FINAL REPORT

RESEARCH ON PHASE DIAGRAMS OF COMPLEX PRECIPITANTS

(With Special Emphasis on the Use of Chemical Speciation Modeling)

Compiled
by

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December 1992

Report to the Water Research Commission on Project 309 entitled
Research on Phase Diagrams of Complex Precipitants

Head of Pollution Research Group : Professor C.A. Buckley
Project Leader : Dr. Carol A. Kerr

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EXECUTIVE SUMMARY

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Supplementary to FINAL REPORT which is the full report
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1 BACKGROUND TO THE PROJECT

The limited amount of water available in the Republic of South Africa, together with environmental considerations, has resulted in many industries employing some sort of desalination measure in order to recover and reuse water and chemicals and to reduce the volume of effluent requiring disposal. The desalination equipment, generally crystalising evaporators, reverse osmosis or electrodialysis plants, is used either as an end-of-line effluent treatment process, or as part of a closed loop recovery system within the production process. Regardless of the desalination technology used, fouling and scaling of heat or mass transfer surfaces is a common problem which often results in equipment being used below design specifications, in order to avoid the precipitation of unwanted solid phases. This can lead to increased water and chemical consumption and effluent production, as operators try to suppress precipitation through dilution or the use of scale inhibitors. Thus the equipment, designed to remove dissolved salts, can be the point of entry of additional chemicals to the aquatic environment. Industries (including water and wastewater treatment) which use precipitation as part of their process operations encounter problems such as under-recovery of a solid phase, or high residual concentrations of product in the supernatant liquid phase. Mal-operation of a precipitation circuit, can threaten the aquatic environment as the effluents produced may contain chemicals or metals which could cause contamination of the surface and groundwater supplies.

The reasons for unwanted precipitation are varied. Consequently, equipment vendors and operators have few guide-lines to help them demarcate areas of safe operation. The basis of this research project was to provide assistance to industry to deal with precipitation problems.

2 PROJECT AIMS

The aims of this project were to :

(i) develop techniques for the determination of a phase diagram of complex precipitates which occur in desalination plants,

(ii) acquire graphical or tabular data indicating envelopes of precipitation,

(iii acquire solubility design data for the barium carbonate sulphate removal process,

(iv) generate data which could assist in the verification of computer models of aquatic equilibria (such as STASOFT).

3 PROJECT OBJECTIVES

The aims of the project were to be realised through practical means. Ideally a graphical or tabular representation of precipitation envelopes, or safe zones of operation, would be produced which would be of practical use to operators of equipment where precipitation problems were encountered.

Identification of the commonly occurring precipitate phases and production of graphical representations of the chemistry involved, eventually could lead to the production of an atlas-type document, which could be consulted to identify the likely precipitates for a given system and the safe operating regimes. This ambition proved to be unrealistic as even in chemical systems with a small number of chemical components, the interactions and interdependence of the chemical species involved, defied representation by simple graphical means.

In defining the methods by which the project aims would be fulfilled, several factors had to be taken into account. These were that :

(i) any solution reached had to of general interest to the industrial community and not tailored to site specific cases.

(ii) the feed solution entering desalination equipment is often the result of a number of other processes and can not be considered in isolation.

(iii) the desalination equipment might be an integral part of process operations and a key component of a recycle loop. Any solution reached, would have to be capable of being demonstrated without disruption of factory operations.

(iv) the adoption of a pollution prevention and waste minimisation philosophy, would offer longer term benefits to a company, and ultimately to the country, than the production of a phase diagram which might only hold for a specific feed solution and which could not readily be modified for changing plant circumstances.

The achievement of the project aims therefore centred around finding a method to enable operators to predict the behaviour of their chemical systems in a concentrating or precipitating environment. The method had to be sufficiently flexible, so as to accommodate changing factory conditions, or plant upsets, or changes in process methods. Computer modeling of chemical systems offered the flexibility required.

3.1 Identification of Problems and Methodology to Achieve Objectives

Discussions with factory personnel indicated that while there was a general awareness that different chemical species of a given ion could exist in solution, few process chemists had considered examining the chemical speciation of their systems in order to determine which species could be controlling the system chemistry. There was also an ignorance of how to determine which species were present in an aqueous system. The term used to describe the nature of individual components in solution is *chemical speciation*.

It was determined that the most feasible way of introducing the concept of chemical speciation and to demonstrate the benefits of having a full chemical speciation of a water, would be through the use of chemical equilibrium speciation computer programs. Chemical speciation studies would enable :

(i) the precipitation potential of feed streams to be determined.

(ii) the characterisation of a water by chemical species rather than by total concentration of ions. This would give greater insight and understanding of the chemistry of a system and would allow better understanding of precipitation and how it might be prevented.

(iii) modeling of various treatment scenarios and their impact on the distribution of species.

(iv) the influence of changing concentration and hence ionic strength, changing temperature, or the addition of another chemical to be predicted.

(v) a deeper understanding of the chemical behaviour of systems.

(vi) operators of desalination equipment to model their own site specific cases and arrive at their own conclusions.

4 SUMMARY OF RESULTS

The release, by the U.S. EPA, in August 1990, of the MINTEQA2. Version 3.0 chemical speciation program, reduced the level of expertise required for chemical speciation modeling. The power of the technique, and the extensive thermodynamic database, including solid phases, lead to its extensive application in this project to augment the more practical approach initially adopted.

The report includes precipitation problems which have been encountered during the course of this project. They are presented as a series of examples of how a knowledge of chemical speciation helped in understanding the problem. They illustrate the practical use of computer speciation programs. In chosing this format for the report, it is hoped that equipment operators and managers, or research personnel will be stimulated to try chemical speciation computer modeling as an aid to problem solving. The cases presented range from problems where a literature search was sufficient to provide information to enable a solution to a problem to be outlined, to more complex problems where a complete understanding of the problem required the modeling of organic complexation combined with adsorption phenomena. The order of presentation reflects the growth curve of modeling skills which a newcomer to chemical speciation modeling would encounter.

4.1 Application of Chemical Speciation

The general nature of the examples presented in this report include :

the importance of an adequate knowledge of the chemical system involved.

Some of the problems encountered could be solved by reference to the scientific literature. This reflects an overall management or information transfer deficiency rather than a technical problem.

an examination of the role of ion pair formation on the precipitation of a solid phase.

Chemical speciation showed that incomplete sulphate removal from solutions and effluents containing magnesium, calcium and sulphate, when treated with barium carbonate, was due to the presence of magnesium sulphate ion pairs. Addition of lime together with barium carbonate, removed magnesium as magnesium hydroxide, and allowed complete removal of sulphate ions from solution.

the optimisation of chemical dosing and process control.

Chemical speciation of a sulphate-rich zinc plant effluent indicated that when removing zinc from solution by the classical metal hydroxide precipitation method, careful pH control was required to prevent the resolubilisation of zinc hydroxide. A technique for determining optimum dosing of lime to effluents being treated to remove sulphate ions with barium carbonate, was demonstrated.

the determination of the degree of saturation in a concentrating system.

Chemical speciation was used to calculate the molar activities of the chemical components of a particular solid phase. Molar activities take account of the influence of all other ions, ionic complexes and ion pairs on the chemical reactivity of the system. Differences of up to 40 % between the total dissolved concentrations and the molar ion activities were found for some ions. These discrepancies would lead to significant errors in the prediction of the degree of saturation.

the effect of temperature on the solubility and nature of the solid phase.

Changes in solubility, or phase changes brought about by changing temperature can be investigated and may offer a solution to the prevention of an unwanted precipitate.

the effect of oxidation state.

