carbonate concentration on calcite precipitation.

5.7.2   EFFECT OF TEMPERATURE ON CALCITE PRECIPITATION

This relationship is depicted in **Fig 5.6** where it can be seen that the lower the temperature the lower is the tendency of calcite to precipitate.
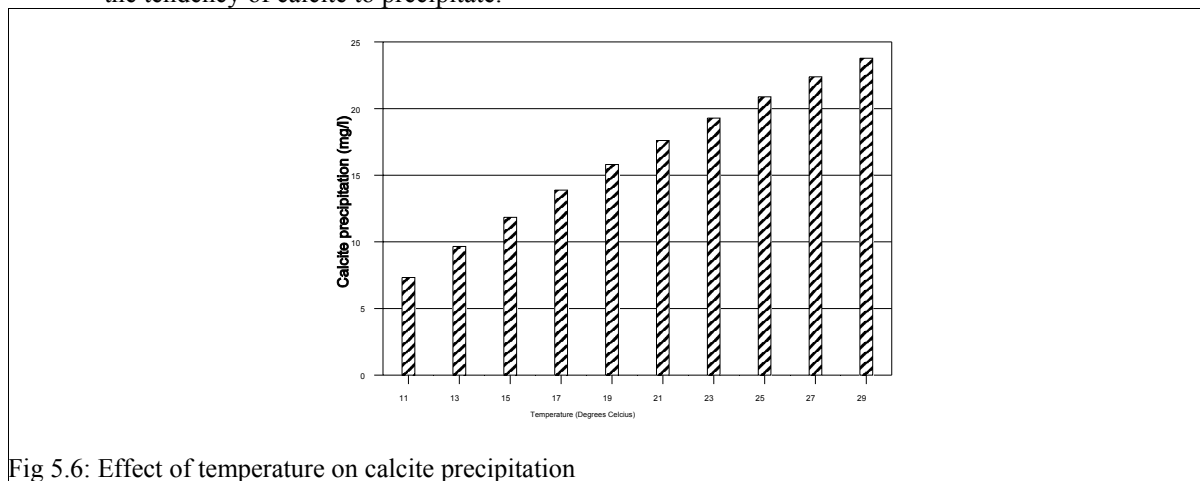
Fig 5.6: Effect of temperature on calcite precipitation

The log $(-\lvert G^0/298*R)$ value for calcite entered in MINTEQA2 is 8.4570. In the case of calcite this is the same as pKsp. Hence, using a calculation by Cobble and Lin:

$$\log K_{sp} = (6391.00/T) - 1.78868 + 2 \log K_w \text{ (at infinite dilution)}$$

the figures produced in **Table 5.11** were obtained.

TABLE 5.11
Relationship between pK_{sp} and temperature

Temp ($^\circ$C)	0	5	10	15	20	25	30	35	40	45	50
pK_{sp}	8.27	8.27	8.27	8.29	8.31	8.33	8.36	8.40	8.44	8.48	8.52

In order to clarify whether these pK_{sp} values would influence results in terms of calcite precipitation, MINTEQA2 runs were undertaken at 10, 25 and 40 $^\circ$C, using the above and MINTEQA2 K_{sp} values alternately. The mass of calcite predicted to precipitate was identical in each case and hence MINTEQA2 values were considered to be valid.

5.7.3   EFFECT OF CALCIUM CONCENTRATION ON CALCITE PRECIPITATION

Speciation predictions from a typical cooling water analysis indicate that at 25 $^\circ$C, even reducing the calcium concentration to 0.67 millimolar i.e. 27 mg/l, will not prevent calcite precipitation. The effect of changing calcium concentrations on a solution can be seen in **Fig 5.7.** As calcium was decreased, nitrate was decreased to maintain electroneutrality of the solution. Nitrate was chosen as it does not affect calcite precipitation.
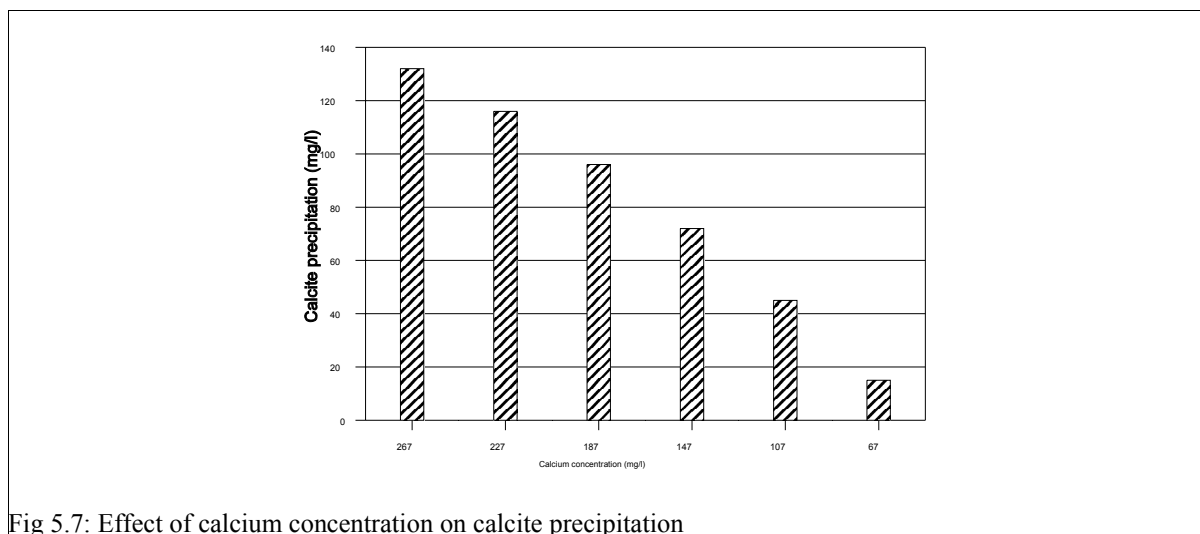
Fig 5.7: Effect of calcium concentration on calcite precipitation

5.7.4   EFFECT OF pH ON CALCITE PRECIPITATION

The effect of changing pH on calcite precipitation was then studied. Reduction in pH is accompanied by a reduction in the quantity of calcite precipitating and at a pH of 8.0 and below calcite no longer precipitates (**Fig 5.8**).
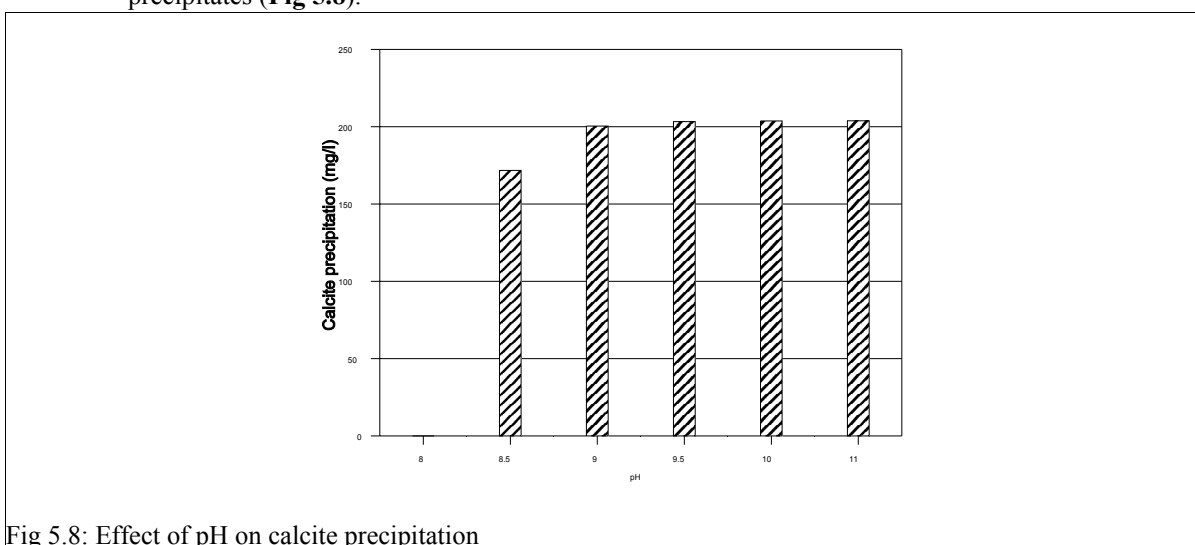
Fig 5.8: Effect of pH on calcite precipitation

Hence the figure indicates that at a pH value of 9 and above, increasing the pH does not have a marked difference on the amount of calcite precipitating.

5.7.5   EFFECT OF CARBON DIOXIDE ON CALCITE PRECIPITATION

Speciation indicates that the addition of carbon dioxide will reduce the calcite precipitation, while increasing the total carbonate in the system. The reason for this is the accompanying decrease in pH. This

relationship is depicted in **Fig 5.9**. Theoretically, the addition of carbon dioxide is expected to depress the pH markedly thereby allowing higher concentrations of calcium and total carbonate to be present in the system without the precipitation of calcite occurring. The distribution of carbonate species changes with increasing carbon dioxide content, with CO_3^{2-} decreasing, HCO_3^- decreasing slightly and H_2CO_3aq increasing.
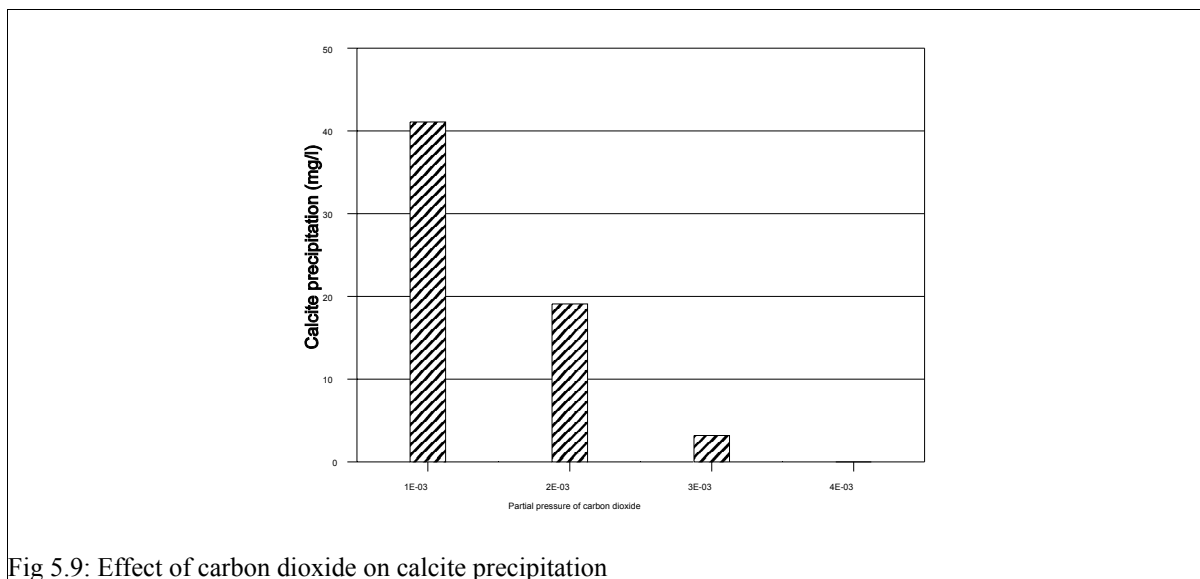
Fig 5.9: Effect of carbon dioxide on calcite precipitation

5.7.6 EFFECT OF ORGANIC MATTER ON CALCITE PRECIPITATION

The DOM sub-model was used to investigate the effect of organics in the water on precipitation of calcite. The greater the amount of organic matter in the water, the lower is the tendency of calcite to precipitate. For example in the recarbonated water, if the DOM is doubled the amount of calcite likely to precipitate is decreased by 12.5%. The reduction in calcite precipitation is due to the bonding of calcium with dissolved organic matter, which can be as high as 50 %, thereby reducing the amount of calcium available to bond with carbonate. The presence of dissolved organic matter will also reduce the tendency for magnesium bearing minerals to precipitate due to bonding, however to a much lesser extent than calcium. Since the DOM sub-model simulates what occurs with random organic matter in the environment, it was used to give an indication of the effect of organic matter. However, certain organics introduced into the cooling water system would be expected to have stronger complexing properties e.g. scale inhibitors, and hence the reduction in calcite precipitation would be greater than that predicted using the DOM sub-model

.5.7.7 EFFECT OF OTHER SPECIES ON CALCITE PRECIPITATION

Other species which are found in high concentrations in the cooling water are sodium, chloride and

sulphate and hence their concentrations were varied to see whether any significant changes to the outputs would occur.

For both chloride and sodium a large increase in their concentrations results in a very minor decrease in the quantity of calcite precipitating and also does not lead to the precipitation of any other mineral. Therefore, varying concentrations of these two elements does not have any significance to this assessment of calcite precipitation. The only change that occurs to the final solution is the ionic strength and hence the activity coefficients of all the species.

As the concentration of sulphate is increased, the amount of $CaSO_4aq$ bound in solution is increased and therefore less calcium is available for calcite precipitation. Using MINTEQA2 it was found that if sulphate concentration is increased by a factor of 2.3 calcite precipitation is decreased by a factor of 1.2.

5.8   EFFECT OF IRON IN SOLUTION

As described in **Chapter 4**, ferric chloride was dissolved in raw water at a pH value of 7. The solution was analysed immediately and then at half hourly intervals for 5.5 hours. In order to determine the final amount of iron in the solution it was again analysed after 3 days. The Fe^{3+} in solution decreased according to **TABLE 5.12.**

TABLE 5.12
Rate at which Fe^{3+} precipitates from water with a neutral pH

TIME (in hours)	Fe^{3+} in solution (mg/L)	Reduction in Fe^{3+} (%)
0.0	9.21	0.00
0.5	8.29	9.99
1.0	8.11	11.94
1.5	7.17	22.50
2.0	6.74	26.82
2.5	7.56	17.92
3.0	6.10	33.77
3.5	5.62	38.98
4.0	5.37	41.69
4.5	5.00	45.71
5.0	4.91	46.64
5.5	4.86	47.23
96.0	1.18	87.17
96.5	0.99	89.26
97.0	1.06	88.45
97.5	1.00	89.13

The precipitate formed after 96 hours was found to be non-crystalline by XRD. EDAX analysis showed that the

following elements were present in the precipitate;

Fe^{3+} (as Fe_2O_3)   90%
Cl   (as Cl_2)   10%

The chloride was probably present, since the precipitate was not prewashed, however, Fe^{3+} must have precipitated

as an oxide or hydroxide.

The amount of precipitated iron found in a Matla cooling water sample was found to be 4.15 mg/L as Fe. The major

difference in MINTEQA2 outputs with and without the iron is that iron causes copper to precipitate as cupricferrit.

Also, since one of the minerals predicted to precipitate contains the chloride ion, 0.4 % chloride is predicted to

precipitate from solution. The solids predicted to precipitate can be found in **TABLE 5.13**.

TABLE 5.13
Comparison of MINTEQA2 outputs for a cooling water solution with and without the presence of

precipitated iron

	Without Iron	With Iron
Solids	**Amount precipitating (Molar)**	**Amount precipitating (Molar)**
Leonhardite	6.497E-7	None
Barite	1.216E-6	1.216E-6
Quartz	2.656E-5	2.887E-7
$Fe(OH)_{2.7}Cl_3$	None	5.856E-5
Ca - Nontronite	None	7.868E-6
Cupricferrit	None	1.036E-9

5.9   THE EFFECT OF OTHER DETERMINANDS IN SOLUTION

The efect of other determinands in solution was simulated using MINTEQA2. The addition of 26.6 mg/l dissolved

organic matter to a typical cooling water sample reduced the amount of calcite expected to precipitate by 13.44 %.

The addition of 0.26 mg/l phosphate further reduced the amount of calcite expected to precipitate by 1.53 % with

an additional mineral expected to precipitate namely hydrapatite.

5.10   SURFACE ADSORPTION MODELLING

5.10.1   ADSORPTION MODELLING AT A FIXED pH OF 8.196

The cooling water results obtained on 1 April 1994, day 10, were modelled using the Diffuse Layer Model

for adsorption onto an amorphous iron oxide surface. The figures used for input into the surface adsorption

model were;

- **Solids concentration** = 3,422 g/l
- **Amorphous iron concentration** = 0.721 mg/g
- **Specific surface area** = 600 m^2/g
- **High energy site density** = 1,922e-4 moles/l
- **Low energy site density** = 7,690e-3 moles/l

These figures were extracted from a paper on MINTEQA2: Additional Modeling Problems (Kerr, 1994).

The equilibrated mass distribution obtained is given in **Table 5.14**, and is compared to the MINTEQA2

output obtained when adsorption modelling was not carried out.

TABLE 5.14

Equilibrated mass distribution of a cooling water sample with a conductivity of 1099 uS/cm and pH of 8.5,

with and without adsorption modelling

NAME	PERCENT DISSOLVED		PERCENT ADSORBED	PERCENT PRECIPITATED	
	WITHOUT	WITH		WITHOUT	WITH
Sodium (Na)	100	100	0	0	0
Potassium (K)	100	100	0	0	0
Magnesium (Mg)	54.5	54.4	0	45.5	45.6
Calcium (Ca)	15.9	15.9	35.6	48.5	84.1
Chloride (Cl)	100	100	0	0	0
Nitrate (NO$_3$)	100	100	0	0	0
Sulphate (SO$_4$)	100	97.5	2.4	0	0
Fluoride (F)	100	100	0	0	0
Copper (Cu)	15.3	0	100	84.7	0
Strontium (Sr)	100	100	0	0	0
DOM	100	100	0	0	0
Carbonate (CO$_3$)	40.1	48.7	0	59.9	51.3
Iron (Fe)	100	0	0	100	100
Aluminium (Al)	1.1	1.1	0	98.9	98.9
Barium (Ba)	12.3	12.4	12.5	87.7	58.4

Hence copper has a strong tendency to adsorb onto an iron hydroxide layer. Calcium, barium and sulphate

will also adsorb but to a lesser extent. In comparison, when adsorption is not allowed, 15.3 % of copper

is predicted to remain dissolved in solution with the remaining 84.7 % precipitating. All of the calcium and

barium which was predicted to adsorb is predicted to precipitate and the small amount of sulphate predicted

to adsorb remains dissolved in the solution.

The solids concentration was varied between 1 and 10 g/l, but this did not make a significant difference to

the output.

5.10.2   ADSORPTION MODELLING OVER A RANGE OF pH

Using the multiproblem generator, the same water sample as above was modelled at pH values of 7, 8, 9, 10 and 11. The distribution of calcium among the dissolved, adsorbed and precipitated states was of interest and is depicted in **Fig 5.10**. The amount of adsorbed calcium remains fairly constant over the pH range. At pH values lower than 8.5 the majority of calcium remains in solution wheras at pH values above 8.5 the amount of calcium expected to precipitate increases rapidly.
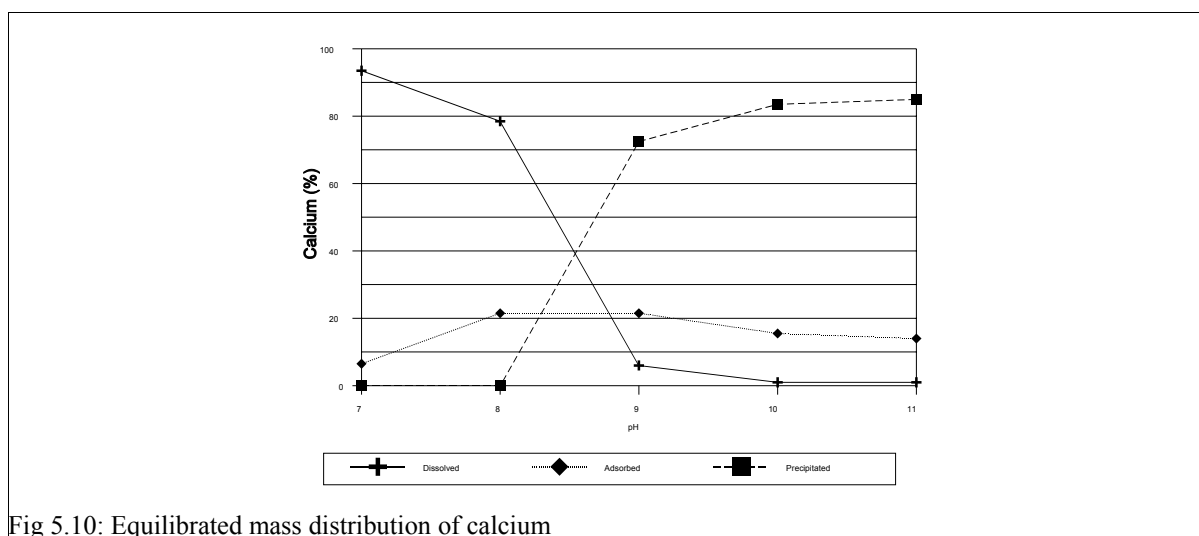
Fig 5.10: Equilibrated mass distribution of calcium

Inspection of **Fig 5.10** indicates that the greatest changes occur between pH values of 8 and 9. More detail of what occurs between these two pH values is depicted in **Fig 5.11**.
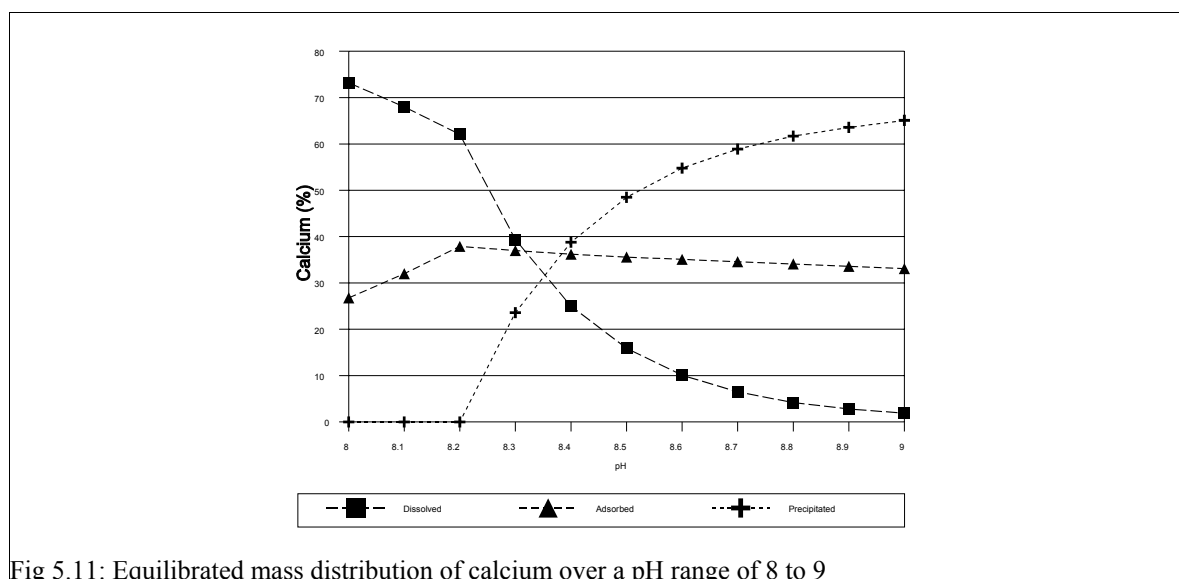
Fig 5.11: Equilibrated mass distribution of calcium over a pH range of 8 to 9

Another element of interest which is distributed among the three phases is barium and its distribution is depicted

in **Fig 5.12**. None of the other species are distributed among the three phases over the pH range of from 8 to 9.