The accurate measurement of the oxidation potential of a water is difficult, and in many cases this chemical parameter is not measured in routine laboratory analyses. Where data is lacking or unreliable, limiting case scenarios can be modelled. The effect of different oxidation potentials on the distribution of species can be evaluated and possible treatment schemes indicated.

the effect of dissolved organic material on metal complexation.

Chemical speciation modeling of cooling circuit water, taking into account the effect of the presence of dissolved organic matter, indicated that organic matter can significantly alter the distribution of chemical species, to the extent that organic complexation can out compete adsorption and precipitation processes. Speciation modeling with hypothetical or composite organic ligands is preferable to ignoring the possible impact of organic matter on a system.

the effect of adsorption on the distribution of chemical species.

Chemical speciation modeling of Inanda Dam water, taking into account the possibility of adsorption on to particulate surfaces, indicated that adsorption can significantly affect the distribution of species. Where site specific soil data is lacking, the assumption that the dominant adsorbing surface will be amorphous iron oxide, is preferable to ignoring the impact of adsorption on the species distribution. In cases where adsorption is shown to be an important mechanism in a system, modeling scenarios can be undertaken to investigate the conditions under which desorption could occur.

the difficulty in modeling environmental problems.

Chemical speciation is a necessary tool if any appreciation of the dynamic and complex interactions occurring in a natural system is to be achieved. Because of the breadth of information required, and the spread of expertise necessary to make meaningful assessments, a multi-disciplinary team approach should be adopted. Chemical speciation can provide a basis on which decisions such as clean-up activity, toxicological impacts and risk assessments can be made.

The varied nature of the examples presented, indicates the potential of chemical speciation as an aid to problem solving. Without the computer programs, few of the examples cited could have been studied to the same extent.

4.2 Practical control of the precipitation process

Although the use of chemical speciation programs has provides a means to deal with precipitation problems with greater insight, there remains a need for practical methods to monitor the degree of saturation of concentrating solutions, with respect to the common scaling minerals. A number of small-scale tests have been developed which help determine the fouling potential of streams undergoing concentration. A patent describing a precipitation controller has been lodged in the name of the Water Research Commission. This apparatus will allow on-line monitoring of the degree of saturation of a stream with respect to a chosen set of solids. Laboratory experiments to test the validity and potential of the precipitation controller are continuing.

5 REALISATION OF PROJECT OBJECTIVES

The project objectives have been met by adoption of a different methodology than that initially visualised. It was realised that the production of phase diagrams or diagrams indicating envelopes of precipitation was not realistic and furthermore, was a static method of presenting precipitation information. The use of chemical speciation computer modeling however, offered a dynamic method of investigation in which diagrams relevant to each site specific case could be generated. The use of such programs have allowed the chemistry of waters and wastewaters to be studied from a perspective not usually available outside large analytical laboratories. In addition, the acquisition of chemical speciation data, enables the fundamental reasons for precipitation problems to be determined, and chemical modeling allows possible remedial measures to be investigated. Examples of site specific cases and the type of information obtained by chemical modeling are given in the main report. From this aspect, the project objectives have been exceeded in that a tool has been identified which will allow a large variety of industries to gain greater understanding of the chemistry of their aqueous streams and to find their own solutions to their own particular problems. Reaction from industry to the use of computer models, in particular MINTEQA2, has been encouraging.

The secondary aims of the project, ie, the acquisition of solubility data for the barium carbonate sulphate removal process and the generation of data which could assist in the verification of computer models of aquatic equilibria (such as STASOFT), have been addressed in some of the examples cited in the report.

6 CONCLUSIONS

Conclusions reached from the work undertaken during the course of this project are:-

(i) Chemical speciation computer programs are suitable for application to precipitation problems.

(ii) MINTEQA2 is a versatile and easy to use tool which can be used to examine aspects of aquatic chemistry, such as ionic and organic complexation, solubilities of solids in ionic solutions, and adsorption phenomena. These phenomena have a direct bearing on the precipitation process.

(iii) The use of chemical equilibrium speciation programs offers access to speciation data, to engineering and water scientists who traditionally would not have used this technique.

(iv) Personnel from individual plants and factories are the people best suited to model site specific problems. An outsider might be capable of technically executing the chemical modeling but factory personnel are familiar with their chemical systems and can appreciate the interactions between different areas of the plant and are in a better position to critically evaluate the computer predictions.

(v) Interest in the application of chemical equilibrium modeling to operational problems is considerable. Requests for a copy of the MINTEQA2 program have been received from both academic and commercial institutions.

(vi) Publications resulting from work undertaken during the course of this project have included, 2 published papers and 4 presentations at local conferences.

(vii) A measure of the success of this project will be the extent to which chemical speciation modeling is assimilated into the daily routine of both research and operational personnel.

7 RECOMMENDATIONS

Recommendations arising from this project are that :

(i) chemical speciation as a technique to analyse aqueous systems should be encouraged. It is a technique which is applicable to all fields of water related activities.

(ii) the use of chemical speciation computer programs, particularly MINTEQA2 should be promoted. This could be achieved by holding introductory workshops and seminars for interested parties. In this way a base of users could be established.

(iii) advanced workshops for MINTEQA2 users should be held regularly to ensure that new skills, approaches and information about new areas of applicability are disseminated throughout the user body.

(iv) the formation of a MINTEQA2 User's Group should be considered.

(v) close contact with the U.S. EPA should be maintained.

(vi) new areas of application for MINTEQA2 should be investigated. This could involve working with physical chemists to tailor the data base for site specific cases or for South African conditions. Possible areas for application are, power station or petrochemical water circuits, sewage treatment processes, eutrophic impoundments and leachates. The extension of the use of MINTEQA2 into the field of high salinity waters could also be investigated.

(vii) clean technologies, waste minimisation and pollution prevention techniques should be the first consideration in solving precipitation problems.

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GLOSSARY OF TERMS

Adsorption	The accumulation of matter at the interface between two phases (usually a liquid and a solid) such that a three dimensional molecular arrangement does not develop. (Sposito, 1986)
Chemical speciation	The determination of the species present in an chemical system and their relative concentrations.
Components	The smallest number of individual chemical constituents which can be used to describe all possible variations in the composition of every phase For example in the system $CaCO_3$ -H_2O, the components are: Ca^{2+}, CO_3^{2-} and H^+. All reactions occurring in this system can be described by these components. MINTEQA2 has a predefined set of components.
DOM	Dissolved Organic Matter. Name of composite ligand in MINTEQA2 database (identification number 145) which represents dissolved organic matter from the Suwannee River, Fargo, Georgia, USA.
EDR	Electrodialysis Reversal
Eh	The redox potential of an aqueous system. Eh values may be positive or negative depending on the ratio of oxidised/reduced species in the redox pair being considered. Increasing Eh values indicate increasingly oxidising conditions and decreasing Eh values indicate increasingly reducing conditions. The quantities Eh and pε are related by the equation $p\epsilon = 16.90\ Eh$
IAP	The Ion Activity Product of a species A_mB_n formed in the reaction $mA^{-n} + nB^{-m} \leftrightarrow A_mB_n$ is $\{A^{-n}\}^m\ \{B^{-m}\}^n$
pε	The negative log of the electron activity
pC	The negative log of the molar concentration of C

Phase	A physically homogeneous portion of a system with a definite boundary,
pH	The negative log of the hydrogen ion activity
SI	Saturation Index. A measure of the degree of saturation of a solution with respect to a given mineral. In MINTEQA2, the saturation index gives the relationship between the ion activity product (IAP) of the components of a precipitate and the corresponding formation constant (K), after the solution has been equilibrated. The logarithmic ratio of these terms is the Saturation Index (SI). It is used to establish the stability order for precipitation (or dissolution) of solids. If $\log\left(\frac{IAP}{K}\right) < 0$ undersaturation $\log\left(\frac{IAP}{K}\right) = 0$ at equilibrium $\log\left(\frac{IAP}{K}\right) > 0$ oversaturation
Solubility product K_{sp}	For a solid dissolving in water according to the reaction $A_mB_n(s) \Leftrightarrow mA^{+n}(aq) + nB^{-m}(aq)$ the solubility product is defined as $K_{sp} = \{A^{+n}(aq)\}^m \{B^{-m}(aq)\}^n$ where { } denotes the activity of the ions.
Species	Species are chemical entities formed from the components of a system. For a system containing the components Ca^{2+}, CO_3^{2-} and H^+, the following species are possible : $CaOH^+$ (cationic complex), OH^- (anionic complex), HCO_3^- (anionic complex), $CaCO_{3aq}$ and H_2CO_{3aq} (uncharged ion pairs) and $CaCO_{3s}$ (solid phase). The relative concentrations of species will change with pH of the system.
TRO	Tubular Reverse Osmosis

CHAPTER 1
INTRODUCTION

The limited amount of water available in the Republic of South Africa, together with environmental considerations, has resulted in many industries employing some sort of desalination measure in order to recover and reuse water and chemicals and to reduce the volume of effluent requiring disposal. The desalination equipment, generally crystallising evaporators, reverse osmosis or electrodialysis plants, is used either as an end-of-line effluent treatment process, or as part of a closed loop recovery process within the production line. Regardless of the desalination technology used, fouling and scaling of heat or mass transfer surfaces is a common problem which often results in equipment being used below design specifications, in order to avoid the precipitation of unwanted solid phases. Apart from inefficient operation of equipment, scaling problems can lead to increased water and chemical use as operators try to suppress precipitation through dilution or the use of scale inhibitors. Thus the equipment, designed to remove dissolved salts, can be the point of entry of additional chemicals to the aquatic environment. Stoppages due to precipitation problems can result in low morale among the work force and can earn equipment an undeserved bad reputation.

Problems are also encountered in industries (including water and wastewater treatment) which use precipitation as part of their process operations. Under-recovery of a solid phase, or high residual concentrations of product in the supernatant liquid phase is a common problem. Apart from economic implications, mal-operation of a precipitation circuit, can threaten the aquatic environment as the effluents produced may contain chemicals or metals which could cause contamination of the surface and groundwater supplies.

The reasons for unwanted precipitation in desalination equipment, and inefficient operation of precipitation processes, are varied and because of this, equipment vendors and operators have few guide-lines to help them demarcate areas of safe operation. Assistance to industry to deal with precipitation problems was the basis of this research project.

The aims of this project were :

(i) to develop techniques for the determination of a phase diagram of complex precipitates which occur in desalination plants,

(ii) to acquire graphical or tabular data indicating envelopes of precipitation,

(iii to acquire solubility design data for the barium carbonate sulphate removal process,

(iv) to generate data which could assist in the verification of computer models of aquatic equilibria (such as STASOFT).

These aims were to be realised through practical means. Ideally a graphical or tabular representation of precipitation envelopes, or safe zones of operation, would be produced which would be of practical use to operators of equipment where precipitation problems were encountered.

Identification of the commonly occurring precipitate phases and production of graphical representations of the chemistry involved, could eventually lead to the production of an atlas-type document, which could be consulted to identify the likely precipitates for a given system and the safe operating regimes.

This approach was thought to be a more useful way of helping with precipitation problems, rather than a mathematical approach where the calculations involved in determining the distribution of species in, and precipitating from, a solution are complex and not readily understood.

In the early stages of this project it seemed doubtful if even this practical approach was going to be the best way to solve the problems encountered and to reach the stated objectives. It became apparent that the feed solution entering desalination equipment is often the result of a number of other processes and can not be considered in isolation. Frequently the desalination equipment is an integral part of the process operation and is a key component of a recycle loop. The adoption of a waste minimisation philosophy and regular site audits of water and chemical usage seemed to offer longer term benefits to a company, and ultimately to the country, than the production of a phase diagram which might only hold for a specific feed solution and which could not readily be modified for changing plant circumstances. Furthermore any solutions were likely to be site specific and not of general benefit to the country as a whole.

The achievement of the project aims therefore centred around finding a method to enable operators to predict the behaviour of their chemical systems in a concentrating or precipitating environment. The method had to be sufficiently flexible, so as to accommodate changing factory conditions, or plant upsets and be capable of accommodating a wide variety of chemical compositions. Computer modeling of chemical systems offered the required flexibility.

CHAPTER 2

PRECIPITATION PROBLEMS

Problems involving precipitation are common in a wide variety of industries in South Africa. This is partly due to the need to conserve the available water supplies of the country. As a result, the ratio of product to water consumption is high in comparison to other industrial countries. The pulp and paper industry and the electrical generating industry are examples of industries whose water consumption is low by international standards. Relatively low water consumption is achieved by operation at high water recoveries and high cycles of concentration. A penalty for efficient use of water, is that operations are conducted at the edge of precipitation regimes, where relatively minor changes in the bulk composition of the water streams, can lead to precipitation problems.

Visits to several factory sites to ascertain and understand the reasons for their precipitation problems gave greater insight into the magnitude and range of the problem (Kerr, 1991, 1992). Discussions were held with factory personnel, both equipment operators and effluent managers. From these visits and discussions several points emerged:

(i) **desalination philosophy**

The reason for the installation of desalination equipment at a factory varied. Either the equipment formed part of a closed-loop within the production process or it was installed as an end-of-line effluent treatment process.

(ii) **need for flexible solutions**

The different niches occupied by desalination equipment dictated that flexibility would be required in any method presented as a solution to precipitation problems. Also any possible solution would have to be demonstrated without disruption of existing operational procedure. While factory management might be prepared to experiment with "new ways" of running an effluent treatment plant, few would contemplate experimenting with an established production process.

(iii) **existence of a knowledge gap**

Factory personnel, understandably, become so involved with their particular problems on their site, that an appreciation that others might have experienced similar problems, or have found methods to solve the problem, is lost. Factory secrecy agreements can contribute to this isolation. Few personnel, particularly those in small industries, have the time nor the resources to peruse the scientific literature and to read references relevant to their particular chemical system. As a result a knowledge gap quickly develops, regardless of technical ability and often the only access to current developments is through equipment vendors.

(iv) **need for pollution prevention and waste minimisation measures**

The precipitation problems reported by a factory, were often of their own making. This was particularly true where desalination equipment, generally evaporators, were seen as an effluent treatment process. The *precipitation problem* in many instances, could be solved by adopting pollution prevention measures such as segregation of effluent streams, good housekeeping and non-generation of effluent through minor process changes. An example is detailed in **Appendix 1**.

(v) **need for a generic approach**

If the aims of the project were to be met in a way that would be beneficial to all industry rather than solving site specific problems, then a generic approach would have to be adopted. Computer modeling of chemical systems would provide this generic approach. If it could be demonstrated that a knowledge of the chemical speciation of a given system would lead to greater understanding of why precipitates formed, then operators and managers would be able to make more informed decisions as to changes in operations, or chemical treatments which would overcome the precipitation problem.

2.1 The Need for Chemical Speciation

Discussions with factory personnel indicated that process chemists were aware, in a general way, that the behaviour of their chemical systems was dependent on the presence in solution of ionic complexes and ion pairs. Most knew that the presence of these complexes could affect solubilities of phases and that this might explain unplanned precipitation of one phase or lack of formation of another phase. While there was a general awareness that different chemical species of a given cation could exist in solution, few process chemists had considered examining the chemical speciation of their systems in order to determine which species could be controlling the system chemistry. There was also a general lack of awareness of how to determine the species present in an aqueous system. The term used to describe the nature of individual components in solution is *chemical speciation*.