Copper remains 100 % adsorbed over this pH range and the sulphate distribution between the dissolved and

adsorbed phases is given in **Table 5.15**.

TABLE 5.15
Distribution of sulphate between the dissolved and adsorbed phases

pH	8.0	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	9.0
Dissolved sulphate (%)	95.4	96.4	97.2	98.0	98.6	99.0	99.3	99.6	99.7	99.8	99.9
Adsorbed sulphate (%)	4.5	3.6	2.8	2.0	1.4	1.0	0.6	0.4	0.3	0.2	0.1

5.11   RELATIONSHIP BETWEEN MINTEQA2 SPECIATED RESULTS, CALCITE PRECIPITATION AND CHEMICAL INDICES ON COOLING WATER SAMPLES

Eskom uses chemical indices on all chemical aspects of the plant in order to determine how efficiently the plant is
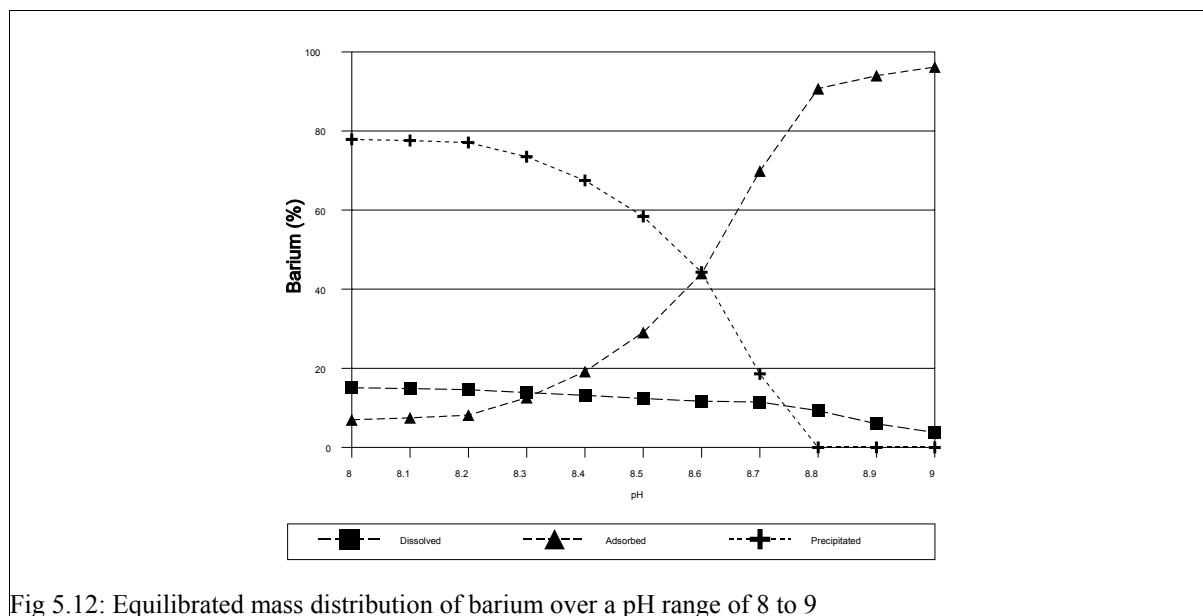
Fig 5.12: Equilibrated mass distribution of barium over a pH range of 8 to 9

running. The relationship between chemical indices for cooling water samples and the calcite precipitation potential

calculated by MINTEQA2 are shown in **TABLE 5.16**.

TABLE 5.16
Relationship between cooling water chemical indices and calcite precipitation potential obtained from

MINTEQA2

	Specification	CWS Day 98	Sim 1	Sim 2	Sim 3	Sim 4
pH @ 25 °C	8.2 - 8.6	8.4	8.4	8.4	8.4	8.4
Conductivity @ 25 °C (F S/cm)	<3 000	2 110	N/A	N/A	N/A	N/A
Turbidity (NTU)	<75	25	25	25	25	25
P-alkalinity (mg/l CaCO$_3$)	<5	10.04	N/A	N/A	N/A	N/A
Malkalinity (mg/l CaCO$_3$)	<120	103	**206**	**51.5**	103	103
Chloride (mg/l Cl)	<250	240	240	240	**480**	**120**
CaH (mg/l CaCO$_3$)	**269**	268	**536**	**134**	268	268
MgH * SiO$_2$ (mg/l CaCO$_3$* SiO$_2$)	<25 000	159.6	N/A	N/A	N/A	N/A
Sulphate (mg/l SO$_4$)	<850	611	611	611	**1222**	**306**
Sodium (mg/l Na)	<250	253	253	253	**701**	**56**
Potassium (mg/l K)	<60	56.5	56.5	56.5	56.5	**10**
Phosphate (mg/l PO$_4$)	<1.0	0.08	0.08	0.08	0.08	0.08
Nitrate (mg/l NO$_3$)	<1.0	4	4	4	4	4
OA (mg/l O$_2$)	<20	10.7	N/A	N/A	N/A	N/A
COD (mg/l O$_2)$	<200	74	74	74	74	74
Index	0.7	0.64	2.46	1.56	0.84	0.54
Calcite pp (open)	0.58	0.62	2.81	0.32	0.51	0.70

Notes: N/A = not applicable to the MINTEQA2 run
Bold figures indicate changes or estimated figures
CaH = Calcium Hardness
MgH = Magnesium hardness
The chemical index for cooling water is calculated as follows:
$P/7.5 + ABS(110-M)/10 + SO_4^{2-}/1000 + Cl/400 + ABS(300-CaH)/100 + TURB/100$
An index of >0.9 indicates inadequate chemistry control, which does not meet requirements.
Index values between 0.6 and 0.9 indequate adequate chemistry control which meet the requirements for long

term plant health.
An index of <0.6 indicates excellent chemistry control.
For **Sim 1**, the alkalinity and calcium hardness of **CWS, day 98**, have been doubled and the calcite precipitation

potential has increased by the same order of magnitude as the chemical index. However in **Sim 2**, where the

alkalinity and calcium hardness have been halved, the calcite precipitation potential is lower whereas the index is

higher than that obtained for **CWS, day 98**. Increasing and decreasing the chloride and sulphate values,

accompanied by changes in the sodium and/or potassium values (to maintain a cation anion balance) has the

opposite effect on the index (showing the chemistry to be out of control due to potential corrosion problems), compared to the calcite precipitation potential. Hence the calcite precipitation potential obtained from MINTEQA2 is a good indicator of the cooling water quality when scaling is the only potential problem, but not when corrosion is a major factor as in the case high chlorides and sulphates.

Chapter 6

CONCLUSIONS

The primary objective of this project was to evaluate the usefulness of chemical speciation modelling as a predictive tool for the treatment and evaluation of raw and cooling water in the power station environment. A secondary aim was to fully evaluate the MINTEQA2 computer program, the user-friendliness of its inputs and the usefulness and correctness of its output. Finally, an objective was to teach power station personnel how to use the program so that they could have instant answers to the more difficult chemical problems occurring during the day-to-day running of the plant. While undertaking the experimental work several points came to light which are discussed under the heading **GENERAL CONCLUSIONS** below.

6.1   GENERAL CONCLUSIONS

- It has been found that MINTEQA2 is a useful tool for characterising cooling water circuits.

- Many of the results obtained were to be expected and could have been predicted using a conventional approach, however a complex set of equations is required as well as a suitable thermodynamic database. Hence, MINTEQA2 has potential for reaching rapid conclusions, as thermodynamic databases are included in the model.

- It must be borne in mind that MINTEQA2 only addresses which minerals are likely to precipitate from the water and hence result in scaling. One must therefore be cautious in relying too much on its outputs, as the aggressive and corrosive properties must also be taken into consideration, prior to recommending other treatments of the cooling water. This was proven in **Chapter 5**, when calcite precipitation potentials were compared to chemical indices. The calcite precipitation potentials compared well with the chemical indices when

the calcium and total alkalinity values were out of specification on the high side. However, corrosion is a major problem on cooling circuits and the chemical indices will show the cooling water chemistry to be out of contol when the corrosive determinands such as chloride and sulphate are increased. The calcite precipitation potential, in this case does not indicate that the cooling water quality is out of control.

- The mineral predicted to precipitate by MINTEQA2 was not always what is found in practice. This could be due to a number of factors, some of which are:

It is not always practical to carry out a fully comprehensive chemical analysis on water samples, particularly in the power station environment. For example, iron analysis and total organic carbon analysis are not carried out on most water samples however the presence of these two constituents can make a major difference to the species which are predicted to precipitate. Hence if the input to the program does not contain all of the relevant chemical constituents, the predicted precipitate and the actual precipitate will not correspond.

If carbon dioxide is entered into MINTEQA2 the user must be careful to allow equilibration at atmospheric pressure to be modelled as complete equilibration does not occur with a dynamic system such as a cooling water circuit. This can be demonstrated by the differences in total alkalinity values obtained between the T-R-I and Matla power station laboratories, where it can be assumed that equilibration with carbon dioxide had occurred with the T-R-I samples, resulting in lower total alkalinity values being read at the T-R-I laboratory.

Kinetic considerations, e.g. a mineral which takes centuries to form (e.g. dolomite) would not be a factor of importance in a cooling water system.

MINTEQA2 assumes a standard enthalpy change of reaction (ΔH). This means that using the program as is, one cannot have a temperature at which a minimum/maximum solubility occurs. This can be overcome by changing the log K value during a MINTEQA2 run,

however this was only attempted in the case of calcite precipitation. Changing the log K values at different temperatures did not make a difference to the predicted quantity of calcite precipitating, however this was only carried out over a limited temperature range where the changes to log K values were insignificant.

- Since starting this project MINTEQA2 has been used within Eskom to carry out predictive modelling in other types of waters e.g. effluents, concentrated brines and ground water. It has proven to be a useful tool for the assessment of these waters. The program has not been used for the modelling of condensate or boiler water as there are specific programs available for the modelling of these low TDS waters.

- MINTEQA2 outputs were used to predict conductivities. All calculated results were within 21 % of the measured value with the majority of calculated values being higher than the measured values. There was one exception and in this case the measured value was found to be inaccurate. Hence, the calculation of conductivity using MINTEQA2 outputs could be useful, (particularly if the programme is modified to obtain closer correlations to verified analytical results), and possibly be used to validate analytical results, if the analytical results are in question.

- Speciated and non-speciated balances were compared and were found to correlate well in most cases.

- Comparison of results carried out on site and those transported approximately 120 km to the T-R-I laboratory showed good correlation except for the total alkalinity and pH values. This led to the conclusion that these analyses should only be carried out on site.

- The properties of minerals predicted to precipitate were evaluated and based on their likelihood of formation a decision was made as to whether they should be included or excluded as precipitates.

- Surface adsorption modelling using the diffuse layer model makes a significant difference to the precipitation potentials of calcium, copper and barium because of their tendency to be adsorbed onto the iron hydroxide layer. The use of this model will be of assistance in other projects being carried out by Eskom e.g. the use of anion-free flocculant for the clarification of cooling water.

6.2   VALIDATION OF MINTEQA2

When sufficient time was allowed for equilibration of the synthetic samples, excellent correlations between MINTEQA2 predictions and measured values were obtained in terms of calcite precipitation. For the synthetic samples, magnesite was also predicted to precipitate, but there was no change in the magnesium concentration over the period of study and hence magnesite was excluded as a precipitate.

6.3   RAW WATER

Usutu river water is a preferable raw water source to Usutu-Vaal river water from a speciation aspect because the quantities of minerals predicted to precipitate by MINTEQA2 were lower for Usutu water. However, there are many other aspects to consider when the quality of water supply alters e.g. flocculation. Efficient flocculation can be more difficult to achieve with low TDS waters than high TDS waters.

6.4   COOLING CIRCUIT DURING CONCENTRATION-SOUTH SIDE

 Information has been gained on how rapidly precipitation starts occurring from cooling water as it concentrates by speciating each water sample. The calculated concentration of contaminants in the cooling water system was based on sodium values and fairly good correlations were obtained when all contributing factors were assessed e.g. the addition of ferric chloride and sulphuric acid. MINTEQA2

was used to predict the concentration of calcium and magnesium in the cooling water after clarification, if portlandite was dosed in such a way as to obtain the analysed total alkalinity values. The predicted values were lower than the actual values in most cases, however certain reasons have been postulated for this discrepancy;

- DOM does not adequately represent the adsorptive properties of the organics present in the cooling water, and the DOM predictions may have been incorrect, as only six analytical values were obtained over the period studied,

- Overdosing of portlandite could have occurred,

- Sulphuric acid and ferric chloride dosing could have been higher than predicted,

- Total alkalinity values, on the days on which analytical results were not available, could have been different to those predicted.

On day 18, where the ferric chloride and sulphuric acid dosing could be calculated from the values obtained on the clarified cooling water, there was good correlation between the predicted and actual total alkalinity and magnesium results, however the predicted calcium result was substantially lower than the actual calcium result.

If a speciation profile is carried out in future it would be better to carry out more analyses over a shorter period e.g. three times per day for twenty days. All water samples should be analysed at this frequency i.e. raw water, cooling water and clarified cooling water. This would eliminate the need for many of the assumptions that have been made.

6.5 CALCITE

It was found that calcite ($CaCO_3$) was the major precipitate from the cooling water circuit at Matla power station. The parameters which most affect the precipitation of calcite were investigated. These were temperature, calcium, carbonate, pH, carbon dioxide, dissolved organic matter and sulphate. Calcite precipitation is decreased when pH, temperature, calcium concentration and carbonate concentration are decreased and when the concentrations of dissolved carbon dioxide, dissolved organic material and sulphate concentrations are increased.

6.6 THE EFFECT OF DETERMINANDS IN SOLUTION ON PRECIPITATION POTENTIALS

As many determinands as possible should be entered into MINTEQA2 in order to obtain a true picture as to what should precipitate from the water. The determinands which are particularly prone to precipitate are those which are normally found in trace level quantities, however only low masses of these solids were predicted to precipitate.

It is necessary to measure all of the major elements (sodium, potassium, calcium, magnesium, chloride, nitrate and sulphate) and total alkalinity and pH, as their concentrations affect the cation /anion balance of the solution. Other determinands which are of importance are barium, silica, organic matter and phosphate. However, whenever the quality of the raw water changes, a trace element analysis should be carried out, because a significant increase in any one of the trace elements analysed in this thesis will result in a significant precipitation problem.

6.7 THE USE OF MINTEQA2 AT POWER STATION LABORATORIES

The validation of analytical results: The speciated cation anion/balance is obtained, together with the other useful outputs such as the ionic strength of the solution. The program will immediately simulate the precipitation of an element from the constituents present in the water if it cannot exist in a dissolved state under given conditions e.g. iron at a certain pH value, which will eliminate analytical errors of this kind.

Ascertaining which analyses are of importance in terms of precipitation i.e. at the levels of concentration studied, certain elements do not take part in the precipitation process e.g. chloride. Due to the significance of organic material in inhibiting precipitation it is considered worthwhile to include routine COD or total organic carbon (TOC) determinations on all sample types.

For determining which parts of the cooling water circuit are most at risk of precipitation. The precipitation potential for calcite and silica-containing minerals is higher at the condenser than any other part of the cooling water circuit, because of the higher temperature of the cooling water at this part of the circuit.

MINTEQA2 can be used as a teaching tool for new members of staff.

Chapter 7

RECOMMENDATIONS

This **Chapter** will commence with suggestions on improvements which could be made to MINTEQA2. Recommendations will then be given on future work which should be undertaken to enhance the understanding and use of chemical speciation models relative to cooling water circuits and raw water supplies. The **Chapter** will be concluded with general recommendations.

7.1 IMPROVEMENTS THAT COULD BE MADE TO MINTEQA2

- The program should be transferred from being DOS-based to WINDOWS-based, since all computer users are more familiar with WINDOWS.

- The free energies of formation in the database should not be limited to a linear relationship with temperature. If this is corrected it will enable the user to determine minimum and maximum solubilities and the program would be more accurate at higher temperatures.

- One of the major reasons for how cumbersome the use of the program is, is its inability to allow solids to precipitate when alkalinity values are part of the input. If this problem were overcome, i.e. by automatic conversion of alkalinity to carbonate, the programming could be speeded up considerably.

- Due to the dynamic nature of cooling water circuits, the MINTEQA2 algorithm should be incorporated in a dynamic simulation package. These programs have recently become available for rental, at a cost of R 66 000.00 per annum.

7.2   FUTURE WORK

● Since dissolved carbon dioxide makes a substantial difference to the MINTEQA2 output, it is essential that this parameter be quantified. Therefore, the use of a carbon dioxide probe for the on-site analysis of raw, cooling and clarified cooling water should be investigated.

● The simulation of organics in the water can be improved, particularly if the database is expanded to include specific organic material, such as antiscalants.

● More time should be spent on the validation procedure. Only the validity of calcite precipitation has been investigated. The validity of the predicted precipitation of $CaSO_4$ should be investigated. Changes in variables such as temperature, pH and dissolved gases should also be validated.

● If the opportunity arises to study the circuit as the concentration of contaminants increases again, then all variables should be noted i.e. exact quantities of treatment chemicals, water flow rates, etc. As mentioned in **Chapter 6**, the frequency of analysis should be increased over the first twenty days. It would also be of benefit to analyse the sludge from the clarifier to determine exactly what minerals are removed during the clarification process.

● Further investigations should be carried out in order to make MINTEQA2 an improved predictive tool, particularly with respect to the relationship between total alkalinity, calcium and magnesium, and portlandite dosing.

● The advantage of using iron hydroxide as a flocculant and adsorbent has already been recognised at Eskom and its ability in removing solutes should be investigated further.

● All samples should be analysed for their dissolved organic matter content, either by TOC or by COD analyses.

7.3   GENERAL CONCLUSIONS

- MINTEQA2 results are qualitative rather than quantitative for cooling circuit applications because of the dynamic nature of the problem

- Power station personnel have been taught how to use MINTEQA2. It has been found that the input is too lengthy and complicated for personnel to use the program on a routine basis therefore it is recommended that the program only be used for problem solving purposes.

- The use of chemical speciation modelling could be included in the various chemical courses available as it is an excellent teaching tool.

- It is not recommended that MINTEQA2 is used to replace the chemical indices currently used in Eskom to evaluate the quality of the cooling water, since corrosive waters containing high chlorides and sulphates do not effect precipitation potentials.

References

AFRICAN NATIONAL CONGRESS (1994) The Reconstruction and Development Programme. A Policy Framework. ABC Printers and Book Printers, Cape Town.

ALLISON, JD, BROWN, DS and NOVO-GRADAC, KJ (1990) MINTEQA2 / PRODEFA2. A Geochemical Assessment Model for Environmental Systems. Version 3.0 User's Manual.

ANON Chemistry Standards and Procedures for the Closed Cooling Systems at Kendal Power Station. PO Box 1091 Johannesburg 2000.

ASTM Standard Methods Volume 11.01, 1992.

BALL JW, JENNE EA, CANTRELL MW (1981) WATEQ3: A Geochemical Model with Uranium added. U.S. Geological Survey, Washington, DC. Open File Report 81-1183.

BARTHOLD, LO and WILSON, DD (1988) The US Power System - A Study in Pluralism. Power Technology International, 61 - 63.

BETZ HANDBOOK (1980) Betz Handbook of Industrial Water Conditioning (8th edn.). Betz Laboratories, INC, Trevose, Pennsylvania.

BRITISH ELECTRICITY INTERNATIONAL (1992) Modern Power Station Practise. (3rd edn.) Volume E. 77.

BROUCKAERT, BM, BROUCKAERT, CJ and BUCKLEY, CA (1996) The Prediction of Electrical Conductivity from Chemical Speciation. The Water Institute of Southern Africa, Biennial Conference and Exhibition, Port Elizabeth, Feather Market Centre, 20-23 May 1996. (Poster)

BROUCKAERT, CJ (1992) Final Report to the Water Research Commission on Research on the Modelling of Tubular Reverse Osmosis, WRC Project Number **325** Pretoria, South Africa.

BUCKLEY, C and WINSHIP, S (1995) The Production of an Anion - Free Flocculant. TRR/S/95/027, Eskom, Johannesburg, South Africa.