The importance of chemical speciation in fields as diverse as toxicology, geochemical cycling of metals, and water treatment has been highlighted in the literature in recent years. In many of the cases studied, one or two chemical *species* exert a controlling influence on the system at given conditions. If system conditions change, then another set of chemical *species* may assume control.

In order to study the precipitation phenomenon, account of chemical species present in solution and their relative concentrations would have to be investigated.

There are three main techniques to determine the chemical speciation of an aqueous system :-

(i) analytical chemistry

(ii) numerical or graphical methods

(iii) computer modeling using rigorous numeric techniques

The use of analytical chemistry to determine aqueous species present and their relative concentrations, was not considered a feasible option, since access to sophisticated laboratory equipment, and personnel with the expertise to conduct the experimental work would be required.

It was considered that the determination of chemical speciation by classical numerical equilibrium chemistry calculations would meet with resistance. The calculations are cumbersome. They also require a fairly detailed knowledge of the chemistry of the system and the ability to write appropriate chemical equilibrium reactions. Even if an exact mathematical solution is not required, useful information can be obtained by constructing graphical representations of a chemical system. An example is the construction of a diagram showing the variation in chemical species with changing pH conditions, e.g. the species distribution of the carbonate system is a familiar diagram of this type. However, this method also presupposes the ability to choose and write appropriate equilibrium equations and have access to the required equilibrium constants. While factory managers or research personnel might be comfortable with these numerical methods of determining chemical speciation, they are not attractive to equipment operators who see little relationship between numerical calculations and the problems they experience on site.

The determination of chemical species present in a system, and their concentrations, has become easier and more accessible to a wider audience, through the development of chemical equilibrium computer programs. Some of these are designed for specific chemical systems and have thermodynamic databases which contain only those equilibrium constants pertinent to the system for which designed. Others contain larger databases which can be used for general speciation problems. By using these computer programs, it is not necessary to explicitly specify the specific equilibrium reactions.

By studying the chemical speciation of waters and effluents streams that give rise to precipitation problems, the reason for precipitation can be better understood. The use of computer programs has the additional advantage that changes to the system can be simulated and the resultant effects studied. A knowledge of chemical speciation could lead to better understanding of the system chemistry, which in turn would lead to more informed judgements being made concerning the possible degree of saturation of solutions undergoing desalination, and better operation of the desalination equipment.

Several different programs were available. Two programs, STASOFT and BACO3 were designed for specific chemical systems, while two others, MINEQL and MINTEQA2 were of more general application.

CHAPTER 3
CHEMICAL EQUILIBRIUM COMPUTER SPECIATION PROGRAMS

Four different computer programs have been used. The choice of program was determined by the complexity of the problem and the amount of information available. A brief description of each program is given. No attempt has been made to evaluate or compare the merits or disadvantages of each program code. The programs are described from the point of view of a user wishing to determine the chemical speciation of a given system, or trying to use the computer models as a problem solving tool.

For general comparisons of chemical equilibrium computer programs, a review paper by Nordstrom, et al. (1979) is useful.

3.1 MINEQL

In the early and late 1970's a number of chemical speciation programs were developed. Two programs dominated; REDEQL (Morel and Morgan, 1972) and GEOCHEM (Mattigod and Sposito, 1978). Most speciation programs have their roots in one or other of these programs. MINEQL (Westall, et al., 1976) developed from REDEQL and has a more general computational method than the earlier programs but, because the computer code is written in FORTRAN it has a rigid input format. For someone not familiar with FORTRAN, the program is difficult to use with any degree of confidence. Because it is an early program, written at a time when "user-friendly" was not a consideration in the minds of computer code writers, it is difficult to extract information from the output files. While suitable as a research tool for persons with high level computer skills and chemical knowledge, it is not a program which can be readily accepted by potential converts to computer speciation modeling.

3.2 STASOFT

The computer model STASOFT, (Loewenthal et al., 1988) can be used to resolve a wide variety of conditioning and dosing problems arising in the treatment of terrestrial waters for municipal use. However, STASOFT is restricted to low salinity waters with total dissolved solids (TDS) less than 1 000mg/ℓ. More recently Friend (1990) has extended the model of Loewenthal to incorporate ion pairing effects between principal cation species (Ca^{2+}, Mg^{2+} and Na^+) and anion species (SO_4^{2-}, CO_3^{2-} and HCO_3^+), so that the model can be applied to waters with TDS values up to about 15 000 mg/ℓ (STASOFT. Version 3). STASOFT however was designed for, and is applicable only to, aqueous solutions where the carbonate system dominates weak acid interactions. The only solid precipitants considered are calcite ($CaCO_3$) and brucite ($Mg(OH)_2$). Thus its database does not encompass the wide variety of chemical species encountered in complex industrial effluents and so it can not be used to solve general speciation applications. The program is user friendly and has been favourably received by the water industry.

3.3 BACO3

BACO3 is a equilibrium chemistry program developed by Prof. R.E. Loewenthal of the University of Cape Town to describe the treatment of sulphate-rich water with barium carbonate (Water Research Commission project No. 203, *The Chemical Removal of Sulphates Using Barium Salts*).

In this project a treatment scheme was outlined to treat sulphate-rich waters with barium carbonate. At the time (1988/90) this scheme attracted much attention and a consultant engineering firm were appointed to evaluate the economic feasibility of the scheme. Trusler, (1988) outlined the theoretical and experimental basis of the treatment scheme. If the scheme proved economically attractive, then solubility data would be required. Because the chemistry of the systems involved were well known, and the required thermodynamic data available in the literature, chemical modeling was used to acquire the solubility data, and the program BACO3 was written specifically for this purpose. The acquisition of solubility data formed the third aim of this project.

BACO3 was used to model the chemical interactions occurring when a variety of sulphate rich waters were treated with barium carbonate. Effects such as variation in original water chemistry and chemical dosing were modelled and the equilibrium chemical composition of the treated water was predicted (**Appendix 2**).

BACO3 is a user-friendly program and well suited to its design task but, because of the limited thermodynamic database, it is not suitable for general chemical speciation problems.

3.4 MINTEQA2

A copy of a geochemical equilibrium speciation model, MINTEQA2, Version 3.0. (Allison et al., 1990) was obtained from the United States Environmental Protection Agency (EPA), Centre for Exposure Assessment Modeling (CEAM).

This program is an amalgamation and update of three earlier programs, WATEQ3 (Ball et al., 1981), MINEQL (op cit), and MINTEQ (Felmy et al. 1984).

In the development of MINTEQA2, the basic mathematical structure of MINEQL was retained and combined with the thermodynamic data base of WATEQ3. This database consisted of thermodynamic data for naturally occurring minerals. Another feature adopted from WATEQ3 was the algorithms for correcting changes in water temperature and ionic strength. These combinations together with algorithms for calculating adsorption, resulted in the program MINTEQ (Felmy et al. 1984) which was a prototype of MINTEQA2.

The major refinements made to MINTEQ since 1984, largely consist of the development of an interactive preprocessor, PRODEFA2, which is used to create input files and to specify system parameters. The thermodynamic database and the number of modeling options has also been expanded.

As with all chemical equilibrium models, two types of data are required; thermodynamic data and water quality data. The incorporation of PRODEFA2 into the program makes presenting water quality data to the computational part of the program an easy task. Other relevant measurements for the system, such as pH, Eh or partial pressure of gases, can also be specified in PRODEFA2.
The thermodynamic data are contained in the accompanying database and for most problems no additional input by the user is required.

The success with which computer programs model real systems depends largely on the translation, by the user, of physical conditions into chemical constraints on the system to be modelled. PRODEFA2 enables the user to progressively become more skilful in creating input files and to choose the model options applicable to the problem.

Of the programs used, MINTEQA2 has the greatest potential to be accepted as a tool for analysis of a chemical system. PRODEFA2 removes the aspects of input file creation, such as rigid input formats, activity guesses and ionic strength estimations required by some other programs. These aspects are intimidating for users familiar with working with total concentrations of cations or anions. Wrong initial guesses can lead to non-convergence of the problem which is discouraging and can lead to premature abandonment of chemical modeling. The non-intimidating nature of PRODEFA2 creates a *comfortableness factor* which enables the user to become skilful at input file creation and allows more effort to be devoted to thinking about the problem and to the interpretation of results.

CHAPTER 4

APPLICATION OF CHEMICAL SPECIATION TO SELECTED PROBLEMS

Some examples are given of problems were a knowledge of chemical speciation aided understanding of the chemical system involved and in some cases led to problem solutions. They are typical of the questions and problems encountered during the course of this project. Some were laboratory problems while others were problems encountered at specific factory sites. They are presented in increasing degree of complexity, in terms of using the various computer programs, or in effort required to solve the problem. This arrangement reflects the progression, during the period of the project, of a growing appreciation of the usefulness of chemical speciation modeling, of accumulating skills in presenting problems to a computer model, and of increasing ability to interpret computer predictions in terms of the problem. The cases presented represent some of the potential areas where a knowledge of chemical speciation could be applied. Chemists or aquatic scientists, involved with chemical speciation, will find little conceptually remarkable or new in this report. However, for those who are unfamiliar with chemical equilibrium calculation, or who find their execution difficult, the use of computer chemical speciation programs provides a working tool to bridge the transition from text book chemistry to the practical implications of chemical speciation. It offers an opportunity to demonstrate the advantages of having a complete chemical speciation of a water, to those who daily deal with scaling and precipitation problems. Hopefully it will stimulate an interest in understanding the chemistry of their systems more thoroughly and that they will be motivated to adopt chemical speciation modeling as a tool to help them solve their specific problems.

The general nature of the example presented are :

(i) the importance of an adequate knowledge of the chemical system involved

(ii) an examination of the role of ion pair formation on the precipitation of a solid phase

(iii) the optimisation of chemical dosing and process control

(iv) the determination of the degree of saturation in a concentrating system

(v) the effect of temperature on the solubility and nature of the solid phase

(vi) the effect of oxidation state on the distribution of chemical species

(vii) the effect of dissolved organic material on metal complexation

(viii) the effect of adsorption on the distribution of chemical species

(ix) the difficulty in modeling environmental problems

4.1 The Importance of an Adequate Knowledge of a Chemical System

In several cases, precipitation problems arose due to lack of adequate knowledge of the chemistry of the particular system. The reasons for this were varied but generally involved changes in personnel at a factory combined with a lack of accurate or meaningful comments in equipment manuals. In these cases, a retrospective literature search can recapture the appropriate physico-chemical data required to solve the precipitation problem.

4.1.1 Example 1 : How to prevent formation of the double salt, $(NH_4)_2SO_4.Na_2SO_4.4H_2O$, in the Na_2SO_4 - $(NH_4)_2SO_4$ - H_2O system.

An evaporator was a critical part of a salt recovery closed loop circuit at a vanadium pentoxide production plant (**Appendix 3**). The plant was situated in an arid and water sensitive area. Mal-operation of this evaporator would lead to contamination of the Steelpoort Valley. It was suspected that groundwater contamination had already occurred on a farm adjacent to the plant. The company subsequently purchased the farm and undertook clean-up activities on the groundwater.

The liquor fed to the evaporator was a mixture of sodium sulphate, ammonium sulphate, and vanadium in the form of ammonium metavanadate and sodium vanadate. The purpose of the evaporator was to crystallise sodium sulphate which, after centrifugation and drying, could be reused in the production process. The remaining ammonium sulphate rich liquor could also be reused. The unwanted precipitation of a double salt, $(NH_4)_2SO_4.Na_2SO_4.4H_2O$ (ammonium sodium sulphate), caused operational problems which resulted in loss of vanadium from the production circuit. To avoid the precipitation of this double salt, the evaporator was operated at low water recoveries resulting in the discharge of the mixed brine.

Plant personnel had been provide with a barely legible copy of the phase diagram for the Na_2SO_4 - $(NH_4)_2SO_4$ - H_2O system by the equipment vendors, but knowledge on how to use this diagram to determine safe operational regimes had been lost through changes in personnel.

A literature search revealed that the chemistry of the Na_2SO_4 - $(NH_4)_2SO_4$ - H_2O system was first studied systematically by Dawson in 1918, who compiled a phase diagram for the system. It was this phase diagram which the evaporator operators had acquired. The original data, given by Dawson, was redrawn using a Jänecke plot. In this type of plot the total amount of salt is normalised and the amounts of the two end member salts are expressed as percentages of the total. Temperature is plotted on the vertical axis (Figure 1). This plot shows clearly that, provided that the total amount of ammonium sulphate present does not exceed 23 % of the total salt present, then over a range of temperatures from -20 to 100 °C, the field of the double salt is not intersected.

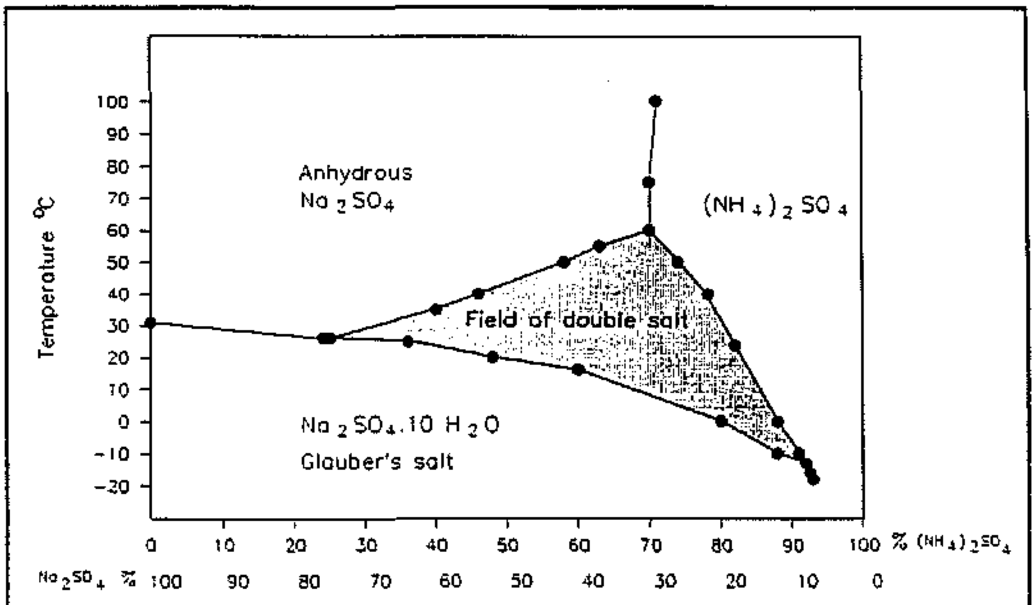

FIGURE 1 : *Jänecke Plot for the* Na_2SO_4 - $(NH_4)_2SO_4$ - H_2O *system*

This diagram was more readily understood by the evaporator operators. Control of the concentration of ammonium sulphate in the evaporator feed was achieved by careful control of an upstream operation.

Solution 1 : Redrawing the phase diagram of the system in a way that could be easily interpreted for evaporator control.