CENTRAL ELECTRICITY GENERATING BOARD (1971,a) Modern Power Station Practise: Planning and Layout (2nd Edn.). **1**.

CENTRAL ELECTRICITY GENERATING BOARD (1971,b) Modern Power Station Practice; Chemistry and Metallurgy (2nd Edn.). **5**.

CENTRE FOR EXPOSURE ASSESSMENT MODELLING (1991) Summary of Modifications and New Features in MINTEQA2 and PRODEFA2 Versions 3.10, 3.11.

CHUKROV F (1973) Izv. Akad. Nauk SSSR, 23.

COBBLE JW and LIN S (1987) The ASME Handbook on Water Technology for Thermal Power Systems, Chapter 8, Paul Cohen, editor. EPRI Research Project No. RP 1958-1.

CORROSION INSTITUTE OF SOUTHERN AFRICA (July, 1994) Corrosion Control in Southern Africa, ISBN 0 86999 927 3.

CORROSION SCHOOL (1993) Handout material.

DEPARTMENT OF WATER AFFAIRS (1986) Management of the Water Resources of the Republic of South Africa. Department of Water Affairs ISBN 0621110043. Pretoria, South Africa.

DEPARTMENT OF WATER AFFAIRS AND FORESTRY (1994) White Paper on Water Supply and Sanitation policy. Pretoria, South Africa.

DEPARTMENT OF WATER AFFAIRS AND FORESTRY (1995) You and Your Water Rights ISBN 0-621-16752-5. Pretoria, South Africa.

DERNAT, M, HOCQUAX, H and OHANNESSIAN L (1985) Cooling Water Treatments Studied by Glow Discharge Lamp. Proceedings of the 6th European Symposium on Corrosion Inhibitors (6SEIC) Ann. Univ. Ferrara, N.S., Sez. V, Supp No 8.

DOBBS JC, SUSETYO W, CARREIRA LA and AZARRAGA LV (1989) Competitive Binding of protons and metal ions in humic substances by lanthanide ion probe spectroscopy. Anal. Chem., 61, 1519-1254.

DREW PRINCIPLES OF INDUSTRIAL WATER TREATMENT (1979) Third Edition. Published by Drew Chemical Corporation.

DZOMBAK DA and MOREL FMM (1990) Surface Complexation Modelling: Hydrous Ferric Oxide. John Wiley and Sons, New York, NY.

ESKOM (1994) Annual report to staff. Communication Services Megawatt Park (CG U39) PO Box 1091 Johannesburg 2000 South Africa.

EUROPA WORLD YEAR BOOK (1995) 36th Edition. Volume 2 Europa Publications, 2772.

FAUST GT, HATHAWAY JC and MILLOT G (1959) A restudy of stevensite and allied minerals.

Am. Miner. 44, 342-370.

FELMY AR, GIRVIN DC, JENNE EA (1984) MINTEQ. A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032, U.S. EPA. Athens Georgia, GA.

FRIEND JFC (1990) Chemical Conditioning of Low and Medium Salinity Waters. M. Sc (ENG) UCT.

FRONDEL-DANA'S SYSTEM OF MINERALOGY (1962) Seventh Edition. Volume 3.

HANEKOM D (1997) Personal Communication.

HERBIN HC (1993) Performance of Nuclear and Fossil - Fired Power Plants : A Worldwide Perspective. Conference paper from Power - Gen Europe '93 **5 - 6**, 217.

HEWETT NH and HUFTON PF (1993) Electricity Generation, Energy Efficiency and the Environment. Conference Papers from Power - Gen Europe '93 **1 - 4** 367.

JCPDS (1994) International Centre for Diffraction Data (Database installed on T-R-I XRD).

KERR, CA (1993) Final Report to the Water Research Commission on Research on Phase Diagrams of Complex Precipitates, WRC Project Number 309, Pretoria, South Africa.

KERR, CA (1994) MINTEQA2: Additional Modelling Problems and case studies of Advanced Modelling Problems PRG University of Natal, Durban, South Africa.

KREBS WD, BJORNARD TA AND SOFER (1993) Advanced Fuel Technology by Siemens for Economic Nuclear Power Generation and Ecological Use of Fuel Resources. Conference Paper from

Power - Gen Europe '93 Vol 5 - 6, 97.

LOEWENTHAL RE, EKAMA GA AND MARAIS GVR (1988). STASOFT: An Interactive Computer Program for Softening and Stabilization of Municipal Waters. Water Research Commission, PO Box 824, Pretoria 0001, South Africa.

LOUX NT, BROWN DS, CHAFIN CR, ALLISON JD and HASSAN SM (1990) Modelling Geochemical Processes attenuating Inorganic Contaminant Transport in the Subsurface region: Adsorption on Amorphous Iron Oxide. In Proceedings, Environmental Research conference on Groundwater Quality and Waste Disposal. Muraka I and Cordle S (Eds.). EPRI EN-6749. Electric Power Research Institute, Palo Alto, CA.

LUJAN M JR AND PECK DL PHREEQE user manual, U.S. Department of the Interior and U.S Geological Survey.

LUMSDON DG, EVANS LJ Predicting Chemical Speciation and computer simulation. Chemical Speciation in the Environment. AM Ure and CM Davidson (Eds), Blackie Academic & Professional, London ISBN 0751400211.

MANIATOPOULOS CS (1993) Legal and Economic Framework. Conference Paper from Power Gen Europe '93 Volume **1-4**, 12 - 23.

MARTYNOVA OI, VASINI LG, BOGLOVSKY AV, GYSEVA OV (1991) Alkaline Scale Formation Restriction in Desalination Plants by means of Antiscalant Additives. Proceedings of the Twelth International Symposium on Desalination and Water Re-use.

MCKELVEY KK AND BROOKE M (1959) The Industrial Cooling Tower Elsevier Publishing Company. Library of Congress Catalog Card Number 58- 10156

MERRITT SD (1993) Applications of soil and cement chemistry to stabilization / solidification. Transportation Research Record n 1424, 1-7.

MORGAN (1994) Eskom Annual Report to Staff. Message from our Chief Executive. PO Box 1091 Johannesburg 2000 South Africa.

MULLER A M (1994) The challenge of Reconstruction and Development : from theory to implementation in water and sanitation. Water Sewage and Effluent Volume 14 No. 4 December 1994.

MULLER M (1996) Water Law Review: The Current Status. A paper presented at the Water Institute of South Africa Biennial Conference and Exhibition (WISA - May 1996).

NALCO WATER HANDBOOK (1988). Second Edition. Mc Graw Hill. ISBN 0070458723.

OHLER B R AND HOLLINGSHAD WR (1985) Cooling Water Product Evaluation and Selection: A Case Study. Official Proceedings The International Water Conference 46th Annual Meeting.

PALACHE C, BERMAN H & FRONDEL C (1951a) Dana's System of Mineralogy, Seventh Edition, Volume 1.

PALACHE C, BERMAN H & FRONDEL C (1951b) Dana's System of Mineralogy, Seventh Edition, Volume 2.

PARKER SP (1992) Editor in Chief. McGRAW-HILL Encyclopedia of Science and Technology Vol. 6, 240 - 241.

POLLUTION RESEARCH GROUP, UNIVERSITY OF NATAL (May 1992) Introduction to MINTEQA2 Version 3.0.

POPCZYK J AND KEDZIERSKI Z (1993) Restructuring of the Polish Power Industry Achievements and Challenges. Conference Paper from Power - Gen Europe '93 Vol 1 - 4, 161.

POSTGATE JR (1981) The sulphate-reducing bacteria. ISBN 0 521 22188 9.

POZYN (November 1994) Fuel & Water, Water Statistics. PO Box 1091 Johannesburg 2000 South Africa

PRESSLY J T (1989) Control of Scale Formation in Mine Cooling Water Systems, Journal of Mine Ventilation Society of South Africa, v42 n5.

PUCKORIUS PR & STRAUSS SD (May, 1995) Special Report Cooling Water Treatment, Power, McGraw-Hill.

RADIOMETER USERS MANUAL FOR THE OPERATION OF THE CDM 83 CONDUCTIVITY METER.

SERKIZ SM, ALLISON JD, PERDUE EM, ALLEN HE and BROWN SD (1996) Rapid Communication: Correcting Errors in the Thermodynamic Database for the Equilibrium Speciation Model MINTEQA2. Wat. Res. Vol 30, No 8, pp 1930-1933.

STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER, APHA, AWWA, WPCF 16 Ed, 1989.

STOLLENWERK KG (July 1994) Geochemical interactions between constituents in acidic groundwater and alluvium in an aquifer near Globe, Arizona. Applied Geochemistry v9 n4, 353-369.

STUMM W & MORGAN JJ (1981) Aquatic Chemistry An Introduction Emphasizing Chemical Equilibria in Natural Waters. 2nd Edition. John Wiley & Sons.

SUSETYO W, CARREIRA LA, AZARRAGA LV and GRIMM DM (1991) Fresenius J. Anal. Chem., 339, 624-635.

THOMPSON H (1993) The Constitution of the Republic of South Africa, Understanding the Existing Framework of the Water Law and Preparing for a New Law.

VENTER PN (1984) Scale Prevention in Ash Water Return Systems. TRR/C84/019 PO Box 1091 Johannesburg 2000 South Africa.

WATER RESEARCH COMMISSION (1993) Annual Report. Pretoria, South Africa.

WESSELS F (1996) Personal Comminication.

WESTALL JC (1986) MICROQL. A Chemica Equilibrium Program in BASIC. Report No. 86-02 Oregon State University, Corvallis, OR.

WESTERN CAPE ENVIRONMENTAL MONITORING GROUP (1993), Clean Production.

WOEST M &MACLONS P (1992) Cause and inhibition of dezincification (selective leaching) in inhibited admiralty brass condenser tubing - progress report. TRR/S92/159/lcvdm PO Box 1091 Johannesburg 2000 South Africa.

ZIJL G J L AND SEP N V (1993) A Transfrontier Approach to Cost - Effective Reduction of Air Pollution. Conference Proceeding fromPower - Gen Europe '93 Vol 1 - 4, p25.

Appendix A1
DESCRIPTION OF ANALYTICAL TECHNIQUES

TABLE A 1.1
Table of determinand and technique used by the T-R-I laboratory

DETERMINAND	TECHNIQUE
Conductivity	Electrometric - Conductivity Meter
pH	Electrometric - pH Meter
Total Alkalinity	Titrimetric
Sodium	ICP
Potassium	ICP
Magnesium	ICP
Calcium	ICP
Chloride	IC
Nitrate	IC
Sulphate	IC
Fluoride	Fluoride - Ion Selective Electrode
Aluminium	ICP
Barium	ICP
Copper	ICP
Iron	ICP
Zinc	ICP
Silica	ICP
Strontium	ICP

TABLE A1.2
Table of determinand and technique used by the Matla power station laboratory

DETERMINAND	TECHNIQUE
Conductivity	Electrometric - Conductivity Meter
pH	Electrometric - pH Meter
Total Alkalinity	Titrimetric
Sodium	AA
Potassium	AA
Magnesium	Titrimetric: Total hardness-calcium hardness
Calcium	Titrimetric: Calcium hardness
Chloride	Titrimetric
Nitrate	Spectrometric
Sulphate	EMA titration
Phosphate	UV-spectroscopy
Chemical Oxygen Demand	Titrimetric
Silica	UV-spectroscopy

A 1.1   ION CHROMATOGRAPHY

All chromatography methods make use of a stationary phase and a mobile phase. Components of a mixture are carried past the stationary phase by the flow of the mobile one; separations are based on differences in migration rates among the sample components due to their differential adsorption to the stationary phase.

An ion exchange membrane is used to effect chemical suppression. This results in the background conductivity being reduced to a negligible level and the sample ions are converted to a highly conductive form. Continuous diffusion of hydrogen ions occurs across the membrane resulting in the following reactions;

$$CO_3^{2-} + H^+ \, {}^* \, HCO_3^- \qquad (A - 1)$$

$$HCO_3^- + H^+ \, {}^* \, H_2CO_3 \qquad (A - 2)$$

$$Cl^- + H^+ \, {}^* \, HCl \qquad (A - 3)$$

$$NO_3^- + H^+ \, {}^* \, HNO_3 \qquad (A - 4)$$

$$SO_4^{2-} + 2H^+ \, {}^* \, H_2SO_4 \qquad (A - 5)$$
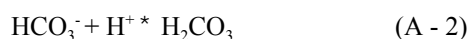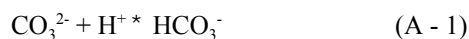
It can be seen from equations A - 1 and A - 2 that the mobile phase is converted to weakly conducting carbonic acid and from equations A - 3, A - 4 and A - 5 that the anions are converted to their corresponding strongly conducting mineral acids.

Fig A1-1 is a schematic diagram of a typical ion chromatograph configuration.

Fig A1-1: Schematic representation of a typical ion chromatograph configuration
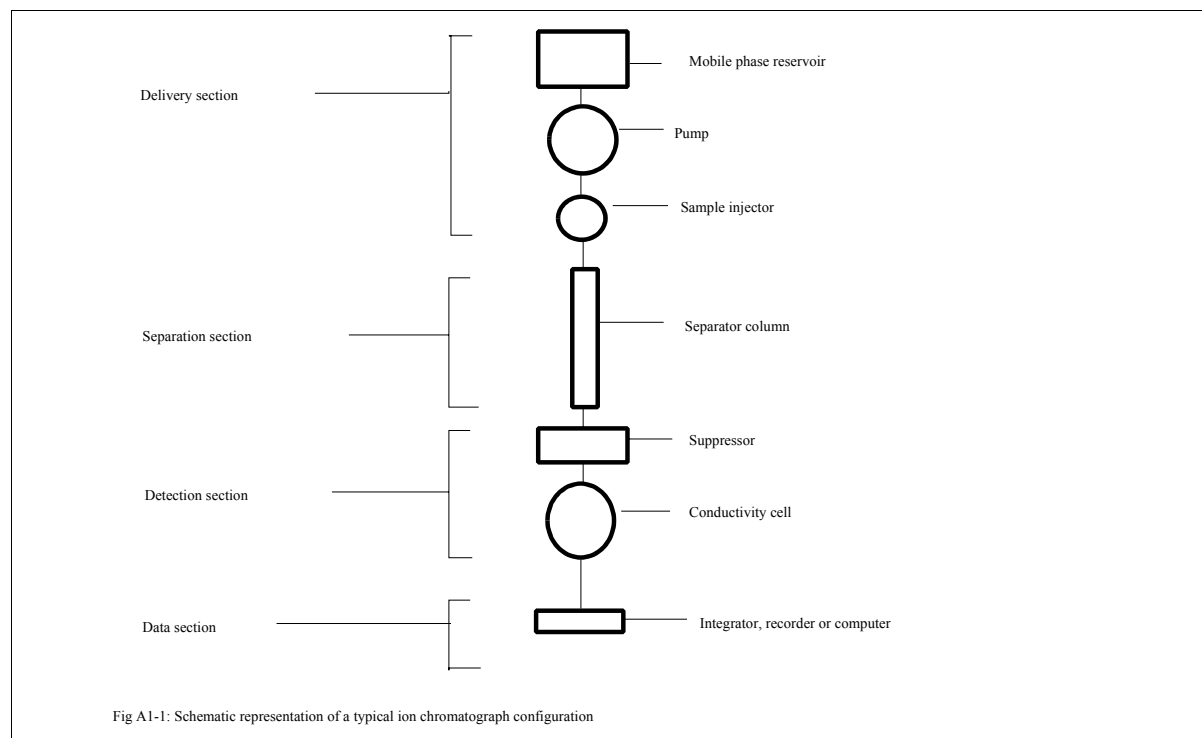
The order in which the anions elute from the ion exchange column is dependant on their charge to mass ratio, ion mobility, diffusivity, etc. The lower the charge to mass ratio the faster the ion will elute e.g. in a homologous series, fluoride will elute before chloride and nitrite will elute before nitrate. A standard solution is prepared and injected prior to injection of the sample of interest. Concentrations can be determined using the standard chromatogram.

A 1.2   INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY

Inductively coupled optical emission spectroscopy involves the emission of electromagnetic radiation of atoms or ions, based on a plasma source. Atomic spectra are obtained by atomisation, a process whereby the molecular constituents of a sample are decomposed and converted to atomic particles. The plasma used is argon which is a conducting gaseous mixture and an electrode discharge produces the heating. The sample is carried into the hot plasma by argon flowing through a central quartz tube. The sample is nebulised by the flow of argon and the resulting finely divided droplets are carried into the plasma. In the region of 10 to 30 Fm above the central core of the plasma, it is optically transparent and this is where spectral observations are made. By the time the sample atoms have reached the observation point they will have resided for about 2 ms at temperatures ranging from 6 000 to 8 000 K.

A 1.3 X - RAY DIFFRACTION SPECTROMETRY

X-rays are defined as short wavelength electromagnetic radiation produced by the deceleration of high-energy electrons or by electronic transitions involving electrons in the inner orbitals of atoms. Interaction between the electric vector of X-radiation and the electrons of the matter through which it passes results in scattering. When X-rays are scattered by the ordered environment in a crystal, both constructive and destructive interference takes place among the scattered rays. This phenomenon occurs because the distances between the scattering centres are of the same order of magnitude as the wavelength of the radiation. To interpret the spectra obtained by this technique, the Bragg equation is used. Therefore, the identification of a species from its diffraction pattern is based upon the position of the lines in the spectrum and their relative intensities. The diffraction angle is determined by the spacing between a particular set of planes. Line intensities depend upon the number and kind of atomic reflection centres that exist in each set of planes.

A 1.4 CONDUCTIVITY

The electrical conductivity of a solution is the reciprocal of the resistance in ohms measured between the opposite faces of a centimeter cube of an aqueous solution at a specified temperature. Conductivity is a number which reflects the ability of an aqueous solution to carry an electric current.

A 1.5 TOTAL ALKALINITY AND pH

The alkalinity of water is its acid - neutralising capacity i.e. the sum of all the titratable bases. For alkalinity measurements the sample is titrated with standard 0.1 molar nitric acid to a designated pH of 4.5, the end point being determined electrometrically.

A 1.6 SCANNING ELECTRON MICROSCOPE COUPLED TO ENERGY DISPERSIVE ANALYSIS OF X-RAYS

With this method, x-ray emission is stimulated on the surface of the sample by a narrow focussed beam of electrons. The resulting X-ray emission is detected and analysed with an energy dispersive spectrometer. The microscope is used to locate the area to be bombarded.

A 1.7 ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption (AA) spectroscopy is a complimentary technique to ICPOES where sample molecules are dissociated into their atoms in a flame. The difference between ICPOES and AA is that in emission spectroscopy radiation is emitted by atoms which are in excited energy states, whereas in absorption spectroscopy the atoms which

can absorb energy are in the ground state. Also, instead of a plasma, a flame is used which is comprised of fuel and oxidant. The fuel - oxidant mixture used for the determination of sodium and potassium is air - acetylene. The flame temperature is approximately 2 450 K.

A 1.8   EQUIVALENT MINERAL ACIDITY TITRATION

This titration is used as an indirect determination of sulphate. The equivalent mineral acid (EMA) in water is the amount of acid liberated from natural waters when the sample is passed through a strong acid cation exchange resin in the hydrogen form. Hydrogen ions are exchanged for other cations in the water passing through the column. The titration is carried out in order to determine total anions in solution and sulphate is calculated by subtracting the known quantity of other anions in solution.

A 1.9   TITRIMETRIC, UV-SPECTROSCOPIC METHODS AND SPECTROMETRIC METHODS

The methods used can be found in any text book of standard methods for the analysis of water and therefore are not described in detail in this **appendix**.

Appendix A2

CHEMICAL ANALYSES OF WATER AT MATLA POWER STATION

Table A 2.1

Comparison between Usutu-Vaal and Usutu waters (February 1994)

Determinand	Percentage Error	Usutu-Vaal water	Usutu water
Conductivity @ 25 °C (FS/cm)	+/- 0.16	237	79
Conductivity (calculated)		284	70
pH @ 25 °C	+/- 0.14	7.72	7.22
Total Alkalinity (mg/l CaCO$_3$)	+/- 2.0	90.54	24.77
Sodium (mg/l Na)	+/- 0.2	15.82	6.56
Potassium (mg/l K)	+/- 6.0	3.82	2.34
Calcium (mg/l Ca)	+/- 2.1	19.46	5.51
Magnesium (mg/l Mg)	+/- 1.3	12.88	3.06
Total Hardness (mg/l CaCO$_3$)	+/- 3.4	101.6	26.4
Zinc (mg/l Zn)	+/- 0.4	0.020	<0.005
Chloride (mg/l Cl)	+/- 1.9	8.40	4.29
Sulphate (mg/l SO$_4$)	+/- 0.7	20.6	7.4
Nitrate and Nitrite (mg/l N)	+/- 6.0	<0.1	<0.1
Fluoride (mg/l F)	+/- 2.0	0.17	0.16
Barium (mg/l Ba)	+/- 3.7	0.067	0.022
Copper (mg/l Cu)	+/- 5.6	0.029	0.043
Iron (mg/l Fe)	+/- *8.0*	0.289	0.137
Silica (mg/l Si)	+/- 3.3	2.15	0.44
Manganese (mg/l Mn)	+/- 3.2	0.063	0.040
Speciated Balance (%)		6.5	6.0
Calculated Balance (%)		6.5	6.2
Calculated TDS (mg/l)		178	59

TABLE A 2.2

Table of distribution (%) of species obtained from MINTEQA2 for Usutu-Vaal and Vaal waters

Species	Distribution	Usutu-Vaal water	Usutu water
SO_4	SO_4^{2-}	89.9	96.3
	$MgSO_4$ (aq)	4.8	1.6
	$CaSO_4$(aq)	5	2
CO_3^{2-}	H_2CO_3	3.8	11.5
	HCO_3^-	94.9	88.2
Ca	Ca^{2+}	96	98.4
	$CaHCO_3^+$	1.4	
	$CaSO_4$(aq)	2.2	1.1
Mg	Mg^{2+}	96.2	
	$MgHCO_3^+$	1.5	
	$MgSO_4$(aq)	1.9	
H_2O	OH^-	3.8	2.7
	$FeOH_2^+$	36.5	62.5
	$FeOH_3$(aq)	31.5	17.6
	$FeOH_4^-$		2.7
	$Cu(OH)_2$(aq)	4.3	13
H	H_2CO_3	7.4	20.8
	HCO_3^-	92.6	80
Mn	Mn^{2+}	95.4	
	$MnSO_4$(aq)	2	
	$MnHCO_3^+$	2.4	
F	F^-	97.2	
	MgF^+	2.5	
Zn	Zn^{2+}	51.2	
	$ZnOH^+$	2.4	
	$Zn(OH)_2$(aq)	1.4	
	$ZnSO_4$(aq)	1.4	
	$ZnHCO_3^+$	8.2	
	$Zn(CO_3)_2^{2-}$	3.6	

TABLE A 2.2 (continued)

Table of distribution (%) of species obtained from MINTEQA2 for Usutu-Vaal and Usutu waters

Species	Distribution	Usutu-Vaal water	Usutu water
Cu	Cu^{2+}	1.6	12.5
	$CuCO_3(aq)$	26.6	21.2
	$CuOH^+$		1.9
	$Cu(OH)_2(aq)$	69.9	61.8
	$CuHCO_3^+$	1	2.5
Fe	$Fe(OH)_2^+$	52.6	82
	$Fe(OH)_3(aq)$	30.3	15.4
	$Fe(OH)_4^-$	17	2.7
Na	Na^+	100	100
K	K^+	100	100
Cl	Cl^-	100	100
NO_3	NO_3^-	100	100
Ba	Ba^{2+}	100	100
Si	H_4SiO_4	100	100

TABLE A 2.3

Table of saturation indices of minerals obtained from MINTEQA2 for Usutu-Vaal and Vaal waters

Mineral	Usutu-Vaal water	Usutu water
Anhydrite	-2.642	-3.497
Aragonite	-0.501	-2.033
Barite	-0.283	-0.085
Calcite	-0.596	-1.894
Chalcedony	-0.596	-1.284
Cristabolite	-0.532	-1.22
Dolomite	-0.635	-3.777
Ferrihydrite	*2.905*	*2.286*
$FeOH_{2.7}Cl_{0.3}$	*7.424*	
Fluorite	-2.678	-3.176
Goethite	*7.296*	*6.677*
Gypsum	-2.431	-3.286
Hematite	*19.6*	*18.361*
Jarosite Na	*0.575*	-0.890
Jarosite K	*3.327*	*2.032*
Magnesite	-0.769	-2.378
Quartz	-0.113	-0.801
SiO_2 (A,GL)	-1.101	-1.789
SiO_2 (A,PT)	-1.409	-2.097
Rhodochrosit	-1.056	-2.237
$Cu(OH)_2$	-1.456	-1.339
Tenorite	-0.436	-0.319
Cupricferrit	*16.897*	*15.775*
Smithsonite	-2.311	
Zn CO_3, 1 H_2O	-2.501	
$Zn(OH)_2$ (E)	-2.982	
ZnO (ACTIVE)	-2.791	
Zincite	-2.621	

TABLE A 2.3 (continued)

Table of saturation indices of minerals obtained from MINTEQA2 for Usutu-Vaal and Vaal waters

Mineral	Usutu-Vaal water	Usutu water
ZnSiO₃	1.47	
Willemite	-2.412	
Malachite	-1.281	-1.092
Azurite	-3.186	-2.924
Mag-ferrite	10.858	8.055
Lepidocrocit	6.425	5.806

Note : All minerals with SI values <-3. 000 have not been included in this table

TABLE A 2.4

Table of results obtained on raw water supplied to Matla power station

from 28 March to 16 June 1994 by the T-R-I laboratory

Determinand	Day									
	8	**11**	**14**	**16**	**18**	**39**	**67**	**73**	**81**	**87**
Conductivity @ 25 ℃ (*F*S/cm)	255	240	237	237	239	223	229	231	233	233
Conductivity (calculated)	288	279	277	275	274	231	240	246	250	249
pH @ 25 ℃	6.93	6.73	6.69	6.54	7.63	6.79	7.04	7.18	7.26	8.01
Total Alkalinity (mg/l CaCO₃)	87.3	81.4	80.2	79.9	79.8	73.1	73.4	73.4	74.6	75.2
Sodium (mg/l Na)	16.7	16.3	16.7	15.9	15.8	10	10	11	11	11
Potassium (mg/l K)	3.5	3.3	3.4	3.8	3.4	2.8	2.1	2.1	2.1	2.3
Magnesium (mg/l Mg)	12.8	13.4	12.6	13	13.3	12.1	11.1	11.5	11.5	11.8
Calcium (mg/l Ca²)	20.4	19.4	20.2	18.8	19	17.5	17.1	17.6	17.6	18.4
Chloride (mg/l Cl)	10.4	10.2	10.4	10.5	10.1	9.8	9.6	10.1	10.5	10.1
Nitrate (mg/l NO₃)	0.92	0.82	0.78	0.58	1.12	1.24	<0.10	<0.10	<0.10	<0.10
Sulphate (mg/l SO₄)	21.3	21.5	21	20.9	21	19.6	20.3	20.5	22.2	19.1
Fluoride (mg/l F)	0.28	0.28	1.10	0.27	0.16	0.28	0.42	0.42	0.35	0.38
Aluminium (mg/l Al)	0.19	<0.05	0.17	<0.05	<0.05	0.13	0.13	N/A	N/A	0.17
Barium (mg/l Ba)	0.16	0.08	<0.01	0.1	0.07	0.09	0.05	0.86	0.8	0.13
Copper (mg/l Cu)	0.03	0.03	0.01	0.03	0.03	<0.01	<0.01	0.01	0.02	0.02
Iron (mg/l Fe)	0.07	0.17	<0.01	0.24	<0.01	<0.01	<0.01	0.03	0.02	0.07
Zinc (mg/l Zn)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silica (mg/l H₄SiO₄)	7.87	7.97	7.97	8.34	6.81	6.53	1.92	2.22	1.2	1.03
Strontium (mg/l Sr)	0.12	0.11	0.11	0.11	0.11	0.2	0.1	0.1	0.1	0.1
Speciated Balance (%)	7.2	9.4	9.2	9.0	9.5	4.5	1.7	3.8	2.3	4.9
Calculated Balance (%)	7.3	9.3	9.9	9.0	9.4	4.7	1.7	3.5	2.4	5.3
Calculated TDS (mg/l)	191	180	178	178	179	167	172	173	175	175

KEY: N/A - Sample not analysed for this constituent.

TABLE A 2.5

Table of distribution (%) of species obtained from MINTEQA2 using raw water results from Table A 2.4

Species	Distribution	Day									
		8	11	14	16	18	39	67	73	81	87
SO_4	SO_4^{2-}	89.8	89.8	89.8	100	89.9	90.5	90.9	100	100	90.4
	$MgSO_4$ (aq)	4.7	5	4.7		5	4.7	4.3			4.5
	$CaSO_4$(aq)	5.2	5	5.2		4.9	4.7	4.6			4.9
CO_3^{2-}	H_2CO_3	19.6	27.9	37.5	37.5	4.6	25.3	16	12.1	10.3	2
	HCO_3^-	79.6	71.4	61.9	61.9	94.2	74.1	83.3	87.1	88.9	96.3
Ca	Ca^{2+}	96.3	96.4	96.5	96.5	96.2	96.6	96.5	96.5	96.3	96
	$CaHCO_3^+$	1.3	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1
	$CaSO_4$(aq)	2.3	2.3	2.3	2.3	2.3	2.2	2.3	2.3	2.5	2.1
Al	$Al(OH)_2^+$	4.9		3.9			7.4				
	$Al(OH)_4^-$	44.7		5.9			35.3				91.5
	AlF^{2+}			2.2			2.4				
	AlF_2^+			41.1							
	AlF_3(aq)			30.3							
	$Al(OH)_3$(aq)	49.1		15.8			53.8				8.4
Mg	Mg^{2+}	96.4	96.5	96.4	96.6	96.4	96.7	96.6	96.6	96.4	96.3
	$MgHCO_3^+$	1.5	1.4	1.4	1.4	1.3	1.3	1.3	1.3	1.3	1.3
	$MgSO_4$(aq)	2	2	2	2	2	1.9	2	2	2.2	1.9
H_2O	OH^-					40.4			11	15.1	3.6
	$MgOH^+$					2.7					
	$Cu(OH)_2$(aq)					56.2			8.4	21.8	1.8
	$FeOH_2^+$	8.5	88.6		93.1				61.1	44.8	2.5
	$FeOH_3$(aq)	1.2	7.8		5.3				15.3	13.5	4.2
	$Fe(OH)_4^-$								3.3	3.5	6.1
	$AlOH_2$(aq)	39	1.8	59.4			50.6	38			5.2
	$Al(OH)_4^-$	47.4		29.4			44.3	59.2			76.3
	$Al(OH)_2^+$	2.6		9.7			4.6	2			
H	H_2CO_3(aq)	33.2	43.8	54.6	54.7	8.9	40.7	27.9	21.7	18.7	4
	HCO_3^-	67.3	56	45.1	45.2	90.4	59.5	72.4	77.8	80.7	97.2

TABLE A 2.5 (continued)

Table of distribution (%) of species obtained from MINTEQA2 using raw water results from Table A 2.4

Species	Distribution	Day									
		8	11	14	16	18	39	67	73	81	87
F	F^-	96.1	97.1	78.3	100	97.1	95.1	96.9	100	100	97.4
	MgF^+	2.5	2.6	2		2.6	2.4	2.2			2.3
	AlF_2^+			8.9			1.6				
	$AlF_3(aq)$			9.9							
Cu	Cu^{2+}	18.2	27.3	35.7	35.7	2.3			11	8.6	1.4
	$CuCO_3(aq)$	47.9	42.5	35.3	35.3	27.9			42.7	40.9	13.7
	$CuOH^+$	1.3	1.2	1	1				1.3	1.3	
	$Cu(OH)_2(aq)$	21	12.6	6.8	6.9	67.5			39.4	44.7	84.9
	$CuHCO_3^+$	11.2	15.8	20.3	20.3	1.3			5.6	4.5	
Fe	$FeOH_2^+$	90.7	94.1		96.1				83.8	80.7	29.8
	$FeOH_3(aq)$	8.5	5.5		3.7				14	16.2	33.6
	$Fe(OH)_4^-$								2.3	3.1	36.6
H_4SiO_4	H_4SiO_4	100	100	100	100	100	100	100	100	100	98.7
	$H_3SiO_4^-$										1.3
Na	Na^+	100	100	100	100	100	100	100	100	100	100
K	K^+	100	100	100	100	100	100	100	100	100	100
Cl	Cl^-	100	100	100	100	100	100	100	100	100	100
NO_3	NO_3^-	100	100	100	100	100	100	100	100	100	100
Ba	Ba^{2+}	100	100	100	100	100	100	100	100	100	100
Sr	Sr^{2+}	100	100	100	100	100	100	100	100	100	100

TABLE A 2.6

Table of saturation indices of minerals obtained from MINTEQA2 using raw water results fromTable A 2.4

Mineral	Day									
	8	11	14	16	18	39	67	73	81	87
$Al(OH)_3(A)$	0.159		-0.38			`0.034	-0.05			-0.66
$Al_4OH_{10}so_4$	1.778		0.392			1.531	0.702			-3.68
Alunite	0.459		-0.01			0.357	-0.74			
Anhydrite	-2.61	-2.62	-2.62	-2.65	-2.64	-2.69	-2.68	-2.669	-2.64	-2.68
Aragonite	-1.28	-1.53	-1.71	-1.74	-0.65	-1.56	-1.31	-1.162	-1.08	-0.31
Barite	0.107	-0.19		-0.1	-0.25	-0.16	-0.4	0.84	0.842	-0.01
Boehmite	1.961		1.421			1.836	1.749			1.146
Calcite	-1.14	-1.39	-1.57	-1.6	-0.52	-1.42	-1.17	-1.023	-0.94	-0.17
Celestite	-3.33	-3.37	-3.38	-3.38	-3.37	-3.13	-3.41	-3.41	-3.38	-3.44
Chalcedony	-0.56	-0.59	-0.56	-0.54	-0.63	-0.65	-1.18	-1.114	-1.38	-1.45
Christabolite	-0.5	-0.49	-0.49	-0.47	-0.56	-0.58	-1.11	-1.05	-1.32	-1.39
Diaspore	3.666		3.126			3.541	3.454			2.851
Dolomite	-2.22	-2.68	-3.08	-3.1	-0.92	-2.72	-2.27	-1.963	-1.79	-0.27
Ferrihydrite	1.735	1.937		1.906				1.585	1.472	2.334
$Fe(OH)_{2.7}Cl_{0.3}$	6.519	6.778		6.808				6.29	6.158	6.79
Fluorite	-2.24	-2.25	-1.23	-2.29	-2.74	-2.3	-1.94	-1.922	-2.08	-1.99
Gibbsite (C)	1.769		1.229			1.644	1.557			0.953
Al_2O_3	-1.9		-2.98			-2.15	-2.33			-3.53
Goethite	6.127	6.328		6.297				5.976	5.863	6.725
Gypsum	-2.4	-2.41	-2.4	-2.44	-2.43	-2.48	-2.47	-2.458	-2.43	-2.47
Hematite	17.26	17.66		17.6				16.96	16.73	18.46
Jarosite Na	-0.52	0.688		1.135				-1.907	-2.42	-2.22
Jarosite K	2.175	3.364		3.883				0.743	0.234	0.474
Jarosite H	-3.38	-1.96		-1.32				-4.839		
Maghemite	6.867	7.27		7.208				6.566	6.34	8.063
Magnesite	-1.58	-1.78	-2.01	-1.99	-0.9	-1.81	-1.59	-1.436	-1.35	-0.59
Quartz	-0.08	-0.08	-0.08	-0.06	-0.15	-0.16	-0.69	-0.631	-0.9	-0.97
SiO_2 (A,GL)	-1.07	-1.06	-1.06	-1.04	-1.13	-1.15	-1.68	-1.619	-1.89	-1.96

TABLE A 2.6 (continued)

Table of saturation indices of minerals obtained from MINTEQA2 using raw water results from Table A 2.4

Mineral	Day									
	8	11	14	16	18	39	67	73	81	87
SiO$_2$ (A,PT)	-1.38	-1.37	-1.37	-1.35	-1.44	-1.46	-1.99	-1.927	-2.19	-2.27
Strontianite	-2.92		-3.39	-3.39	-2.3	-2.91	-2.96	-2.817	-2.73	-1.99
Witherite	-3.66	-4.19		-4.29	-3.36	-4.12	-4.12	-2.743	-2.69	-2.73
Cu(OH)$_2$	-1.96	-2.19	-2.93	-2.45	-1.46			-2.167	-1.81	-1.53
Tenorite	-0.94	-1.17	-1.91	-1.43	-0.44			-1.147	-0.79	-0.51
Cupricferrit	*14.05*	*14.23*		*13.91*				*13.545*	*13.68*	*15.68*
Analcime	-0.59		-1.51			-1.24	-2.14			-2.28
Halloysite	*3.911*		*2.841*			*3.498*	*2.26*			*0.503*
Kaolinite	*7.179*		*6.109*			*6.766*	*5.528*			*3.771*
Leonhardite	*13.84*		*10.16*			*12.01*	*8.392*			*7.712*
Low Albite	-0.55		-1.47			-1.28	-2.71			-3.13
Analbite	-1.47		-2.38			-2.2	-3.63			-4.05
Muscovite	*9.219*		*7.213*			*8.365*	*6.634*			*5.007*
Anorthite	-2.09		-3.94			-2.84	-3.59			-3.38
Pyrophyllite	*6.329*		*5.271*			*5.754*	*3.453*			*1.145*
Laumontite	*0.704*		*-1.14*			*-0.21*	*-2.02*			*-2.36*
Malachite	-1.52	-1.79	-3.09	-2.14	-1.25			-2.249	-1.61	-1.81
Mag-Ferrite	*6.936*	*6.96*		*6.507*				*7.097*	*7.03*	*10.26*
Leucite	-1.21		-2.14			-1.73	-2.75			-2.9
Microcline	*0.515*		*-0.41*			*-0.09*	*-1.65*			*-2.07*
H Sandine	*0.069*		*-0.86*			*-0.53*	*-2.09*			*-2.51*
Lepidocrocit	*5.256*	*5.457*		*5.426*				*5.105*	*4.992*	*5.854*
Na-Nontronite	*17.48*									*15.44*
K-Nontronite	*18.22*									*16.19*
Ca-Nontronite	*24.34*									*22.35*
Mg-Nontronite	*24.04*									*22.06*
Montmorillon	*6.289*									*2.675*

Note : All minerals with SI values <-3. 000 have not been included in this table

TABLE A 2.7

Table of results obtained on raw water at Matla power station from 21 March to 27 June 1994 (Matla

laboratory results)

Determinand	Day						
	1	8	21	49	63	77	98
Conductivity @ 25 °C (FS/cm)	278	263	241	230	231	234	238
Conductivity (calculated)	325	312	277	267	267	272	275
pH @ 25 °C	7.99	7.98	7.95	8.12	8.30	8.07	8.3
Total Alkalinity (mg/l CaCO₃)	105	106	89	82	83	83	84
Sodium (mg/l Na)	15	16	13	14	12	22	13
Potassium (mg/l K)	4.0	5.0	4.4	4.4	5.0	2.8	2.2
Magnesium (mg/l Mg)	12	12	12	12	11	10	12
Calcium (mg/l Ca)	24	22	20	20	20	18	23
Chloride (mg/l Cl)	11	10.5	10.5	10.5	11	12	13
Sulphate (mg/l SO₄)	21	20	18	20	18	15	15
Silica (mg/l H₄SiO₄)	4.8	3.2	4.3	2.2	2.4	0.5	0.5
Speciated balance (%)	1.7	1.4	4.3	7.2	4.4	8.9	8.0
Calculated Balance (%)	1.6	1.4	4.2	7.1	4.3	8.7	7.8
Calculated TDS (mg/l)	209	197	181	173	173	176	179

TABLE A 2.8

Table of distribution (%) of species obtained from MINTEQA2 using raw water results from Table A 2.7

Species	Distribution	Day						
		1	8	21	49	63	77	98
SO_4	SO_4^{2-}	89.4	89.8	90.1	90.1	90.4	91	89.4
	$MgSO_4$ (aq)	4.3	4.4	4.5	4.5	4.2	3.8	4.4
	$CaSO_4$(aq)	6	5.5	5.2	5.2	5.2	4.8	5.9
CO_3^{2-}	H_2CO_3	2.1	2.1	2.3	1.5	1	1.7	1
	HCO_3^-	96.1	96.2	96.1	96.4	96.4	96.5	96.2
	CO_3^{2-}					1.1		1.1
Ca	Ca^{2+}	95.4	95.5	96	95.7	95.4	96.2	95.7
	$CaHCO_3^+$	1.5	1.5	1.3	1.2	1.2	1.2	1.2
	$CaSO_4$(aq)	2.2	2.1	1.9	2.2	2	1.7	1.6
	$CaCO_3$(aq)					1.5		1.5
Mg	Mg^{2+}	95.8	95.8	96.3	96.1	95.9	96.5	96.2
	$MgHCO_3^+$	1.7	1.7	1.5	1.4	1.4	1.4	1.4
	$MgSO_4$(aq)	1.9	1.8	1.7	1.9	1.7	1.5	1.4
H_2O	OH^-	93.5	93.6	93.5	93.6	94	94.5	93.4
	$MgOH^+$	5.5	5.5	5.6	5.6	5.2	4.7	5.6
	$CaOH^+$	1						
H	H_2CO_3	4.1	4.2	4.5	3.1	2.1	3.4	2
	HCO_3^-	95.1	95.1	94.8	96.2	97.3	95.9	97.2
H_4SiO_4	H_4SiO_4	98.8	98.8	98.9	98.4	97.6	98.5	97.5
	$H_3SiO_4^-$	1.2	1.2	1.1	1.6	2.4	1.5	2.5
Na	Na^+	100	100	100	100	100	100	100
K	K^+	100	100	100	100	100	100	100
Cl	Cl^-	100	100	100	100	100	100	100

TABLE A 2.9

Table of saturation indices of minerals obtained from MINTEQA2 using raw water results from Table A 2.7

Mineral	Day						
	1	8	21	49	63	77	98
Anhydrite	-2.56	-2.61	-2.68	-2.64	-2.68	-2.798	-2.71
Aragonite	-0.09	-0.13	-0.27	-0.32	0.044	-0.221	0.107
Calcite	*0.051*	*0.01*	-0.13	*0.002*	*0.183*	-0.082	*0.245*
Chalcedony	-0.78	-0.96	-0.83	-1.12	-1.09	-1.767	-1.77
Chrysotile	-3.2	-3.61	-3.51	-3.08	-2.04	-4.886	-3.29
Clinoenstite	-3.11	-3.31	-3.23	-3.18	-2.83	-4.001	-3.47
Cristobalite	-0.72	-0.9	-0.77	-1.06	-1.03	-1.703	-1.71
Diopside	-3.35	-3.78	-3.66	-3.57	-2.82		-4.09
Dolomite	*0.07*	*0.025*	-0.21	*0.05*	*0.375*	-0.150	*0.478*
Gypsum	-2.35	-2.4	-2.47	-2.43	-2.47	-2.587	-2.5
Magnesite	-0.48	-0.48	-0.58	-0.45	-0.3	-0.564	-0.26
Nesquehonite	-2.89	-2.89	-2.99	-2.86	-2.71	-2.972	-2.67
Quartz	-0.31	-0.48	-0.35	-0.64	-0.61	-1.284	-1.29
SiO_2 (A,GL)	-1.29	-1.46	-1.34	-1.63	-1.6	-2.272	-2.28
SiO_2 (A,PT)	-1.6	-1.77	-1.64	-1.94	-1.9	-2.580	-2.58
Talc	-2.68	-3.44	-3.08	-3.24	-2.13		-4.75