While the solution to this particular problem did not involve a knowledge of chemical speciation, it does illustrate the importance of knowing as much as possible about the chemistry of the system. Ideally, relevant literature should be available on site or a listing of the literature should be compiled by the head office and given to personnel on site. Chemical speciation of the evaporator feed would reveal the controlling species and additional refinements to operational control might be possible.

4.2 Ion Pairs as a Barrier to Precipitation

The non-appearance of a wanted precipitate or a greatly reduced mass of precipitate was a common problem. The precipitation of a solid phase in a system is dependent of the solubility product of the solid phase.

For a solid dissolving in water according to the reaction

$$A_mB_n(s) \rightleftharpoons mA^{+n}(aq) + nB^{-m}(aq)$$

the *solubility product*, K_{sp}, is defined as

$$K_{sp} = \{A^{+n}(aq)\}^m \{B^{-m}(aq)\}^n$$

where { } denotes the activity of the ions.

Published values of solubility products are fundamental thermodynamic quantities. It is difficult to apply these values to real solutions because it is necessary to know all the chemical species present and the activity of all the ionic species. In addition, because activities are not generally known, total concentrations of anions and cations are often used to gauge the degree of saturation or precipitation potential of the system.

Given these difficulties it is not surprising the K_{sp} values are not of direct use as an indicator of precipitation in water systems with high total dissolved solids (TDS) concentrations.

4.2.1 Example 2 : Incomplete sulphate removal from underground mine water when treated with barium carbonate.

The treatment of sulphate-rich waters using barium carbonate was investigated by Trusler, (1988) and is reported in WRC Report No 203/1/90, (1990). Computer modeling of the treatment process was undertaken using the computer program BACO3, and is reported in Appendix 2. Laboratory experiments with pure chemical solutions and various sulphate-rich effluents indicated that when magnesium was present in the water, there was incomplete removal of sulphate, and that the degree of sulphate removal was dependent on magnesium concentration (Figure 2a). Addition of barium carbonate to a simulated underground mine water also resulted in incomplete sulphate removal (Figure 2b).

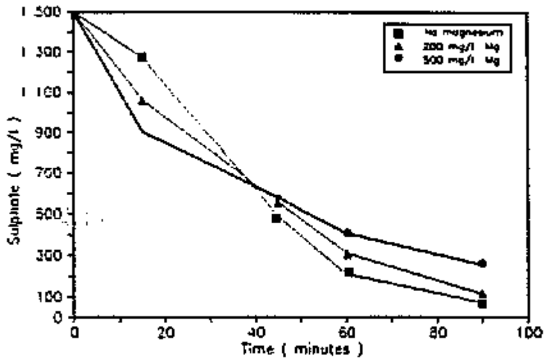

Fig. 2a

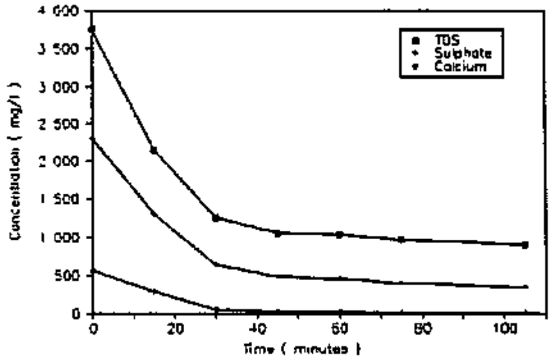

Fig. 2b

FIGURE 2a : *The incomplete removal of sulphate from calcium sulphate solutions containing varying concentrations of magnesium (added as magnesium chloride) when treated with barium carbonate.*

FIGURE 2b : *Incomplete sulphate removal from simulated underground mine water after treatment with barium carbonate. Both figures after Trusler (1988)*

The precipitation reactions involved for a water containing calcium, magnesium ions as well as sulphate ions are :

$$CaSO_4 + BaCO_3 \Leftrightarrow BaSO_4(s) + CaCO_3(s)$$

$$MgSO_4 + BaCO_3 \Leftrightarrow BaSO_4(s) + MgCO_3(s)$$

Magnesium carbonate is significantly more soluble that calcium carbonate. As a result it was expected that the K_{sp} of magnesium carbonate would not be exceeded and that no magnesium or carbonate ions would be removed from solution as magnesium carbonate. This would explain the limited magnesium removal from waters containing calcium, magnesium, and sulphate ions but not why the presence of magnesium should retard the removal of sulphate.

MINTEQA2 was used to examine the chemical speciation of the mine water. Figure 3 shows the distribution of magnesium and calcium species present in the mine water over a range of pH values. The most striking feature of this diagram is the high concentration of both calcium sulphate and magnesium sulphate ion pairs. At pH 7, of the total calcium concentration, 27 % is present as the neutral $CaSO_{4\,(aq)}$ ion pair and of the total magnesium concentration, 25 % is present as the $MgSO_{4\,(aq)}$ ion pair.

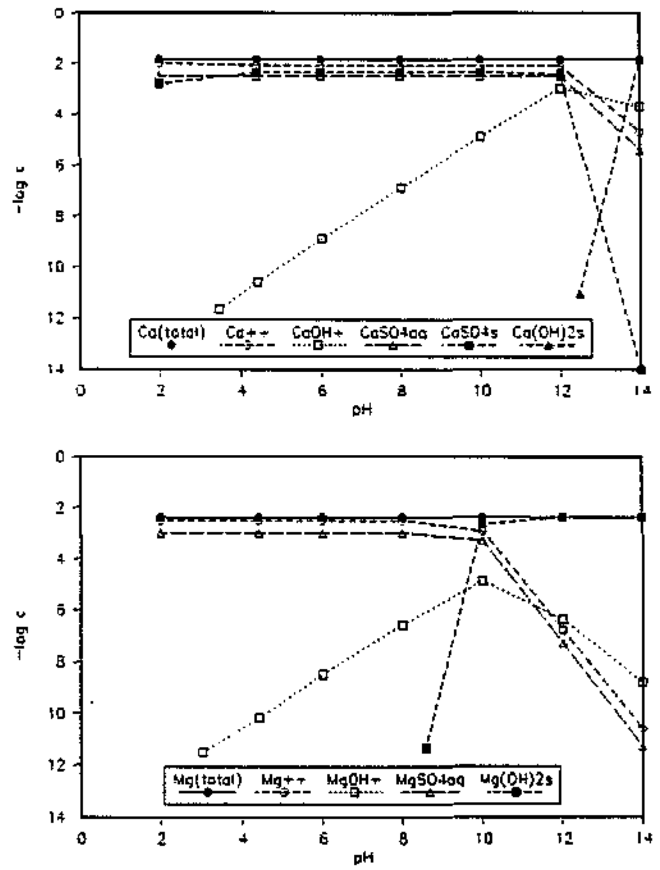

FIGURE 3 : *Variation in the distribution of calcium and magnesium species in underground mine water with pH. Total molar concentrations of these components are : calcium,* 1.45×10^{-2} *(580 mg/ℓ); magnesium,* 4.04×10^{-3} *(97 mg/ℓ)*

The mine water was modelled with the addition of increasing amounts of barium carbonate. At equimolar concentrations of barium and sulphate, it was predicted that 99 % of the calcium ions would be removed from the water as calcium carbonate and that 23 % of the magnesium ions would be removed as magnesium hydroxide. The equilibrium pH of the treated solution was predicted to be 9,7.

Figure 4 shows the changes in the molar concentration of $CaSO_{4\,(aq)}$ and $MgSO_{4\,(aq)}$ with increasing addition of barium carbonate. Although initially, the calcium sulphate ion pair dominates, with increasing addition of barium carbonate, the position is reversed and the magnesium sulphate ion pair dominates until a stoichiometric amount of barium carbonate has been added. It is the stability of the magnesium sulphate ion pair which is responsible for the incomplete removal of sulphate in the presence of magnesium ions.