Note : All minerals with SI values <-3. 000 have not been included in this table

TABLE A 2.10

Table of results obtained on cooling water south at Matla power Station

from 28 March to 16 June 1994 by the T-R-I laboratory

Determinand	Day									
	8	10	12	15	17	19	68	74	82	88
Conductivity @ 25 ℃ (FS/cm)	861	1022	1099	1222	1460	1450	1700	2030	1660	1860
Conductivity (calculated)	1015	1160	1312	1474	1716	1665	2054	2427	1827	2046
pH @ 25 ℃	6.9	7.6	7.7	7.2	8.0	7.0	7.3	6.9	7.2	6.5
Total Alkalinity (mg/l $CaCO_3$)	96.3	109.0	96.5	81.1	93.2	88.8	90.3	98.2	96.5	90.3
Sodium (mg/l Na)	84	101	114	128	135	133	292	302	193	213
Potassium (mg/l K)	17.9	21.4	36.0	33.0	35.6	30.2	30.8	57.3	47.2	50.6
Magnesium (mg/l Mg)	36.1	37.6	39.1	44.9	51.4	49.0	32.0	32.1	35.7	36.8
Calcium (mg/l Ca)	61	68	82	80	108	82	80	103	66	86
Chloride (mg/l Cl)	66	79	90	110	130	146	225	278	208	228
Nitrate (mg/l NO_3)	4.52	5.09	5.01	6.11	7.58	7.84	9.44	10.50	8.23	7.71
Sulphate (mg/l SO_4)	234	268	309	387	449	452	465	574	439	512
Fluoride (mg/l F)	0.82	0.94	1.00	1.10	1.10	0.70	1.20	1.10	1.10	0.96
Aluminium (mg/l Al)	0.88	0.72	0.64	0.77	0.99	0.71	N/A	N/A	N/A	N/A
Barium (mg/l Ba)	0.07	0.17	0.19	0.07	0.20	0.18	0.05	0.17	0.13	0.15
Copper (mg/l Cu)	0.22	0.20	0.38	0.13	0.18	0.01	<0.01	0.02	<0.01	0.21
Iron (mg/l Fe)	<0.01	<0.01	0.51	<0.01	0.13	<0.01	<0.01	0.01	<0.01	0.07
Zinc (mg/l Zn)	0.10	<0.01	<0.01	<0.01	0.02	0.02	<0.01	0.02	<0.01	<0.01
Silica (mg/l H_4SiO_4)	14.9	15.7	16.1	16.2	17.7	12.1	5.8	3.7	4.0	2.6
Strontium (mg/l Sr)	0.28	0.33	0.36	0.33	0.46	0.45	0.60	<0.30	0.40	0.50
Speciated Balance (%)	7.9	6.7	9.8	4.8	4.8	2.9	5.8	1.0	4.2	3.4
Calculated Balance (%)	7.4	6.3	9.2	4.5	4.2	2.5	5.6	1.0	3.8	3.1
Calculated TDS (mg/l)	646	767	824	917	1095	1088	1275	1523	1245	1395

KEY: N/A - Sample not analysed for this constituent

TABLE A 2.11

Table of distribution (%) of species obtained from MINTEQA2 using cooling water results from Table A 2.10

Species	Distribution	Day									
		8	10	12	15	17	19	68	74	82	88
SO_4	SO_4^{2-}	82.9	82.6	82	81.9	79.8	82.1	84.1	83.2	84.9	
	$MgSO_4$(aq)	7.4	7.2	7	7.5	7.7	7.6	4.7	4.3	5.6	
	$CaSO_4$(aq)	8.6	8.9	9.9	9.1	11	8.7	8	9.2	7.1	
	$NaSO_4^-$		1.1	1.2	1.3	1.3	1.3	2.9	2.8	2	
CO_3^{2-}	H_2CO_3	19.7	4.6	3.7	10.7	1.8	15.9	8.6	18.9	10.7	37.3
	HCO_3^-	78.6	92.9	93	87	94	82.1	89.3	79.2	87.5	61.4
	$MgHCO_3^+$					1.1					
	$CaHCO_3^+$					1.2					
Ca	Ca^{2+}	85.2	84	83	80.9	79.7	79.2	79.6	77.7	79.4	78.2
	$CaHCO_3^+$	1	1.1								
	$CaSO_4$(aq)	13.7	14.6	16	18.3	19	20	19.5	21.5	19.6	21
Mg	Mg^{2+}	86.6	85.4	85	82.6	81.6	81.1	81.5	79.7	81.2	80.1
	$MgHCO_3^+$	1.2	1.3	1.1							
	$MgSO_4$(aq)	12.1	13	14	16.3	17	17.8	17.4	19.2	17.5	18.8
Na	Na^+	100	100	100	100	98.9	98.8	98.8	98.6	98.8	98.7
	$NaSO_4^-$					1	1.1	1.1	1.3	1.1	1.2
K	K^+	100	100	99	98.7	98.5	98.5	98.5	98.2	98.5	98.3
	KSO_4^-			1.1	1.3	1.5	1.5	1.5	1.8	1.5	1.7
F	F-	80.1	94.1	94	91.3	93	88.3	95.5	95.5	95.1	
	MgF^+	4.3	5	5	5.4	6	5.4	3.7	3.5	4.2	
	AlF_2^+	8.2			1.2		3.2				
	AlF_3(aq)	6.3			1.3		2.2				
Al	$Al(OH)_2^+$	5.1			2	92	3.9				
	$Al(OH)_4^-$	40.7	81.5	85	61.9		49.6				
	AlF_2^+	5.4			1.2		2.2				
	AlF_3(aq)	2.8					1				
	$Al(OH)_3$(aq)	45.4	18	15	34	7.9	42.9				

TABLE A 2.11 (continued)

Table of distribution (%) of species obtained from MINTEQA2 using cooling water results from Table A 2.10

Species	Distribution	Day									
		8	10	12	15	17	19	68	74	82	88
Cu	Cu^{2+}	21.4	3	2.2	12.5		19.6		23.9		39.7
	$CuCO_3(aq)$	44.5	33.7	27	39.7	15.1	41.8		40.4		26
	$Cu(OH)^+$	1.2			1.3		1.3		1.2		
	$Cu(OH)_2(aq)$	17.6	59.9	68	38	82.9	23.1		16.4		4.5
	$CuSO_4(aq)$	3.4			2.8		5		6.6		10.7
	$CuHCO_3^+$	11.8	1.8	1.1	5.4		9		11.2		17.9
Zn	Zn^{2+}	70.7				39.1	66.2		65.3		
	$Zn(OH)^+$					2.8					
	$Zn(OH)_2(aq)$					2.8					
	$ZnSO_4(aq)$	13				10.7	19.2		20.8		
	$ZnHCO_3^+$	9.8				4.5	7.6		7.7		
	$ZnCO_3(aq)$	5.5				30.9	5.2		4.1		
	$Zn(CO_3)_2^{2-}$					8.4					
Fe	$Fe(OH)_2^+$			55		31.4			92		96.7
	$Fe(OH)_3(aq)$			29		31.8			7.3		3.1
	$Fe(OH)_4^-$			16		36.9					
H_2O	OH^-							89.5	16	88.6	1.3
	$MgOH^+$							8.6	1.4	9.7	
	$CaOH^+$							1.9		1.6	
	$Al(OH)_2^+$	3.3			1.1		2.3				
	$Al(OH)_4^-$	51.9	82.1	65	68.8	86	59.1				
	$Al(OH)_3(aq)$	43.4	13.6	8.5	28.3	5.6	38.3				
	$Cu(OH)_2(aq)$	1.2	3.6	6.6	1.5	3			17.6		10.2
	$Fe(OH)_2^+$			8.1					56.2		83.2
	$Fe(OH)_3(aq)$			6.3		1.4			6.6		4
	$Fe(OH)_4^-$			4.8		2.2					

TABLE A 2.11 (continued)

Table of distribution (%) of species obtained from MINTEQA2 using cooling water results from Table A 2.10

Species	Distribution	Day									
		8	10	12	15	17	19	68	74	82	88
H	H_2CO_3	34.2	9.3	7.6		4	28.5	15.9	31.9	19.3	54.3
	HCO_3^-	68.2	93.5	97		102.7	73.5	82.4	66.7	79.2	44.8
	$CaHCO_3^+$			1		1.3					
	$MgHCO_3^+$					1.2					
H_4SiO_4	H_4SiO_4					98.7					
	$H_3SiO_4^-$					1.3					
Cl	Cl^-	100	100	100	100	100	100	100	100	100	100
Ba	Ba^{2+}	100	100	100	100	100	100	100	100	100	100

TABLE A 2.12

Table of saturation indices of minerals obtained from MINTEQA2 using cooling water results from Table A 2.10

Mineral	Day									
	8	10	12	15	17	19	68	74	82	88
$Al(OH)_3$ (A)	0.792	0.304	0.168	0.609	0.086	0.675				
$AlOHSO_4$	-2.3	-4.14	-4.43	-2.9	-4.98	-2.37				
$Al_4(OH)_{10}SO_4$	5.289	1.985	1.287	4.138	0.487	4.861				
Alunite	4.971	1.575	1.182	4.14	0.278	5.013				
Anhydrite	-1.35	-1.27	-1.17	-1.11	-0.96	-1.06	-1.08	-0.93	-1.16	-1.01
Aragonite	-0.96	-0.18	-0.08	-0.68	0.269	-0.85	-0.58	-0.86	-0.71	-1.35
Barite	0.581	1.002	1.086	0.731	1.21	1.189	0.62	1.205	1.039	1.138
Boehmite	2.594	2.106	1.97	2.411	1.888	2.477				
Calcite	-0.82	-0.04	0.061	-0.54	0.408	-0.71	-0.44	-0.72	-0.57	-1.21
Celestite	-2.13	-2.03	-1.95	-1.91	-1.74	-1.73	-1.62		-1.79	-1.66
Chalcedony	-0.29	-0.26	-0.25	-0.25	-0.22	-0.38	-0.69	-0.89	-0.86	-1.04
Chrysotile		-3.44	-2.82		-0.71					
Clinoenstite	-4.44	-3.02	-2.81	-3.76	-2.09	-4.27	-4.19		-4.49	
Cristobalite	-0.22	-0.2	-0.19	-0.19	-0.15	-0.31	-0.63	-0.82	-0.79	-0.98
Diopside		-3.21	-2.73	-4.71	-1.29					
Dolomite	-1.6	-0.07	0.077	-1.06	0.771	-1.37	-1	-1.67	-1.14	-2.51
Sepiolite (C)		-3.06	-2.63	-4.53	-1.15					
Ferrihydrite			3.126		2.58			0.826		1.297
$Fe(OH)_{2.7}Cl_{0.3}$			7.951		7.362			6.035		6.601
Fluorite	-1.16	-0.88	-0.77	-0.75	-0.63	-1.19	-0.69	-0.69	-0.83	-0.86
Gibbsite (C)	2.402	1.914	1.778	2.219	1.696	2.285				
Al_2O_3	-0.64	-1.61	-1.88	-1	-2.05	-0.87				
Goethite			7.517		6.971			5.217		5.688
Gypsum	-1.14	-1.6	-0.95	-0.9	-0.75	-0.85	-0.87	-0.72	-0.95	-0.8
Hematite			20.04		18.95			15.44		16.38
Huntite		-4.21	-3.97		-2.59					
Jarosite Na			4.174		1.959			0.528		2.933

TABLE A 2.12 (continued)

Table of saturation indices of minerals obtained from MINTEQA2 using cooling water results from Table A 2.10

Mineral	Day									
	8	10	11	14	16	18	67	73	81	87
Jarosite K			*7.042*		*4.748*			*3.173*		*5.676*
Jarosite H			-0.26		-2.84			-3.52		-0.56
Maghemite			*9.648*		*8.557*			*5.049*		*5.99*
Magnesite	-1.27	-0.52	-0.48	-1.01	-0.13	-1.16	-1.06	-1.45	-1.06	-1.8
Nesquehonite	-3.68	-2.93	-2.89	-3.42	-2.54	-3.57	-3.46	-3.89	-3.47	-4.21
Quartz	*0.198*	*0.219*	*0.229*	*0.234*	*0.268*	*0.108*	-0.21	-0.41	-0.37	-0.56
$SiO_2(A,GL)$	-0.79	-0.77	-0.76	-0.75	-0.72	-0.88	-1.2	-1.39	-1.36	-1.55
$SiO_2 (A,PT)$	-1.1	-1.08	-1.07	-1.06	-1.03	-1.19	-1.51	-1.7	-1.67	-1.86
Strontianite	-2.66	-1.85	-1.78	-2.4	-1.43	-2.44	-2.03		-2.26	-2.91
Talc		-1.89	-1.24	-4.1	*0.953*					
Tremolite		-2.03	-0.41		*4.646*					
Witherite	-4.12	-3	-2.92	-3.93	-2.65	-3.7	-3.97	-3.82	-3.61	-4.29
$CuCO_3$	-2.91	-3.07	-2.89	-3.19	-3.47	-4.28		-3.99		-3.16
$Cu(OH)_2$	-1.18	-0.68	-0.35	-1.07	-0.59	-2.4		-2.25		-1.79
Atacamite	-2.09	-1.73	-1.1	-1.96	-1.73	-4.3		-3.63		-2.39
$Cu_2(OH)_3NO_3$			-4.5	-2.69						
Antlerite	-2.59	-2.47	-1.61		-2.81					-3.34
Brochantite	-2.18	-1.56	-0.37	-2.17	-1.8					-3.53
Langite	-3.63	-3.01	-1.82	-3.62	-3.26					-4.99
Tenorite	-0.16	*0.337*	*0.674*	-0.05	*0.434*	-1.38		-1.23		-0.77
Dioptase	-2.84	-2.33	-1.98	-2.7	-2.18	-4.16		-4.52		-4.21
Cupricferrite			*18.45*		*17.12*			*11.95*		*13.35*
Smithsonite	-2.38				-2.32	-3.09		-3.2		
$ZnCO_3,1H_2O$	-2.12				-2.06	-2.83		-2.94		
$Zn(OH)_2 (B)$	-4.12				-2.92	-4.69		-4.93		
$Zn(OH)_2 (G)$	-4.08				-2.88	-4.65		-4.89		
$Zn(OH)_2 (E)$	-3.87				-2.67	-4.44		-4.68		
ZnO (active)	-3.68				-2.48	-4.25		-4.49		

TABLE A 2.12 (continued)

Table of saturation indices of minerals obtained from MINTEQA2 using cooling water results from Table A 2.10

Mineral	Day									
	8	10	12	15	17	19	68	74	82	88
$ZnSiO_3$	0.891				2.159	0.233		-0.52		
Analcime	1.243	1.577	1.611	1.609	1.973	1.236				
Halloysite	5.733	4.8	4.549	5.44	4.463	5.32				
Kaolinite	9.001	8.068	7.817	8.708	7.731	8.588				
Leonhardite	19.15	20.23	20.3	20.04	21.64	18.48				
Low Albite	1.562	1.916	1.962	1.964	2.363	1.466				
Analbite	0.648	1.002	1.048	1.05	1.449	0.552				
Muscovite	12.61	11.98	11.93	12.72	12.09	12.3				
Anorthite	0.008	0.505	0.517	0.377	1.109	-0.15				
Pyrophyllite	8.709	7.818	7.588	8.489	7.58	8.117				
Laumontite	3.361	3.9	3.933	3.803	4.603	3.022				
Wairakite	-1.05	-0.51	-0.48	-0.61	0.193	-1.39				
Malachite	0.104	0.435	0.951	-0.07	0.138	-2.49		-2.05		-0.76
Azurite	-0.7	-0.53	0.167	-1.14	-1.22	-4.66		-3.93		-1.81
Spinel	-3.28	-2.86	-2.93	-3.01	-2.41	-3.26				
Mag-ferrite			11.58		11.16			5.211		5.432
Kalsilite	-1.97	-1.66	-1.46	-1.56	-1.22	-1.86				
Leucite	0.638	0.967	1.175	1.084	1.458	0.656				
Microcline	2.637	2.987	3.206	3.12	3.528	2.566				
H Sanidine	2.191	2.541	2.76	2.674	3.082	2.12				
Nepheline	-2.45	-2.14	-2.11	-2.12	-1.79	-2.37				
Lepidocrocit			6.646		6.1			4.346		4.817
Na-Nontronite			21.92		21.07					
K-Nontronite			22.72		21.84					
Ca-Nontronite			28.58		27.72					
Mg-Nontronite			28.27		27.41					
Montmorrilon			8.696		8.913					

Note : All minerals with SI values <-3. 000 have not been included in this table

TABLE A 2.13

Table of results obtained on cooling water south at Matla power station from 21 March to 27 June 1994 (Matla

laboratory results)

Determinand	Day								
	1	5	8	10	18	49	63	77	98
Conductivity @ 25 ℃ (FS/cm)	278	678	878	1008	1440	1330	1259	2040	2110
Conductivity (calculated)	325	795	958	1155	1624	1338	1203	2061	2255
pH @ 25 ℃	8.03	8.67	8.30	8.83	8.43	8.40	8.47	8.51	8.41
Total Alkalinity (mg/l $CaCO_3$)	105	160	105	124	101	109	123	114	103
Sodium (mg/l Na)	17.5	63	76	92	123	147	126	275	255
Potassium (mg/l K)	9.5	12	22	26	27	30	26	73	57
Magnesium (mg/l Mg)	9.72	32	32	26	41	28	22	34	41
Calcium (mg/l Ca)	30.4	32	67	82	104	70	77	98	107
Chloride (mg/l Cl)	11	47	68	80	134	144	136	226	240
Nitrate (mg/l NO_3)	<0.05	ND	4	ND	ND	14	2.4	2.6	4
Sulphate (mg/l SO_4)	14.4	124	225	256	430	347	284	571	611
Phosphate (mg/l PO_4)	0.04	ND	0.11	ND	ND	0.05	0.41	0.08	0.08
COD (mg/l O_2)	2	ND	45	ND	ND	95	95	155	74
Speciated Balance (%)	7.3	3.0	15	4.5	0.6	31	33	27	16
Calculated Balance (%)	10.2	1.2	5.8	4.0	0.5	2.7	1.9	2.2	0.8
Calculated TDS (mg/l)	209	509	659	756	1080	998	944	1530	1583

TABLE A 2.14

Table of distribution (%) of species obtained from MINTEQA2 using cooling water results from Table A 2.13

Species	Distribution	Day									
		1	1*	5	8	10	18	49	63	77	98
DOM	DOM		62.1		63.9			69	67.7	70.3	65.3
	CaDOM		35.9		32.6			27.7	29.8	26.7	31.9
	MgDOM		2		3.5			3.3	2.5	3	2.8
SO_4	$NaSO_4^-$					1	1.2	1.5	1.4	2.5	2.4
	SO_4^{2-}	88.7	89	86.1	86.4	83.1	81.1	90.1	90.2	89.5	85.8
	$MgSO_4(aq)$	3.4	3.4	7.7	6.1	5	6.4	4.1	3.4	3.7	4.9
	$CaSO_4(aq)$	7.5	7.2	5.2	6.5	10.6	11	4	4.8	3.7	6.5
CO_3^{2-}	H_2CO_3	1.9	1.9								
	HCO_3^-	96.1	96.2	92.9	95.1	88.9	92.8	95.2	94.9	94.1	93.8
	CO_3^{2-}			2.8	1.3	4.1	1.8	1.8	2	2.5	1.9
	$MgCO_3(aq)$			1.3		1.3					
	$CaCO_3(aq)$			1.2		3.6	1.7				
	$CaHCO_3^+$						1.1				
Ca	Ca^{2+}	96	93.2	85.4	61.4	81.1	78.9	42.8	44.4	36.8	55.3
	$CaHCO_3^+$	1.5	1.5	1.7		1					
	$CaSO_4(aq)$	1.5	1.4	8.5	9.1	13.8	1.9	8.3	7.3	9.1	15.4
	$CaCO_3(aq)$			4.5		4	1.3				
	CaDOM		3		27.9			47.7	46.7	53.1	28
Mg	Mg^{2+}	96.3	96	87.4	83.5	83.5	81.1	76.7	78.2	72.3	76.1
	$MgHCO_3^+$	1.7	1.7	1.9	1.1	1.2			1.1		
	$MgSO_4(aq)$	1.3	1.3	7.6	10.8	12.4	17	12.9	11.3	15.6	18.5
	$MgCO_3(aq)$			3.1		2.8	86.4		1.1		
	MgDOM				3.8			8.6	8.2	10.4	3.8
PO_4	$H_2PO_4^-$		7.5		3			2.6	2.2	1.8	2.1
	$MgPO_4^-$		2.7		8.6			8.4	8.1	9.9	9.5
	$MgHPO_4(aq)$		10.1		16.2			12.2	10.1	10.8	13.2
	$CaHPO_4(aq)$		13.6		11.1			7.6	8.9	7.1	11.2
	$CaPO_4^-$		3.7		6			5.3	7.3	6.6	8.1
	HPO_4^{2-}		62.1		54.8			63.4	62.9	62.9	55.1

TABLE A 2.14 (continued)

Table of distribution (%) of species obtained from MINTEQA2 using cooling water results fromTable A 2.13

Species	Distribution	Day									
		1	1*	5	8	10	18	49	63	77	98
H_2O	OH^-	94.2	94.3	88	89	89.6	86.4	91.9	93	91.7	89
	$MgOH^+$	4.5	4.5	11	9.6	8.1	11.1	7.2	5.9	7.3	9.4
	$CaOH^+$	1.3	1.3		1.4	2.3	2.5		1.1		1.7
H	H_2CO_3	3.7	3.7		1.9		1.4	1.5	1.3	1.1	1.4
	$CaHCO_3^+$					1	1.2				
	HCO_3^-	95.4	95.4	97.9	96.7	98	96.5	97.4	97.6	97.6	96.8
Na	Na^+						98.9			98.6	98.5
	$NaSO_4^-$						1			1.3	1.4
K	K^+						98.6	98.8	99	98.2	98.1
	KSO_4^-						1.4	1.2	1	1.8	1.9
Cl	Cl^-	100	100	100	100	100	100	100	100	100	100
NO_3	NO_3^-	100	100	100	100	100	100	100	100	100	100

Note: 1 = speciated results on day 1 without the inclusion of DOM

1* = speciated results on day 1 with the inclusion of DOM

TABLE A 2.15

Table of saturation indices of minerals obtained from MINTEQA2 using cooling water results from Table A 2.13

Mineral	Day									
	1	1*	5	8	10	18	49	63	77	98
Anhydrite	-2.62	-2.636	-1.842	-1.488	-1.218	-0.978	-1.51	-1.521	-1.322	-1.054
Aragonite	*0.054*	*0.039*	*0.737*	*0.334*	*1.098*	*0.701*	*0.254*	*0.442*	*0.387*	*0.485*
Artinite			-2.75	-4.154	-2.707	-3.658	-4.13	-4.045	-3.794	-3.884
Brucite	-4.27	-4.272	-2.57	-3.373	-2.392	-3.039	-3.313	-3.26	-3.087	-3.163
Calcite	*0.193*	*0.178*	*0.876*	*0.473*	*1.237*	*0.84*	*0.393*	*0.58*	*0.526*	*0.624*
Dolomite	*0.158*	*0.141*	*2.03*	*1.025*	*2.256*	*1.554*	*0.909*	*1.13*	*1.153*	*1.237*
Hydrapatite		*2.79*		*5.055*			*3.569*	*6.937*	*4.59*	*5.257*
Gypsum	-2.41	-2.425	-1.631	-1.277	-1.008	-0.767	-1.299	-1.31	-1.111	-0.844
Huntite	-3.99	-4.015	0.255	-1.953	0.21	-1.099	-2.141	-1.854	-1.675	-1.619
Magnesite	*-0.53*	*-0.533*	*0.658*	*0.056*	*0.522*	*0.218*	*0.02*	*0.053*	*0.131*	*0.117*
Nesquehonite	-2.94	-2.941	-1.751	-2.352	-1.886	-2.19	-2.389	-2.355	-2.278	-2.292

Note : All minerals with SI values <-3. 000 have not been included in this table

1 = speciated results on day 1 without the inclusion of DOM

1* = speciated results on day 1 with the inclusion of DOM

TABLE A 2.16

Table of results obtained on clarified cooling water south at Matla power Station from 28 March to 16 June 1994

Determinand	Day									
	8	**10**	**14**	**16**	**18**	**39**	**67**	**73**	**81**	**87**
Conductivity @ 25 °C (F S/cm)	860	887	1178	1370	840	1193	1540	1950	1560	1670
Conductivity (calculated)	982	1042	1358	1597	1491	1408	1605	1806	1715	1854
pH @ 25 °C	7.4	10.3	7.1	10.5	10.4	9.4	10.1	9.5	10.2	10.3
Total Alkalinity (mg/l $CaCO_3$)	81.0	34.5	55.2	37.2	37.6	33.6	39.6	31.6	41.6	37.6
Sodium (mg/l Na)	84	98	109	145	127	164	200	193	192	200
Potassium (mg/l K)	18.0	22.2	23.2	32.4	29.2	34.0	46.6	31.2	47.0	46.2
Magnesium (mg/l Mg)	40.0	22.6	44.7	23.4	23.9	23.8	16.9	22.5	27.6	23.4
Calcium (mg/l Ca)	45.8	58.3	68.9	113.0	89.4	47.1	74.3	88.3	62.0	79.5
Chloride (mg/l Cl)	73	106	123	140	139	173	174	295	212	233
Nitrate (mg/l NO_3)	3.56	4.32	5.94	6.87	7.17	9.83	8.99	10.30	7.90	7.20
Sulphate (mg/l SO_4)	227	262	363	444	437	349	394	371	427	478
Fluoride (mg/l F)	0.54	0.52	0.90	0.56	0.35	1.00	0.86	0.80	0.90	0.76
Aluminium (mg/l Al)	0.08	<0.05	0.06	0.10	0.01	N/A	0.13	N/A	N/A	0.14
Barium (mg/l Ba)	0.07	0.08	0.13	0.15	0.15	0.11	0.08	0.11	0.11	0.11
Copper (mg/l Cu)	0.05	0.04	0.12	0.05	0.05	0.06	<0.01	0.06	0.06	0.11
Iron (mg/l Fe)	<0.01	<0.01	<0.01	1.01	<0.01	<0.01	<0.01	0.01	0.06	0.13
Zinc (mg/l Zn)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silica (mg/l H_4SiO_4)	12.70	6.00	18.60	3.90	3.00	5.80	3.00	2.60	6.40	2.90
Strontium (mg/l Sr)	0.25	0.23	0.38	0.38	0.38	0.30	0.70	0.50	0.30	0.40
Speciated Balance (%)	7.2	2.3	0.9	1.7	8.9	3.1	3.3	4.8	3.6	8.1
Calculated Balance (%)	6.8	2.1	0.9	2.3	4.4	2.6	3.2	4.3	3.0	4.9
Calculated TDS (mg/l)	645	665	884	1028	630	895	1155	1463	1170	1253

KEY: N/A - Sample not analysed for this constituent

TABLE A 2.17

Table of distribution (%) of species obtained from MINTEQA2 using CCWresults from Table A 2.16

Species	Distribution	Day									
		8	10	14	16	18	39	67	73	81	87
SO_4	SO_4^{2-}	83.9	82.6	84.4		85.4	87.6	89.5		64.3	86.4
	$MgSO_4\,(aq)$	8.4	7.8	3.7		3.7	4.4				3.4
	$CaSO_4(aq)$	6.6	8.2	9.7		9.3	5.8	8.3			7.7
	$NaSO_4^-$		1.2	2		1.4	1.8	2.2			2.1
CO_3^{2-}	CO_3^{2-}			15.8		38.1	13.8	32.4	15.8	35.7	38.1
	H_2CO_3	6.9	13.5		37.3						
	HCO_3^-	91.1	84.5	65.1	61.4	21.6	74	36.5	65.1	31.6	26.3
	$MgCO_3(aq)$			3.7		8.9	3.7	5.7	3.7	9.8	8.1
	$CaCO_3(aq)$			12.7		28.9	6.4	21.8	12.7	19.3	23.7
	$NaCO_3^-$			1.4		2.2	1.1	3	1.4	3.1	3.4
Ca	Ca^{2+}	85.3	81.4	80.3	78.2	70.9	78.9	76.7	80.3	75.7	71.3
	$CaCO_3(aq)$			2.6		9.7	2.8	4.6	2.6		9
	$CaSO_4(aq)$	13.6	18	17	21	19	18	18.4	17		19.4
Mg	Mg^{2+}	86.7	83.1	82.4	80.1	73.8	81.2	78.9	82.4	77.9	74.3
	$Mg(OH)^+$					2		1.1		1.3	1.6
	$MgHCO_3^+$	1									
	$MgCO_3(aq)$			1.8		6.8	1.9	3.2	1.8	3.3	6.3
	$MgSO_4(aq)$	12.1	16.1	15.2	18.8	17.2	16.2	16.5	15.2	17.2	17.6
H_2O	OH^-	2.4	1.5	86	1.3	90.7	86.8	82.9	86	88.2	81.3
	$AlOH_3(aq)$	18.1	28.4								
	$AlOH_4^-$	71.6	53.3					11			7.3
	$AlOH_2^+$		1.4								
	$CuOH_2(aq)$	7	14.8	4.1	10.2		5.3		4.1		1.2
	$Fe(OH)_3(aq)$				4						
	$FeOH_2^+$				83.2						
	$FeOH_4^-$			1.5					1.5	2.1	3.3
	$MgOH^+$			6.1		6.3	6.7	4.3	6.1	7.3	5.3
	$CaOH^+$			2.2		2.1	1.2	1.7	2.2	1.5	1.6

TABLE A 2.17 (continued)

Table of distribution (%) of species obtained from MINTEQA2 using CCW results from Table A 2.16

Species	Distribution	Day									
		8	10	14	16	18	39	67	73	81	87
H	H_2CO_3	13.1	24		54.3						
	HCO_3^-	86.1	75.1	120	44.8		100		120		
	$CaHCO_3$			1.2					1.2		
	OH^-							296		138	215.1
	$H_3SiO_4^-$							39.3		33.3	19.6
	$H_2SiO_4^{2-}$							3.1		3.3	2.5
	$MgOH^+$							15.4		11.4	14.1
	$CaOH^+$							6.1		2.3	4.3
	$Al(OH)_4^-$							39.4			19.3
	$Fe(OH)_4^-$									3.2	8.6
	$Cu(OH)_2$ (aq)									1.4	3.2
F	F^-	93.9	93.3	96.3		96.5	96.4	97.2	96.3		96.7
	MgF^+	5.6	5.6	2.7		2.7	3	2	2.7		2.1
Cu	Cu^{2+}	6	19.3		39.7						
	$CuCO_3(aq)$	34.9	33.1		26						
	$CuOH^+$	1.1	1.6								
	$Cu(OH)_2(aq)$	54.2	35.8		4.5						
	$CuSO_4(aq)$		4.3		10.7						
	$CuHCO_3^+$	2.8	5.7		17.9						
Na	Na^+				98.7			98.8		98.8	98.5
	$NaSO_4^-$				1.2			1		1.1	1.2
K	K^+	98.7	98.7		98.3		98.7	98.6	98.7	98.5	98.3
	KSO_4^-	1.3	1.3		1.7		1.3	1.4	1.3	1.5	1.7
Fe	$FeOH_3(aq)$		2.5		3.1				2.5		
	$Fe(OH)_2^+$				96.7						
	$FeOH_4^-$		97.4						97.4		
H_4SiO_4	H_4SiO_4		68.1			21.4	73.2	36	68.1	30.6	25.6
	$H_3SiO_4^-$		31.5			72.9	26.6	61.6	31.5	66.1	70
	$H_2SiO_4^{2-}$					5.6		2.4		3.3	4.4

TABLE A 2.17 (continued)

Table of distribution (%) of species obtained from MINTEQA2 using CCW results from Table A 2.16

		Day									
Species	**Distribution**	**8**	**10**	**14**	**16**	**18**	**39**	**67**	**73**	**81**	**87**
Al	$Al(OH)_4^-$	74.1	54.7								
	$Al(OH)_3(aq)$	25	38.9								
	$Al(OH)_2^+$		2.9								
	ALF_2^+		2								
	$AlF_3(aq)$		1.3								
Cl	Cl^-	100	100	100	100	100	100	100	100	100	100
NO_3	NO_3^-	100	100	100	100	100	100	100	100	100	100
Ba	Ba^{2+}	100	100	100	100	100	100	100	100	100	100
Sr	Sr^{2+}	100	100	100	100	100	100	100	100	100	100

TABLE A 2.18

Table of saturation indices of minerals obtained from MINTEQA2 using CCW results from A Table 2.16

Mineral	Day									
	8	10	14	16	18	39	67	73	81	87
Al(OH)₃(A)	-0.51	-0.44			-4.27		-2.86			-3.03
Al₄OH₁₀SO₄	0.957	0.142								
Alunite	-0.5	1.137								
Anhydrite	-1.48	-1.18	-1.1	-1.01	-1.04	-1.34	-1.14	-1.1	-1.197	-1.09
Aragonite	-0.64	-1.01	0.936	-1.35	1.522	0.701	1.121	0.936	1.055	1.437
Artinite			-1.67		0.673	-1.77	-0.53	-1.67	0.099	0.406
Barite	0.579	0.991	0.899	1.138	1.134	0.931	0.815	0.899	0.977	1.007
Brucite			-1.1		0.634	-1.26	-0.09	-1.1		0.409
Boehmite	1.294	1.361			-2.47		-1.05			-1.23
Calcite	-0.5	-0.87	1.074	-1.21	1.661	0.84	1.26	1.074	1.194	1.576
Celestite	-2.18	-1.86	-1.76	-1.66	-1.78	-1.95	-1.56	-1.76	-1.903	-1.75
Chrysotile	-4.57		5.435		9.745	5.712	8.024	5.435	9.745	9.198
Chalcedony	-0.36	-0.19	-1.21	-1.04	-1.65	-0.83	-1.42	-1.21	-1.165	-1.59
Clinoenstite	-3.42	-3.91	-0.37		0.916	-0.16	0.417	-0.37	1.077	0.754
Christabolite	-0.29	-0.13	-1.14	-0.98	-1.59	-0.77	-1.36	-1.14	-1.101	-1.52
Diaspore	2.999	3.066			-0.76		0.651			0.479
Dolomite	-0.78	-1.66	1.834	-2.51	3.034	1.663	2.157	1.834	2.316	2.907
Diopside	-0.78		2.407		4.96	2.546	4.038	2.407	5.066	4.595
Sepiolite (C)	-3.96	-4.78	1.283		3.422	2.099	2.651	1.283	4.229	3.162
Ferrihydrite			0.36	1.297				0.36	0.477	0.711
Fe(OH)₂.₇Cl₀.₃			4.789	6.601				4.789	4.663	4.879
Fluorite	-1.51	-0.96	-0.96	-0.86	-1.7	-1.01	-0.97	-0.96	-1.03	-1.1
Forsterite					1.382	-1.58	0.159	-1.64	1.22	0.996
Gibbsite (C)	1.102	1.169			-2.66		-1.25			-1.42
Goethite			4.751	5.688				4.751	4.869	5.103
Gypsum	-1.27	-0.97	-0.89	-0.8	-0.83	-1.13	-0.93	-0.89	-0.986	-0.87
Hematite			14.51	16.38				14.51	14.745	15.21
Huntite			-0.73		1.697	-0.77	-0.13	-0.73	0.479	1.485

TABLE A 2.18 (continued)

Table of saturation indices of minerals obtained from MINTEQA2 using CCW results from Table A 2.16

	Day									
Mineral	8	10	14	16	18	39	67	73	81	87
Jarosite Na				2.933						
Jarosite K				5.676						
Jarosite H				-0.56						
Maghemite			4.116	5.99				4.116	4.351	4.819
Magnesite	-0.78	-1.28	0.263	-1.8	0.877	0.327	0.401	0.263	0.626	0.834
Hydrmagnesite					-2.42				-3.743	-2.81
Nesquehonite	-3.19	-3.69	-2.15	-4.21	-1.53	-2.08	-2.01	-2.15	-1.782	-1.57
Quartz	0.127	0.294	-0.73	-0.56	-1.17	-0.35	-0.94	-0.73	-0.682	-1.1
Serpiolite (A)			-1.58		0.555	-0.77	-0.22	-1.58	1.362	0.295
SiO_2 (A,GL)	-0.86	-0.69	-1.71	-1.55	-2.15	-1.33	-1.93	-1.71	-1.67	-2.09
SiO_2 (A,PT)	-1.17	-1	-2.02	-1.86	-2.46	-1.64	-2.24	-2.02	-1.978	-2.4
Strontianite	-2.26	-2.61	-0.64	-2.91	-0.13	-0.82	-0.22	-0.64	-0.565	-0.14
TALC	-3.19	-4.49	5.105		8.534	6.14	7.264	5.105	9.502	8.113
Tremolite			16.2		24.74	17.51	21.62	16.2	25.916	23.58
Witherite	-3.67	-3.93	-2.16	-4.29	-1.39	-2.11	-2.02	-2.16	-1.861	-1.56
$Cu(OH)_2$	-1.33	-1.13	-0.98	-1.79	-1.06	-0.98		-0.98	-0.983	-0.72
Atacamite	-2.87	-1.92	-3.7	-2.39		-3.83		-3.7	-4.51	-4.04
Antlerite	-4.1	-2.67		-3.34						
Brochantite	-3.84	-2.2		-3.53						
Tenorite	-0.31	-0.11	0.037	-0.77	-0.04	0.036		0.037	0.037	0.3
Dioptase	-3.07	-2.7	-3.57	-4.21	-4.1	-3.2		-3.57	-3.351	-3.69
Fosterite			-1.64							
Cupricferrit			12.28	13.35				12.28	12.514	13.25
Malachite	-0.8	-0.24	-2.97	-0.76	-4.24	-2.77		-2.97	-4.012	-3.38
Azurite	-2.35	-1.43		-1.81						
Mag-Ferrite			9.432	5.432				9.432	11.075	11.64
Wollastonite			-1.67		-0.4	-1.75	-0.83	-1.67	-0.459	-0.61
P-Wollastonite			-2.52		-1.25	-2.6	-1.68	-2.52	-1.309	-1.46
Lepidocrocit			3.88	4.817				3.88	3.998	4.232

TABLE A 2.18 (continued)

Table of saturation indices of minerals obtained from MINTEQA2 using CCW results from Table A 2.16

Mineral	Day									
	8	10	14	16	18	39	67	73	81	87
Analcime	*0.323*	*0.501*			-2.88		-1.11			-1.42
Halloysite	*2.992*	*3.46*					-3.84			-4.51
Low Albite	*0.572*	*0.917*			-3.92		-1.93			-2.4
Analbite	-0.34	*0.003*			-4.83		-2.85			-3.31
Anorthite	-1.82	-1.88					-3.16			-3.45
Pyrophyllite	*5.826*	*6.629*					-3.14			-4.13
Laumontite	*1.397*	*1.668*					-2.08			-2.7
Wairakite	-3.01	-2.74								
Kalsilite	-2.82	-2.81			-4.69		-3.15			-3.29
Leucite	-0.28	-0.11			-3.45		-1.68			-1.99
Microcline	*1.649*	*1.989*			-2.81		-0.82			-1.29
H Sandine	*1.203*	*1.543*			-3.26		-1.27			-1.74
Kaolinite		*6.728*			-3.85		-0.57			-1.24
Leonhardite		*15.77*			*2.104*		*8.264*			*7.041*
Muscovite		*9.493*			-2.97		*1.853*			*1.042*
Monticellite			-3.25		-0.25	-3.49	-1.4	-3.25	-0.632	-0.68
Na-Nontronite										*12.08*
K-Nontronite										*12.84*
Ca-Nontronite										*18.65*
Mg-Nontronite										*18.3*
Montmorillon										-0.01

Note : All minerals with SI values <-3. 000 have not been included in this table

TABLE A 2.19

Comparison of results obtained from T-R-I and Matla chemical laboratories on raw and cooling water samples taken

on 28 March 1994

Determinand	Raw water		Cooling water	
	T-R-I Results	**Matla Results**	**T-R-I Results**	**Matla Results**
Conductivity @ 25 °C (µS/cm)	255	263	861	878
pH @ 25 °C	6.93	7.98	6.9	8.3
Total Alkalinity (mg/l CaCO$_3$)	87.3	106	96.3	105
Sodium (mg/l Na)	16.7	16	84	76
Potassium (mg/l K)	3.5	5.0	17.9	22
Magnesium (mg/l Mg)	12.8	12	36.1	32
Calcium (mg/l Ca)	20.4	22	61	67
Chloride (mg/l Cl)	10.4	10.5	66	68
Sulphate (mg/l SO$_4$)	21.3	20	234	225
Nitrate (mg/l NO$_3$)	NR	NR	4.52	4
Silica (mg/l H$_4$SiO$_4$)	7.87	4.8	NR	NR

NR: Results not relevant as both laboratories did not carry out analyses.

Appendix 3

MINERALOGY

TABLE A 3.1

Solids predicted to precipitate by MINTEQA2 from cooling water south over the concentration period

	Day									
Mineral	**8**	**10**	**12**	**15**	**17**	**19**	**67**	**73**	**81**	**87**
Barite	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Calcite	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Ca - Nontronite	No	No	Yes	No	Yes	No	No	No	No	No
Diaspore	No	No	No	No	No	No	No	No	No	No
Hematite	No	No	No	No	No	No	No	Yes	No	Yes
Leonhardite	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No	No
Tenorite	Yes	Yes	Yes	Yes	Yes	No	No	No	No	Yes
Tremolite	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	No
Zinc Silicate	Yes	No	No	No	Yes	Yes	No	Yes	No	No

Appendix 4

MINERALS

Alunite: $KaAl_3(SO_4)_2(OH)_6$

Reference: Palache (b) p555-556

Chemical information: Crystals of the members of the alunite group are small, imperfect and rare.

Occurrence: Found in altered or mineralised organic rocks. Large deposits have been found world-wide and has been mined as a raw material in the production of alum or as a source of potash.

Artificial production: Alunite has been crystallised by heating a solution of alum and aluminium sulphate in a sealed tube at 230 °C.

Exclude as a precipitate

Aragonite: $(CaCO_3)$

Reference: Palache (b) p182-192

Chemical information: Aragonite is polymorphous with calcite and vaterite. Aragonite is unstable relative to calcite at atmospheric pressure and at all normal temperatures. It is only likely to form below 100 °C or when foreign elements are present in solid solution.

Occurence: Aragonite is much less widespread and abundant than calcite. In all of its occurrences it is a low-temperature near-surface deposit.

Artificial production: Aragonite has been synthesised from solutions by metathical reaction of calcium salts with alkali carbonates and its crystallisation is favoured over calcite in the presence of small amounts of barium, strontium, magnesium or lead salts, or if calcium sulphate is present in solution.

Exclude as a precipitate

Barite: $BaSO_4$

Reference: Palache (b)

Chemical information: Barite is a brittle, colorless to white crystal and can be pigmented by inclusions such as hematite, sulfides and organic matter.