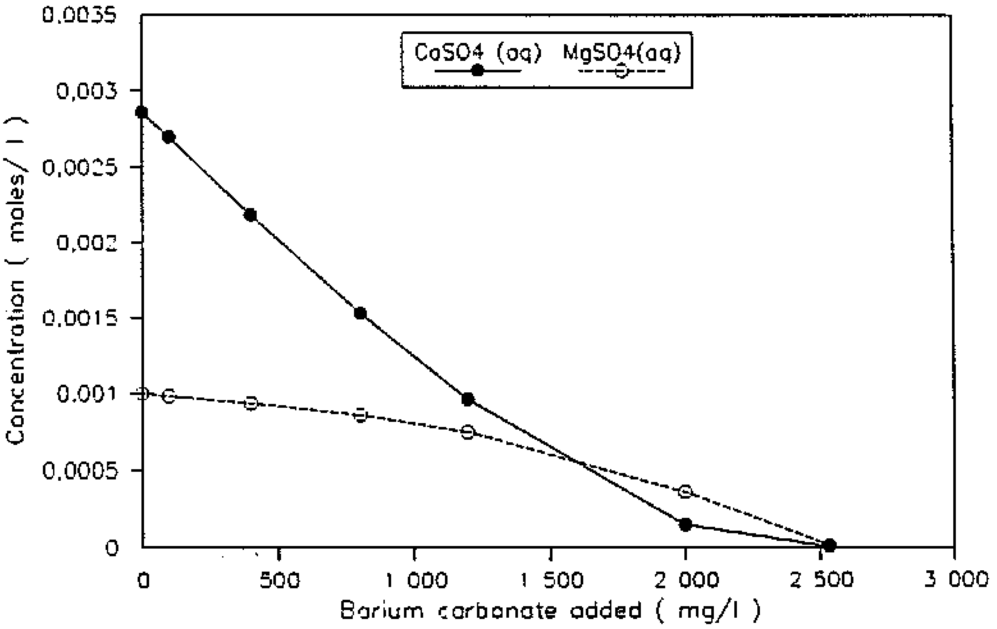

FIGURE 4 : *Molar concentrations of calcium sulphate and magnesium sulphate ion pairs present in underground mine water when treated with increasing amounts of barium carbonate.*

The removal of magnesium ions from the water, would liberate the sulphate associated with the magnesium sulphate ion pair, and allow complete sulphate removal. This could be readily accomplished by increasing the pH of the solution and allowing precipitation of magnesium hydroxide. The lime, in addition to increasing the pH, would ensure that the sulphate ions were associated with calcium ions and thus readily removed from solution. Figure 5 shows that complete sulphate removal from actual underground mine water could be accomplished after 45 minutes reaction time when the water was dosed with 0,8 g/ℓ of calcium hydroxide in addition to barium carbonate. (1 g/ℓ of calcium carbonate seed crystals were also present).

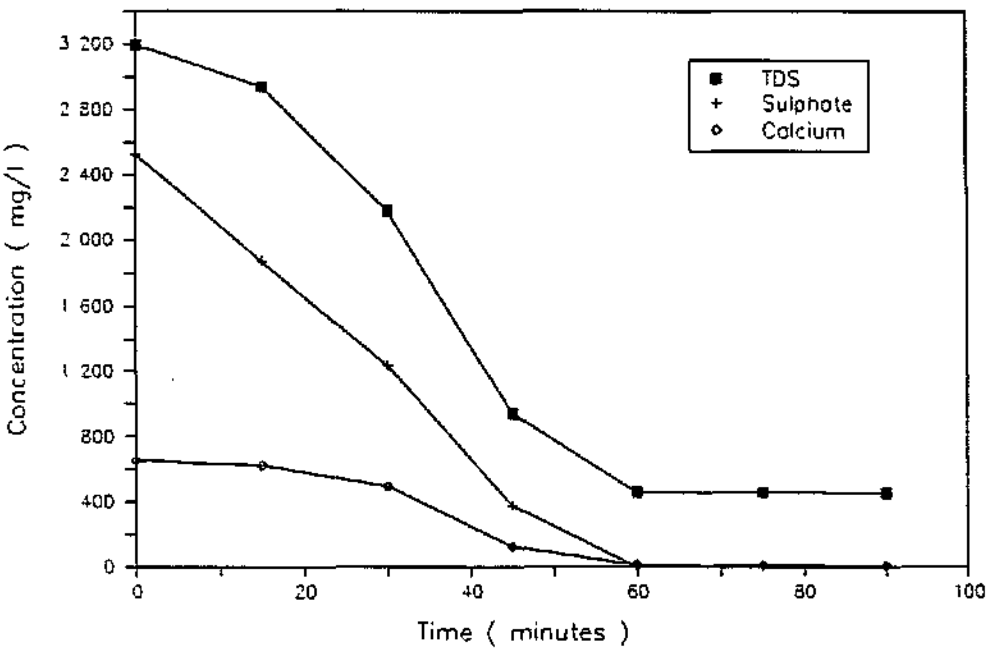

FIGURE 5 : *Complete sulphate removal from underground mine water, after addition of barium carbonate and lime. After Trusler (1988).*

Solution 2 : Removal of magnesium ions from the underground mine water, prevents the formation of magnesium sulphate ion pairs, and results in complete sulphate removal when treated with barium carbonate.

4.3 Optimisation of Chemical Dosing and Process Control

The effective operation of clarifiers and flocculators is dependent on factors such as equipment design and correct chemical dosing. Frequently, excess chemical dosing is practiced, to ensure complete removal of unwanted ions, such as hardness ions, or to ensure that product ions enter the desired phase. For example, in the recovery of heavy metals as the metal hydroxide, excess lime is often added to ensure that the maximum mass of heavy metal is present in the solid phase. Calculations to determine dosing requirements are usually conducted on the basis of total concentrations of cations and anions present in solution. Work by Stumm and O'Melia (1968), Ferguson and King (1977), Buffle et al. (1985) demonstrated that for many common dosing chemicals, such as aluminium and iron salts, the active species responsible for coagulation or precipitation is the highly charged metal hydroxo species. The formation of these species in aqueous solutions depends on parameters such as pH and the nature of the ions present.

Although flocculation is a non-equilibrium process and subject to kinetic control, a knowledge of the equilibria can indicate a limit towards which the system will proceed. The determination of the chemical species present in a water or waste water and their behaviour under changing pH conditions, as would be encountered in flocculation, can assist in optimising the chemical dosing requirements and determining the boundary limits for effective precipitation conditions. Two examples are given where a knowledge of chemical speciation was used to predict optimum dosing requirements and precipitation conditions.

4.3.1 Example 3 : Under precipitation of zinc from a zinc metal plant effluent, when dosed with lime.

The classical metal hydroxide precipitation process was used to precipitate zinc from a zinc plant effluent. Residual concentrations of zinc in the supernatent were higher than expected. MINTEQA2 was used to determine the variation in concentration of the zinc species present in the effluent with changes in pH. (Figure 6) (**Appendix 4**).