Occurence: Barite is the most common mineral containing barium. It forms in hydrothermal metalliferous veins at moderate or low temperatures and is frequently associated with fluorite, calcite, dolomite, quartz, etc.

Artificial production: Crystals have been produced by slow inter-diffusion of dilute solutions of barium chloride and sulphates.

Include as a precipitate

Boehmite: $AlO(OH)$

Reference: Palache (a) p645-646

Chemical information: A basic oxide of aluminium which is dimorphous with diaspore.

Occurrence: Boehmite is widely distributed in bauxite and at times forms the princopal constituent of the rock.

Artificial production: An intermediate product in the dehydration of gibbsite and by heating precipitated hydrous aluminium oxide or gibbsite under pressure.

Exclude as a precipitate

Brucite: $Mg(OH)_2$

Reference: Palache (a) p636-638

Chemical information: Manganese, iron and zinc have been found to substitute for magnesium.

Occurrence: Brucite is associated with many other minerals e.g. calcite, aragonite, hydromagnesite and artinite. It occurs typically as a low-temperature hydrothermal vein mineral in serpentine, dolomitic or chloritic schists.

Artificial production: By mixing solutions of magnesium chloride in an excess of potassium hydroxide at a temperature of 200 °C. Brucite has been found as crystals in steam boilers using waters containing magnesium chloride.

Exclude as a precipitate.

Ca-nontronite $M^+_{0.35}(Mg_{2.88}Mn_{0.02}Fe_{0.02})Si_4O_{10}(OH)_2$. Since calcium has been specified in this mineral, M^+ would be calcium. Calcium can be substituted for by magnesium, sodium and potassium.

Note: This mineral is more widely known as Stevensite.

Reference: Faust et. al. (1959)

Chemical information: Faust et al. (1959) described the mineral as *a random or statistically disordered distribution of vacant sites of octahedrally coordinated atoms which would give a small proportion of domains with few or no vacancies and which have the attributes of talc.* Stevensite belongs to a group of minerals called smectites.

Occurence: Has been found to occur naturally in Japan**.**

Exclude as a precipitate.

Calcite $(CaCO_3)$

Reference: Dana (b) p141-142

Chemical information : Calcite is the thermodynamically stable form of calcium carbonate at all pressures and temperatures thus far investigated. There are two metastable polymorphs, aragonite and vaterite which change irreversibly to calcite on heating. Compositional variation can be large through the substitution of other divalent cation for Ca, the most significant substituents being barium strontium and lead.

Occurence: Calcite in its various forms is one of the commonest and most widely distributed of all minerals.

Artificial production: Calcite and its polymorphs may all be formed by precipitation from solution, this process being largely dependant on temperature and the presence of other substances in the solution.

Include as a precipitate

Cupricferrite: $CuFe_2O_4$

Reference: JCPDS

Artificial production: Stoichiometric amounts of CuO and Fe_2O_3 were heated in a platinum boat in pure oxygen with intermittent grinding at 850 °C for 18 hours.

Exclude as a precipitate.

Diaspore: $HAlO_2$ or $\alpha AlO.OH$

Reference: Dana (b) p677-679

Chemical formula: or $HAlO_2$

Chemical information: This is a hydrogen aluminium oxide mineral belonging to the Goethite group. It differs from other hydroxyl minerals in not having hydroxyl groups and in that H acts as a cation in two-fold coordination between oxygen.

Occurence: Diaspore commonly occurs with corundum as a constituent of emery rock, in part as crusts lining crevices.

Artificial production: Has been reported formed in crystals by heating hydrous aluminium oxide in a NaOH solution under pressure.

Exclude as a precipitate.

Dolomite: $CaMg(CO_3)_2$

Reference: Dana (b) p207-217

Chemical Information: The members of the dolomite group have a structure similar to that of calcite. Iron, and to a lesser extent manganese, cobalt, lead and zinc have been found to substitute for magnesium. several other compositional varieties can occur, resulting in difficulty in the interpretation of some analyses.

Occurence: Massive dolomite rocks are found as extensive strata in many parts of the world. The rocks are

considered to be secondary, transformed from limestone, coral, or marble by the action of solutions containing magnesium.

Artificial production: Dolomite does not crystallise directly at ordinary temperatures and pressures from solutions containing calcium, magnesium and carbon dioxide, or other ions such as chloride, sulphate or sodium. Under such conditions it normally forms fine-grained precipitates, soetimes gelatinous or spherulitic, which apparently consist of admixed calcite and magnesite.

Exclude as a precipitate

Ferrihydrite: $Fe_5O_7(OH).4H_2O$

Reference: Chukrov, 1973

Artificial Production: Prepared by slow hydrolysis of ferric salts at pH >3 and below 9.5.

Include as a precipitate.

Gibbsite: $Al(OH)_3$

Reference: Dana (b) p663-666

Chemical information: Called true gibbsite. small amounts of iron and silica oxides are often found as impurities.

Occurrence: Gibbsite is typically found as a secondary product, rresulting from the alteration of aluminous materials.

Artificial production: Obtained by hydrolysing or passing carbon dioxide into alkali aluminate solutions.

Exclude as precipitate.

Goethite: $HFeO_2$

Reference: Dana (a) p680-684

Chemical information: Goethite is a hydrogen iron oxide with the same composition as lepiddocrocite. The massive varieties often contain a high percentage of adsorbed or capillary water.

Occurrence: Goethite is one of the most common minerals and, after hematite is the commonest of the ferric oxides.

Artificial production: There are several ways in which goethite can be produced, but mainly by the oxidation of solutions of ferrous compounds and by slow hydrolysis of most ferric salts.

Include as precipitate.

Hematite: Fe_2O_3

Reference: Dana (a) p519

Chemical information: Hematite is often found admixed with magnetite. A high percentage of water can also be found in the crystals.

Occurence: Large hematite deposits are normally of sedimentar origin. It is also found in igneous rocks and in crystals formed by volcanic activity.

Artificial production: Hematite can be produced artificially in three ways: (1) Sublimation i.e. by the reaction of ferric chloride vapours and steam. (2) In melts i.e by heating iron oxide in borax and in silicate melts of high iron content. (3) In solution i.e. by heating iron hydrate with water in a closed tube.

Include as precipitate.

Hydro-Apatite: $Ca_5(PO_4)_3(OH)$

Reference: Dana (b) p879

Occurrence: The several members of tha apatite group are among the commonest and most widely distributed of all minerals.

Artificial production: By precipitation of solutions of calcium salts, by ammoniacal solutions of phosphates.

Include as precipitate.

Jarosite K: $KFe_3(SO_4)_2(OH)_6$, known as jarosite.

Reference: Dana (b) p560-563

Chemical information: A basic sulphate of potassium and ferric ion.

Occurrence: Secodary mineral, widespread as crusts and coatings on iron ores and cracks in adjacent rocks.

Artificial production: Synthesised at 110 °C by crystallisation from an acidic solution of K_2SO_4 and an excess of $Fe_2(SO_4)_3$.

Exclude as precipitate.

Jarosite Na: $NaFe_3(SO_4)_2(OH)_6$,, known as natrojarosite.

Reference: Dana (b) p563-564

Chemical information: Isostructural with jarosite.

Occurrence: Found with gypsum, alunite, jarosite, etc.

Exclude as precipitate.

Leonhardite $MgSO_4.4H_2O$

NOTE: This mineral is more widely known as Starkeyite.

Reference: JCPDS

Chemical information: A more commonly known mineral in this series which has 7 coordinated waters is epsom salts, which is highly soluble in water and sparingly soluble in alcohol.

Occurence: This is a sythetic mineral, therefore no natural occurence.

Artificial production: Leonhardite can be recrystallised from a water solution containing magnesium, sulphur and oxygen

Exclude as a precipitate.

Lepidocrocite: $FeO(OH)$

Reference: Dana (a) p642-645

Chemical information: Lepidocrocite is a mononbasic ferric oxide which is dimorphous with goethite.

Occurrence: Often occurs together with goethite with its crystals laying on goethite crusts.

Artificial production: Obtained by oxidation of both ferrous and ferric componds under suitable conditions.

Include as precipitate.

Mag-ferrite: $MgFe_2O_4$ full name is magnesioferrite

Reference: Dana (a) P688

Chemical information: essentially a magnesium, iron spinel.

Occurrence: Magnesioferrite is found mainly in fumaroles, where it is apparently formed by the reaction of steam

and ferric chloride vapours with MgO or other magnesian materials.

Artificial production: Found in sintered magnesite of furnace linings and other refractories.

Exclude as precipitate.

Maghemite: Fe_2O_3

Reference: Dana (A) p708-709

Chemical information: Maghemite is a ferromagnetic feric oxide which is related to magnetite and the spinel group.

Occurence: Forms by slow oxidation at low temperatures and may be derived from magnetite or lepidocrocite.

Artificial production: Easily produced by the oxidation of precipitated magnetite at temperatures below 750 $^\circ$C.

Include as a precipitate.

Magnesite: $MgCO_3$

Reference: Dana (b) p162-165

Chemical information: Magnesite resembles calcite and dolomite.

Occurrence: Magnesite deposits are formed in a number of ways; by the alteration of rocks rich in magnesium, as crystalline beds, as a replacement of calcite rocks by magnesium-containing solutions and as a sedimentary deposit.

Artificial production: Obtained as microscopic crystals by heating $CaCO_3$ with $MgCl_2$ or $MgSO_4$ solution. Precipitation at ordinary temperature and pressure gives either nesquehonite or a basic carbonate.

Maybe include as precipitate.

Malachite: $Cu_2(OH)_2(CO_3)$

Reference: Dana (b) p252-255

Chemical information: Crystals are very rare and once formed the composition does not vary significantly, although a small amount of zinc can substitute for the copper.

Occurrence: Malachite is found naturally as a minor ore of copper, occurring as a secondary mineral in the upper oxidised zone of copper deposits.

Artificial production: Obtained by the actions of alkali carbonates on solutions of cupric salts, heating soluble

cupric salts in contact with calcite in sealed tubes at 150 to 225 ^{0}C and by passing carbon dioxide into suspended cupric oxide.

Exclude as precipitate.

Quartz SiO_2

Reference: Frondel

Chemical information: Quartz shows a significant but very small range in chemical composition The principal elements which enter that enter solid soltion in natural quartz are Li, Na, Al, Ti, Mg and (OH).

Occurence: Silicon, after oxygen, is the second most abundant element, constituting 27.7 % of the Earth's crust by weight. The major part of silicon is combined in silicates, chifly as feldspars. The remaining silicon is present as SiO_2, about 12 %. It is chiefly contained as quartz in igneous rocks, the other polymorphs of silica being relatively rare.

Artificial production: There are four ways in which quartz can be synthesised (1) From solutions at elevated temperatures (200-400 ^{0}C) and pressures (up to 25 000 psi) (2) From water solutions under ordinary conditions. Its formation by the evaporation of silica solutions or sols in water at room temperature has been reported, but not verified. It is thought that the products were only hardened gels (opal). (3) From vapours - crystalline silica has been obtained by the thermal decomposition of $SiCl_4$, and by passing the mixed vapours of NaCl and KCl over silica glass. (4) From dry melts.

Exclude as a precipitate.

Tenorite CuO

Reference: Dana (a) p507

Chemical information: An infusible mineral, which is easily soluble in dilute HCl or HNO_3.

Occurence: Tenorite is a common mineral found in the oxidised portion of copper deposits, but is less abundant than cuprite, Cu_2O. It is also found in crystals on lavas as a product of sublimation.

Artificial production: Powdery or granular black cupric oxide is formed by heating finely divided Cu or Cu_2O in oxygen, by calcining cupric salts or by electrolysis.

Exclude as a precipitate.

Tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$

Reference: JCPDS

Chemical information: Tremolite is a variety of asbestos, with inhalation of dust or fine particles being dangerous.

Occurence: Species have been found in East canaan and in Connecticut and Massachusetts, United States of America.

Exclude as a precipitate.

Zinc Silicate $ZnO.SiO_2$

Reference: JCPDS

Occurence: Synthetic, therefore no natural occurence.

Artificial production: Synthetically formed as spherules in devitrified glass.

Exclude as a precipitate.

Other silicates: Several other silicates were identified as having positive saturation indices, but due to the greater likelihood of an amorphous precipitate being formed, only the type of silicate will be mentioned in this section. **Analbite, low albite** and **analcime** are sodium aluminium silicates. **Anorthite** and **laumontite** are calcium aluminium silicates. **Chrysotile, clinoenstite, forsterite, sepiolite** and **talc** are magnesium silicates. **Diopside** and **huntite** are calcium magnesium silicates. **H sandine, leucite, microcline** and **muscovite** are potassium aluminium silicates. **Halloysite, kaolinite** and **pyrophyllite** are aluminium silicates. **Montmorillon** is a magnesium, iron aluminium silicate.

Appendix A5

MINTEQA2

_____

A 5.1   MINTEQA2 MENU OPTIONS

The are six options on the menu

Edit Level 1

This option is used to enter all the necessary background information ie. titles, type of display, output

complexity, number of iterations, termination of program execution if the charge balance exceeds 30 % and

method used to compute activity coefficients. It is also used to enter or change ionic strength, pH, redox

potentials, temperature, adsorption parameters, inorganic carbon content and precipitation options.

Edit Level 2

This level is used to specify concentrations and types of components, gases, redox aqueous and mineral

species, adsorption sites and reactions and also to add species of all of the above types. However, adding

of species in this way is not ideal as it only applies to the problem in hand. It is preferable to add new

species to the database.

Edit Level 3

This level is used for checking and individually editing all entries.

Edit Level 4

Used to sweep a range of pH, redox potential or dissolved concentration of one particular species.

M Multiproblem Generator

This is used to submit multiple problems back-to-back in one input file. This feature would be used when the standard input file has to be changed in a way that the sweep option does not support eg temperature changes.

X Exit

This writes the current program to a new MINTEQA2 output file and exits the program.

Appendix 6

MINTEQA2 OUTPUT

Appendix 7

CALCULATED INCREASE IN THE CONCENTRATION OF CONTAMINANTS IN MATLA POWER STATION COOLING WATER

TABLE A7.1
Calculated increase in the concentration of contaminants in Matla power station cooling water

	0	1	2	3	4	5	6	7	8	9
Evaporation	1.55	kl/Mw.h								
day	0	1	2	3	4	5	6	7	8	9
Raw Water										
pH	7.99	7.99	7.99	7.99	7.99	7.99	7.99	7.99	7.98	7.57
Na	15	15	15	15	15	15	15.3	15.6	16	16.1
Cl	11	11	11	11	11	11	11	11	11	10.7
K	4	4.1	4.3	4.3	4.4	4.5	4.6	4.8	5	4.4
Ca	24	24	24	24	23	23	23	22	22	21.2
Mg	12	12	12	12	12	12	12	12	12	12.5
SO4	21	20.9	20.8	20.6	20.5	20.4	20.2	20.1	20	20.5
NO3	0.6	0.6	0.65	0.7	0.75	0.8	0.85	0.9	0.92	0.88
Alk	105	105	105	105	105	106	106	106	106	103.6
COD	2	8	8	9	10	10	10	11	11	11
CW analysis										
pH	7.99	8.03				8.67			8.3	
Na	15	17.5				63			105	
Cl	11	11				32			68	
K	4	9.5				12			22	
Ca	24	30.4				32			67	
Mg	12	9.7				32			32	
SO4	21	14.4							225	
NO3	0.6	0				124			4	
Alk	105	105				160			105	
COD		2								
CT temp	25	25	25	25	25	25	25	25	25	25
Clar temp	40	40	40	40	40	40	40	40	40	40
Power	13308	18528	27270	27760	27814	27124	27432	25039	27507	26151
evapn	20627.4	28718.4	42269	43028	43111.7	42042.2	42519.6	38810	42636	40534
RW vol	20627.4	28718.4	42269	43028	43111.7	49842.2	50319.6	46610	46236	44134
cw blow	0	0	0	0	0	7800	7800	7800	3600	3600
calc analysis										
pH	7.99	8.03	8.19	8.35	8.51	8.67	8.55	8.43	8.3	8.57
Na	15	20.62565	28.46	39.98572	51.72063	63.47836	68.34117	72.92	76.14	84.69
SO4	21	28.83841	39.7	55.53066	71.56837	87.55889	93.44713	98.58	101.6	112.1
Cl	11	15.12548	20.87	29.32286	37.92846	46.5508	49.91749	52.9	54.72	60.13
K	4	5.500175	7.641	10.94563	14.38787	17.91519	19.54311	21.16	22.4	24.63
Ca	24	33.00105	40.53	48.44444	49.79353	52.82853	52.55106	53.78	52.52	52.68
Mg	12	16.50052	20.27	24.22222	24.38793	25.00619	23.72833	24.51	23.59	23.76
Alk	105	144.3796	174.8	210.6944	222.1444	233.088	223.0034	210.4	190	179.7
COD	2	5.000349	9.178	16.09423	23.91751	31.756	36.31464	41.23	44.7	51.02
nitrate	0.6	0.825026	1.164	1.702388	2.289134	2.916213	3.272929	3.632	3.897	4.381
Mg no precip	12	16.50052	22.77	31.98857	41.3765	50.78269	54.45544	57.71	59.7	65.88
Ca no precip	24	33.00105	45.53	63.97715	82.753	100.7815	107.332	113.2	115.8	126.7
Mg after clar	12	14	15	15	15.6	16.4	16.9	16.9	14.8	13.9
Ca after clar	24	28	30	31.8	34.8	39.2	41.1	41.5	38.3	38.7
Alk after clar	105	120	130	140	150	160	145	130	105	109
Lime used		91.2	108	126	160	188	137	114	96.9	131
Ml treated		9.6	16.8	22.9	21.5	19.8	18	20.4	26.5	27.3

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	10	11	12	13	14	15	16	17	18	19	20	21	22
Raw Water													
pH	7.13	6.73	6.72	6.71	6.69	6.62	6.54	7.09	7.63	7.73	7.84	7.95	7.89
Na	16.2	16.3	16.4	16.55	16.7	16.3	15.9	15.85	15.8	14.9	14	13	12.8
Cl	10.4	10.2	10.3	10.4	10.4	10.4	10.5	10.3	10.1	10.2	10.3	10.5	10.5
K	3.8	3.3	3.3	3.4	3.4	3.6	3.8	3.6	3.4	3.7	4	4.4	4.3
Ca	22.4	19.4	19.7	20	20.2	19.5	18.8	18.9	19	19.3	19.6	20	19.9
Mg	13	13.4	13.1	12.8	12.6	12.8	13	13.1	13.3	12.9	12.5	12	12
SO4	21	21.5	21.4	21.3	21	21	20.9	20.9	21	20	19	64.78	18.1
NO3	0.85	0.82	0.8	0.79	0.78	0.68	0.58	0.85	1.12	1.12	1.13	1.13	1.14
Alk	101.2	98.8	98.4	97.9	97.4	97.2	97	97	96.9	90.9	84.9	89	89
COD	10	10	9	9	8	8	7	7	7	7	7	7	7
CW analysis													
pH	8.83		7.7			7.2		8	8.43	7			
Na	92		114			128		135	123	133			
Cl	80		90			110		130	134	146			
K	26		36			33		35.6	27	30.2			
Ca	82		82			80		108	104	82			
Mg	26		39			45		51.4	41	49			
SO4	256		309			387		449	430	452			
NO3			5.01			6.11		7.6		7.8			
Alk	124		106			89.2		103	101	97.7			
COD													
CT temp	25	25	25	25	25	25	25	25	25	25	25	25	
Clar temp	40	40	40	40	40	40	40	40	40	40	40	40	
Power	28822	36344	36344	32409	27847	27664	27874	27021	27343	27776	25573	27541	28050
evapn	44674	56333	56333	50234	43163	42879	43205	41883	42382	43053	39638	42689	43478
RW vol	47474	59133	61783	55684	48613	47179	47505	52883	43282	46593	43178	46229	47018
cw blow	2800	2800	5450	5450	5450	4300	4300	11000	900	3540	3540	3540	3540
calc analysis													
pH	8.83	8.4	8.3	8.3	8.3	8.3	8.3	8.3	8.43	8.3			
Na	92.15	101.52	114	121.3	126.2	128.1	131.7	135.1	123.3	133	136.3	137.7	139.6
SO4	121.6	134.01	150.2	159.2	164.7	167	171.8	176.5	161.4	174.5	179.3	218.6	219.8
Cl	64.54	70.063	77.57	81.57	84.01	84.88	87.25	89.33	81.17	87.87	90.94	93.33	96.15
K	26.07	27.59	29.73	30.61	31.02	31.12	31.95	32.56	29.32	31.75	33.1	34.42	35.82
Ca	53.23	56.736	55.89	54.53				108	104.7	98.25			
Mg	22.78	25.707	23.08	17.22				51.4	53.91	40.37			
Alk	178.4	200.2	210.6	187.5				103	175.6	139.9			
COD	55.71	61.505	68.05	71.42	72.44	72.33	72.68	73.05	65.17	69.61	71.06	71.98	73.23
nitrate	4.777	5.2414	5.835	6.144	6.325	6.299	6.304	6.545	6.313	7.091	7.592	7.991	8.434
Mg no precip	71.6	79.172	89.55	95.39	98.9	100.2	103.4	106.5	97.81	106.7	110.7	113.4	116.2
Ca no precip	135.4	147.83	161.2	167.3	171	171.9	175.2	177.7	160.4	172.7	177.9	181.9	187
Mg after clar	15.3	10.3	10.3										
Ca after clar	42.7	37.6	37.6										
Alk after clar	124	115	106	100	94	89	98	103	101	82			
Lime used	131	143	188										
Ml treated	23.3	36.9	33.5										

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	23	24	25	26	27	28	29	30	31
Raw Water									
pH	7.83	7.77	7.71	7.65	7.59	7.53	7.47	7.41	7.35
Na	12.7	12.5	12.3	12.15	12	11.8	11.6	11.5	11.3
Cl	10.4	10.4	10.4	10.3	10.3	10.2	10.2	10.1	10.1
K	4.2	4.2	4.1	4	3.9	3.9	3.8	3.7	3.6
Ca	19.9	19.8	19.7	19.7	19.6	19.6	19.5	19.5	19.4
Mg	12.1	12.2	12.2	12.3	12.4	12.4	12.5	12.6	12.6
SO4	18.2	18.3	18.4	18.5	18.6	18.7	18.8	18.9	19
NO3	1.14	1.15	1.15	1.16	1.16	1.17	1.17	1.18	1.18
Alk	89	89	89	89	88.9	88.9	88.9	88.9	88.9
COD	7	7	7	7	7	7	8	8	8
CW analysis									
pH									
Na									
Cl									
K									
Ca									
Mg									
SO4									
NO3									
Alk									
COD									
CT temp									
Clar temp									
Power	27560	32592	25680	22949	25134	32998	28289	28271	27313
evapn	42718	50518	39804	35570.95	38957.7	51146.9	43847.95	43820.05	42335.15
RW vol	46258	54058	43344	39110.95	42497.7	54686.9	47387.95	47360.05	45875.15
cw blow	3540	3540	3540	3540	3540	3540	3540	3540	3540
calc analysis									
pH									
Na	141.5	142.9	145.8	145.9711	145.1091	144.8871	147.0956	147.5364	147.7707
SO4	221.2	222.3	226.1	226.1413	224.8127	224.7921	229.0167	230.5605	232.0816
Cl	98.85	101.2	104.9	106.3039	106.7862	107.7945	110.9984	112.5563	114.0088
K	37.1	38.25	39.82	40.40556	40.57823	40.97994	42.12069	42.59757	42.95577
Ca									
Mg									
Alk									
COD	74.5	75.59	77.61	78.13004	78.07906	78.46241	81.36674	83.02247	84.56758
nitrate	8.866	9.263	9.797	10.08044	10.25651	10.50041	10.9879	11.29737	11.58631
Mg no precip	119	121.5	125.7	127.2051	127.7644	129.1223	133.1409	135.3415	137.4802
Ca no precip	191.9	196.3	203.1	205.5969	206.3728	208.2345	214.3202	217.3269	220.1303
Mg after clar									
Ca after clar									
Alk after clar									
Lime used									
Ml treated									

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	32	33	34	35	36	37	38	39
Raw Water								
pH	7.28	7.21	7.14	7.07	7	6.93	6.86	6.79
Na	11.1	10.9	10.7	1.5	10.4	10.3	10.2	10
Cl	10.1	10	10	9.9	9.9	9.9	9.8	9.8
K	3.5	3.4	3.3	3.2	3.1	3	2.9	2.8
Ca	19.4	19.3	19.3	19.2	19.2	19.1	19.1	19
Mg	12.7	12.8	12.8	12.9	13	13.1	13.2	13.3
SO4	19	19.1	19.2	19.3	19.4	19.5	19.6	19.6
NO3	1.19	1.19	1.2	1.2	1.21	1.22	1.23	1.24
Alk	88.9	88.8	88.8	88.8	88.8	88.8	88.8	88.8
COD	8	8	8	8	8	8	8	8
CW analysis								
pH								
Na								
Cl								
K								
Ca								
Mg								
SO4								
NO3								
Alk								
COD								
CT temp								
Clar temp								
Power	27324	27101	25938	27347	25962	21834	24961	27538
evapn	42352.2	42006.55	40203.9	42387.85	40241.1	33842.7	38689.55	42683.9
RW vol	45892.2	45546.55	43743.9	45927.85	43781.1	37382.7	42229.55	46223.9
cw blow	3540	3540	3540	3540	3540	3540	3540	3540
calc analysis								
pH								
Na	147.5181	147.1183	146.5101	145.4313	144.7553	143.6374	141.3251	139.907
SO4	232.9917	233.9327	234.7758	235.0149	236.0885	236.4154	234.5206	234.4751
Cl	115.0951	116.0312	116.8442	117.1976	117.9213	118.2121	117.2644	117.2414
K	43.1103	43.17254	43.12659	42.89591	42.72363	42.36184	41.60637	41.0783
Ca								
Mg								
Alk								
COD	85.79725	86.95026	87.97878	88.67889	89.65161	90.24947	89.87817	90.23576
nitrate	11.83315	12.06446	12.28169	12.44561	12.65498	12.8116	12.82302	12.94976
Mg no precip	139.141	140.7823	142.321	143.3411	144.8873	145.9101	145.4227	146.1978
Ca no precip	222.1433	224.0328	225.5959	226.4259	227.8853	228.5013	226.7762	226.8452
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	40	41	42	43	44	45	46	47
Raw Water								
pH	6.92	7.06	7.19	7.33	7.46	7.6	7.73	7.87
Na	10.4	10.8	11.2	11.6	12	12.4	12.8	13.2
Cl	9.9	10	10	10.1	10.2	10.3	10.3	10.4
K	2.9	3.1	3.2	3.4	3.5	3.7	3.8	4
Ca	19.1	19.2	19.3	19.4	19.5	19.6	19.7	19.8
Mg	13.2	13.1	13	12.8	12.7	12.5	12.4	12.2
SO4	19.6	19.7	19.7	19.8	19.8	19.9	19.9	19.9
NO3	1.21	1.18	1.15	1.12	1.09	1.06	1.03	1
Alk	88.1	87.4	86.8	86.1	85.5	84.8	84.1	83.4
COD	8	8	8	8	8	8	8	8
CW analysis								
pH								
Na								
Cl								
K								
Ca								
Mg								
SO4								
NO3								
Alk								
COD								
CT temp								
Clar temp								
Power	27288	27039	27362	28134	27877	28056	27315	23449
evapn	42296.4	41910.45	42411.1	43607.7	43209.35	43486.8	42338.25	36345.95
RW vol	45836.4	45450.45	45951.1	47147.7	46749.35	47026.8	45878.25	39885.95
cw blow	3540	3540	3540	3540	3540	3540	3540	3540
calc analysis								
pH								
Na	139.6426	139.6553	139.922	140.6076	141.8443	143.2546	144.9786	146.658
SO4	235.856	237.0932	238.1125	239.3291	240.8982	242.3079	243.7272	244.6396
Cl	118.0156	118.7536	119.3739	120.1289	121.1407	122.0985	123.0466	123.8021
K	40.87161	40.82447	40.84125	41.05317	41.41115	41.89073	42.44362	43.04839
Ca								
Mg								
Alk								
COD	91.15133	91.95162	92.64425	93.36513	94.21365	94.94963	95.67858	96.19356
nitrate	13.1332	13.2713	13.36743	13.44279	13.51194	13.54325	13.55224	13.51412
Mg no precip	147.9658	149.4429	150.6497	151.8145	153.0157	153.9619	154.7403	155.1241
Ca no precip	228.2129	229.442	230.5406	231.8268	233.5359	235.0794	236.7075	237.9049
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	48	49	50	51	52	53	54	55
Raw Water								
pH	8	8.12	8.14	8.15	8.17	8.18	8.2	8.21
Na	13.6	14	13.9	13.7	13.6	13.4	13.3	13.1
Cl	10.4	10.5	10.5	10.5	10.6	10.6	10.6	10.7
K	4.2	4.4	4.45	4.5	4.55	4.6	4.65	4.7
Ca	19.9	20	20	20	20	20	20	20
Mg	12.1	12	12	11.9	11.8	11.7	11.7	11.6
SO4	20	20	19.9	19.8	19.7	19.5	19.4	19.3
NO3	0.97	0.94	0.91	0.88	0.85	0.82	0.79	0.76
Alk	82.7	82	82	82.1	82.2	82.2	82.3	82.4
COD	8	8	9	9	9	8	9	9
CW analysis								
pH		8.4						
Na		147						
Cl		144						
K		30						
Ca		70						
Mg		28						
SO4		347						
NO3		14						
Alk		109						
COD								
CT temp								
Clar temp								
Power	21137	26555	25292	25598	28240	26820	27212	27295
evapn	32762.35	41160.25	39202.6	39676.9	43772	41571	42178.6	42307.25
RW vol	36302.35	45360.25	43402.6	43876.9	47972	45771	46378.6	46507.25
cw blow	3540	4200	4200	4200	4200	4200	4200	4200
calc analysis								
pH								
Na	147.0813	146.8552	147.1046	146.6823	146.3307	146.8441	146.6988	146.5429
SO4	243.3977	240.9326	238.9463	236.3244	233.9937	233.1334	231.4751	230.0735
Cl	123.3758	122.3653	121.6807	120.6747	119.9158	120.0041	119.6615	119.5465
K	43.32348	43.43921	43.79209	43.99909	44.26897	44.90064	45.34159	45.8424
Ca								
Mg								
Alk								
COD	95.80379	94.91785	95.09216	94.93282	94.86327	94.59691	94.86294	95.20809
nitrate	13.34775	13.10908	12.85853	12.57104	12.28917	12.06594	11.80198	11.54161
Mg no precip	153.9872	152.0625	150.3472	148.3358	146.5017	145.6065	144.2242	143.0767
Ca no precip	236.9514	234.8352	233.397	231.3567	229.6447	229.5526	228.6671	228.0702
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	56	57	58	59	60	61	62	63
Raw Water								
pH	8.23	8.24	8.25	8.26	8.27	8.28	8.29	8.3
Na	12.9	12.8	12.6	12.5	12.4	12.3	12.2	12
Cl	10.7	10.7	10.8	10.9	10.9	10.9	11	11
K	4.75	4.8	4.85	4.9	4.95	5	5	5
Ca	20	20	20	20	20	20	20	20
Mg	11.5	11.4	11.3	11.2	11.2	11.1	11	11
SO4	19.1	18.9	18.8	18.7	18.5	18.3	18.2	18
NO3	0.72	0.69	0.65	0.62	0.58	0.55	0.51	0.48
Alk	82.5	82.6	82.7	82.8	82.9	82.9	83	83
COD	8	9	8	9	13	16	15	16
CW analysis								
pH								8.47
Na								126
Cl								136
K								26
Ca								77
Mg								22
SO4								284
NO3								2.4
Alk								123
COD								
CT temp								
Clar temp								
Power	27268	27228	27087	16708	13867	14029	13145	25840
evapn	42265.4	42203.4	41984.85	25897.4	21493.85	21744.95	20374.75	40052
RW vol	46465.4	46403.4	46184.85	30097.4	25693.85	25944.95	24574.75	40052
cw blow	4200	4200	4200	4200	4200	4200	4200	0
calc analysis								
pH								
Na	146.2604	145.9052	145.3939	144.7877	140.5168	135.5325	130.9378	126.3007
SO4	228.655	227.1613	225.6759	224.1453	217.1525	209.1189	201.7353	194.3727
Cl	119.4652	119.3821	119.3776	119.3305	116.1827	112.4026	109.0082	105.5989
K	46.35825	46.87333	47.38584	47.88194	46.93427	45.686	44.55588	43.3875
Ca								
Mg								
Alk								
COD	94.70234	95.07396	94.56335	94.89967	94.76672	95.00456	94.82556	94.73336
nitrate	11.26907	10.99145	10.70051	10.40401	9.926913	9.425796	8.946588	8.477865
Mg no precip	141.9597	140.8346	139.6981	138.5191	134.0702	129.0644	124.4447	119.8566
Ca no precip	227.5657	227.0844	226.6174	226.1066	219.7847	212.3444	205.5635	198.8022
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	64	65	66	67	68	69	70	71
Raw Water								
pH	7.98	7.66	7.34	7.04	7.06	7.09	7.11	7.13
Na	43	43	43	43	43	10.3	10.5	10.6
Cl	10.7	10.3	10	9.6	9.7	9.8	9.9	10
K	4.2	3.4	2.6	2.1	2.1	2.1	2.1	2.1
Ca	19.3	18.6	17.9	17.1	17.2	17.3	17.4	17.4
Mg	11	11	11.1	11.1	11.2	11.2	11.3	11.4
SO4	18.5	19.3	20	20.3	20.3	20.4	20.4	20.4
NO3	0.44	0.41	0.37	0.34	0.3	0.3	0.3	0.3
Alk	84.5	86	87.5	89.1	89.1	89.1	89.1	89.1
COD	15	15	14	15	14	14	13	13
CW analysis								
pH					7.3			
Na					292			
Cl					225			
K					30.8			
Ca					80			
Mg					32			
SO4					465			
NO3					9.44			
Alk					99.3			
COD								
CT temp								
Clar temp								
Power	27595	27818	27792	28128	27921	26666	26515	22986
evapn	42772.25	43117.9	43077.6	43598.4	43277.55	41332.3	41098.25	35628.3
RW vol	42772.25	43117.9	43077.6	43598.4	44597.55	42652.3	42418.25	36948.3
cw blow	0	0	0	0	1320	1320	1320	1320
calc analysis								
pH								
Na	157.614	191.0542	224.7645	258.4434	292.5294	293.3312	294.434	295.5427
SO4	207.8447	222.8539	238.5331	254.4327	270.5245	280.5735	289.6599	298.4413
Cl	113.3908	121.4009	129.2405	136.7595	144.4487	148.9284	153.0315	157.0711
K	46.44602	49.09012	51.12842	52.7732	54.43787	54.83417	55.1467	55.44278
Ca								
Mg								
Alk								
COD	105.6566	117.3218	116.5441	128.2973	127.5093	139.395	134.9903	146.131
nitrate	8.798281	9.117129	9.407194	9.673492	9.911302	9.91669	9.911338	9.904838
Mg no precip	127.867	136.4214	145.045	153.7389	162.5378	167.7186	172.3789	176.9568
Ca no precip	213.3666	228.3758	242.9575	256.9773	270.5324	277.9865	284.7309	291.3169
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	72	73	74	75	76	77	78	79
Raw Water								
pH	7.16	7.18	7.4	7.62	7.85	8.07	8.07	8.06
Na	10.8	11	13	16	19	22	20	17
Cl	10.1	10.1	10.5	11	11.5	12	11.6	11.2
K	2.1	2.1	2.3	2.5	2.7	2.8	2.7	2.5
Ca	17.5	17.6	17.7	17.8	17.9	18	17.9	17.8
Mg	11.4	11.5	11.1	10.8	10.4	10	10.4	10.8
SO4	20.5	20.5	19	17.7	16.4	15	17	19
NO3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Alk	89.1	89.1	87.6	86.1	84.6	83	84.9	86.8
COD	13	13	13	13	13	13	7	1
CW analysis								
pH			6.9			8.51		
Na			302			275		
Cl			278			226		
K			57.3			73		
Ca			103			98		
Mg			32.1			34		
SO4			574			571		
NO3			10.5			2.6		
Alk			108			114		
COD								
CT temp								
Clar temp								
Power	26441	25545	25656	26960	25930	25777	26896	27879
evapn	40983.55	39594.75	39766.8	41788	40191.5	39954.35	41688.8	43212.45
RW vol	42303.55	40914.75	44416.8	46438	44841.5	44504.35	48738.8	50262.45
cw blow	1320	1320	4650	4650	4650	4550	7050	7050
calc analysis								
pH								
Na	295.705	297.0688	299.6099	287.2005	278.9612	273.3129	266.8859	247.7407
SO4	305.0504	313.4969	320.1071	307.3377	295.2006	282.4723	272.86	254.7213
Cl	160.0865	164.0129	167.8876	162.5768	158.5414	154.9211	151.4912	141.9978
K	55.52291	55.80559	56.17723	53.44665	51.20766	49.16113	47.27892	43.43402
Ca								
Mg								
Alk								
COD	151.3571	157.7235	163.6089	160.2751	157.7008	154.9668	147.811	129.7505
nitrate	9.868658	9.862557	9.849027	9.25861	8.729135	8.235716	7.797149	7.063544
Mg no precip	180.3682	184.8078	188.9273	181.9185	175.6568	169.285	163.3722	151.6469
Ca no precip	296.0144	302.3703	308.2061	296.4429	286.409	276.7883	268.4554	249.9066
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	80	81	82	83	84	85	86	87
Raw Water								
pH	8.05	8.05	8.04	8.03	8.02	8.02	8.01	8.01
Na	14	11	11	11	11	11	11	11
Cl	10.8	10.5	10.5	10.4	10.3	10.2	10.1	10.1
K	2.3	2.1	2.1	2.2	2.2	2.2	2.3	2.3
Ca	17.7	17.6	17.8	17.9	18	18.1	18.3	18.4
Mg	11.2	11.5	11.5	11.6	11.6	11.7	11.7	11.8
SO4	21	22.2	21.7	21.2	20.7	20.2	19.7	19.1
NO3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Alk	88.7	90.6	90.7	90.8	91	91.1	91.2	91.3
COD	1	1	1	1	1	1	1	1
CW analysis								
pH			7.2					
Na			193					
Cl			208					
K			47.2					
Ca			66					
Mg			35.7					
SO4			439					
NO3			8.23					
Alk			106					
COD								
CT temp								
Clar temp								
Power	27839	25596	27071	23389	25443	25623	26014	24653
evapn	43150.45	39673.8	41960.05	36252.95	39436.65	39715.65	40321.7	38212.15
RW vol	50200.45	46723.8	43260.05	37552.95	40736.65	41015.65	41621.7	39512.15
cw blow	7050	7050	1300	1300	1300	1300	1300	1300
calc analysis								
pH								
Na	228.7789	209.4937	191.9852	196.0994	198.9749	202.4192	205.8378	209.2969
SO4	241.2618	230.5992	219.4752	230.9624	239.6368	248.9342	257.7413	266.1033
Cl	133.666	126.1162	118.8704	124.2408	128.3368	132.8582	137.2499	141.6491
K	39.96845	36.76197	33.83375	34.76445	35.44486	36.23654	37.09524	37.95899
Ca								
Mg								
Alk								
COD	114.0327	100.3285	88.31775	87.01678	85.6428	84.35918	83.11098	81.9033
nitrate	6.432285	5.881604	5.382546	5.491286	5.566327	5.656959	5.74697	5.83816
Mg no precip	142.0782	134.089	126.6708	132.722	137.5052	142.8468	148.1956	153.5469
Ca no precip	234.1398	220.2828	206.9982	216.106	223.2198	231.2757	239.3071	247.4994
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

day	88	89	90	91	92	93	94	95
Raw Water								
pH	8.03	8.06	8.08	8.11	8.13	8.16	8.18	8.2
Na	11.2	11.3	11.5	11.6	11.8	11.9	12.1	12.3
Cl	10.4	10.7	11	11.3	11.6	11.9	12.2	12.5
K	23	2.3	2.3	2.3	2.3	2.2	2.2	2.2
Ca	18.8	19.3	19.7	20.2	20.6	21	21.4	21.8
Mg	11.8	11.8	11.8	11.9	11.9	11.9	11.9	12
SO4	18.7	18.3	17.9	17.5	17.1	16.7	16.3	15.9
NO3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Alk	90.7	90.2	89.6	88.9	88.2	87.5	86.8	86.1
COD	1	1	1	1	1	1	1	1
CW analysis								
pH	6.5							
Na	213							
Cl	228							
K	50.6							
Ca	86							
Mg	36.8							
SO4	512							
NO3	7.71							
Alk	99.3							
COD								
CT temp								
Clar temp								
Power	25818	26787	25579	28334	27509	27848	26449	19543
evapn	40017.9	41519.85	39647.45	43917.7	42638.95	43164.4	40995.95	30291.65
RW vol	40917.9	42419.85	40547.45	44817.7	43538.95	44064.4	41895.95	31191.65
cw blow	900	900	900	900	900	900	900	900
calc analysis								
pH								
Na	212.396	217.3272	222.6405	227.5492	233.4411	239.0414	244.8239	250.1872
SO4	273.2478	282.3909	291.5757	299.7059	308.7359	316.9039	324.7772	331.5744
Cl	145.7724	151.3474	157.3548	163.1105	169.8939	176.5341	183.4196	189.94
K	53.58504	54.4193	55.30273	56.09339	57.0497	57.85771	58.67353	59.38925
Ca								
Mg								
Alk								
COD	80.6858	80.10945	79.56984	79.00501	78.52707	78.0337	77.55796	77.05057
nitrate	5.915688	6.042075	6.174585	6.294715	6.43617	6.568336	6.701206	6.820073
Mg no precip	158.3947	164.5816	170.9894	176.8907	183.693	190.1074	196.5304	202.3793
Ca no precip	254.868	264.6839	275.2382	285.2577	297.0502	308.4967	320.2731	331.3336
Mg after clar								
Ca after clar								
Alk after clar								
Lime used								
Ml treated								

Calculated increase in the concentration of contaminants in Matla power station cooling water

	96	97	98
day	96	97	98
Raw Water			
pH	8.23	8.27	8.3
Na	12.5	12.7	13
Cl	12.7	12.9	13
K	2.2	2.2	2.2
Ca	22.2	22.6	23
Mg	12	12	12
SO4	15.6	15.3	15
NO3	0.3	0.3	0.3
Alk	85.4	84.7	84
COD	1	1	1
CW analysis			
pH			8.41
Na			255
Cl			240
K			57
Ca			107
Mg			41
SO4			611
NO3			4
Alk			103
COD			
CT temp			
Clar temp			
Power	13340	11859	12338
evapn	20677	18381.45	19123.9
RW vol	21577	19281.45	23623.9
cw blow	900	900	4500
calc analysis			
pH			
Na	253.1822	254.0216	254.4223
SO4	334.9958	335.5163	335.2847
Cl	194.0343	195.92	197.2715
K	59.66509	59.55184	59.34861
Ca			
Mg			
Alk			
COD	76.35686	75.4997	74.61482
nitrate	6.878608	6.883742	6.87627
Mg no precip	205.873	207.2119	208.028
Ca no precip	338.275	341.4489	343.7845
Mg after clar			
Ca after clar			
Alk after clar			
Lime used			
Ml treated			