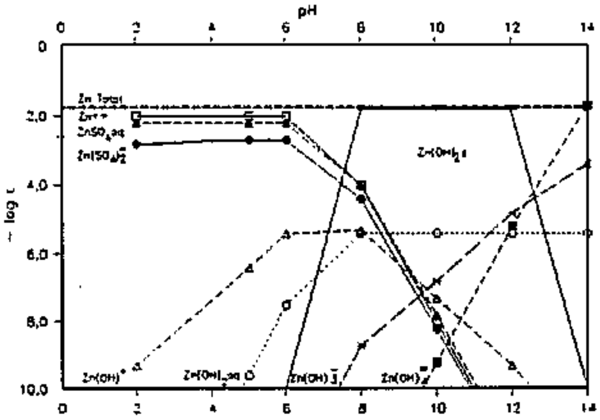

FIGURE 6 : *Variation in zinc species with pH. Total zinc concentration. 1 150 mg/ℓ*

Figure 6 shows that up to pH 8, the dominant zinc species present in the effluent are, in order of decreasing concentration, free zinc ions, Zn^{2+}, the zinc sulphate ion pair, $ZnSO_{4\,(aq)}$, and the negatively charged anionic complex, $Zn(SO_4)_2^{2-}$. From pH 8 to pH 12, the dominant zinc species is the solid phase, zinc hydroxide, $Zn(OH)_2$. At pH values greater than 12,5 the dominant zinc species are the soluble hydroxy species $Zn(OH)_4^{2-}$, $Zn(OH)^-_3$ and $Zn(OH)^+$.

This diagram illustrated the need for strict pH control on the metal hydroxide precipitation process. Indiscriminent dosing with lime could raise the pH of the solution to values greater than pH 12. This would lead to either,

(i) the resolubilisation of already precipitated zinc hydroxide, if lime was added at time intervals greater than the formation rate of zinc hydroxide, or

(ii) to the non appearance of, or reduced mass of zinc hydroxide, if an excess of lime was added at one time.

Solution 3 : Careful pH control of the precipitation process to ensure correct lime dosing and maximum precipitation of zinc hydroxide.

The computer program BACO3 was used to determine the optimum lime dosage required to ensure total sulphate removal in water treatment plants utilising barium carbonate to remove sulphate as outlined by Trusler (1988). Trusler showed that for waters containing magnesium, addition of lime together with barium carbonate, was necessary to ensure complete sulphate removal. The reasons for this have been outlined in Example 2.

4.3.2 Example 4 : Determination of the optimum lime dosage for a water softening plant

Although this example is based on a hypothetical water treatment scheme, the methodology to determine the optimum lime dosage, is applicable to other water softening technologies such as lime clarifiers or hot lime softeners where the chemistry of the treatment scheme is dominated by the carbonate system, and where the dominant solid phases involved are calcite ($CaCO_3$) and brucite ($Mg(OH)_2$).

The acquisition of solubility parameters for the sulphate removal process using barium carbonate, included the determination of the lime addition necessary to ensure complete removal of sulphate from waters containing magnesium as well as calcium and sulphate ions. Such a composition is typical of mine waters. Chemical dosing requirements would affect the sizing of plant equipment such as stirred reaction vessels and clarifiers.

Using the computer program BACO3, the treatment of a partially neutralised underground mine water with barium carbonate was simulated. A series of runs were undertaken where increasing amounts of lime were added to the water to which a stoichiometric amount of barium carbonate (stoichiometric to the concentration of sulphate in the water) had been added. The predicted total calcium and total dissolved salts (TDS) concentrations of the treated water were plotted against the amount of lime added. Figure 7 shows that while lime addition is beneficial to the process, the addition of more than approximately 250 mg/ℓ of lime (as CaO), would result in an increase in the overall TDS of the product water. Total dissolved salt concentration is not a direct output from the program, but can be determined by summing the predicted equilibrium ion concentrations in the treated water. Addition of excess lime would also lead to an increase in the alkalinity of the water.

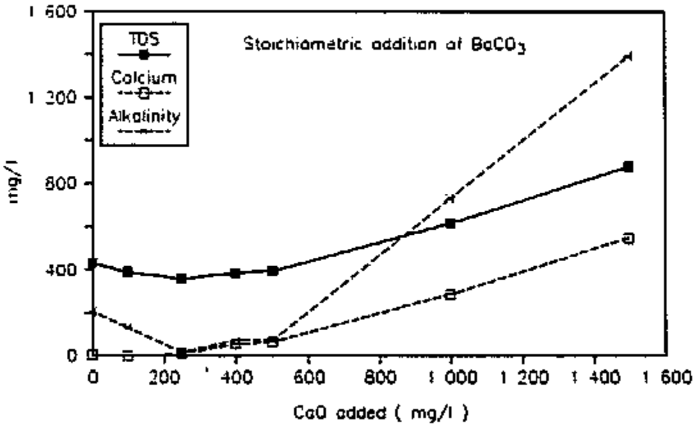

FIGURE 7 : *Effect on TDS, total alkalinity (as CaCO3) and total calcium ion concentration, of increasing addition of lime (as CaO) to partially neutralised underground mine water, together with stoichiometric addition of barium carbonate.*

Solution 4 : The solubility of a precipitate can be reduced by removing a stable ion pair.

4.4 Determination of the Degree of Saturation in a Concentrating System

Scaling and fouling of heat transfer surfaces, such as tubes within an evaporator, or mass transfer surfaces, such as membranes in an reverse osmosis or electrodialysis reversal plant, is a major problem which has financial and environmental implications.

Costs may be incurred in the purchase of cleaning chemicals, replacement membranes or new heat exchangers and unless there is back-up equipment may lead to loss of production. When the equipment is part of a closed loop salt recovery system, down time of the equipment means that makeshift disposal or treatment measures have to be implemented. An example would be the disposal of large volumes of brines to a unlined solar evaporation dam.

Even in equipment where close control is practiced, factory upsets resulting in changes to the composition of feed streams, can result in fouling and precipitation problems. Not surprisingly, the most frequently asked questions encountered during the course of this project have concerned the prediction of the onset of precipitation and methods to avoid precipitation.

Precipitation occurs when a solution becomes oversaturated with respect to a particular solid phase. As discussed in Section 4.2. published data of solubility products are of little immediate use in determining the solubility of solids in a mixed chemical system. The problem reduces to determining the degree of saturation of the solution, with respect to a given mineral. Identification of the scaling mineral is a prerequisite for successful process control in concentrating systems. Plant operators usually have determined the nature and composition of the scaling mineral or minerals in a given system. One of the most commonly occurring scaling mineral is gypsum, $CaSO_4.2H_2O$. The formation of calcite scale, $CaCO_3$, is less problematical as deposits can generally be removed by acid washing.

4.4.1 Example 5 : Determination of the degree of saturation of a solution, with respect to a given mineral.

MINTEQA2 was used to determine the degree of saturation, with respect to gypsum, of brines from the electrodialysis reversal (EDR) plant at the Tutuka Power Station (**Appendix** 5).

Figure 8 shows the position of an EDR feed and brine pair relative to the gypsum saturation curve for the system. The published K_{sp} value has been corrected, by MINTEQA2, for the temperature and the ionic strength of the solution. The diagram illustrates how a knowledge of the chemical speciation can give a more accurate picture of the saturation state of the streams. If no chemical speciation data were available for these streams, then the only available information would be the total dissolved concentrations of the calcium and sulphate ions. Plotting these values would lead to the conclusion that both the feed and the brine were oversaturated with respect to gypsum. This leads to the confusing statement often found in manufacturer's literature that it is possible to operate equipment at saturation levels over 100 % without the formation of precipitates. After speciation, a more accurate representation of the saturation state of the streams can be obtained by plotting the data points as free ion concentrations or preferably as free ion activities. The use of free ion activities is the most accurate representation, as the effect of all other species in solution on the calcium and sulphate concentrations have been taken into account. Examination of the feed and brine compositions, plotted as free ion activities, shows that the feed is undersaturated with respect to gypsum and that the brine is approaching saturation. The impact of the presence of ion pairs and ionic complexes on the total dissolved concentrations is considerable. Table 1 indicates that the effective concentrations of the calcium and sulphate ions can be 40 % less than the total dissolved concentrations of the ions.

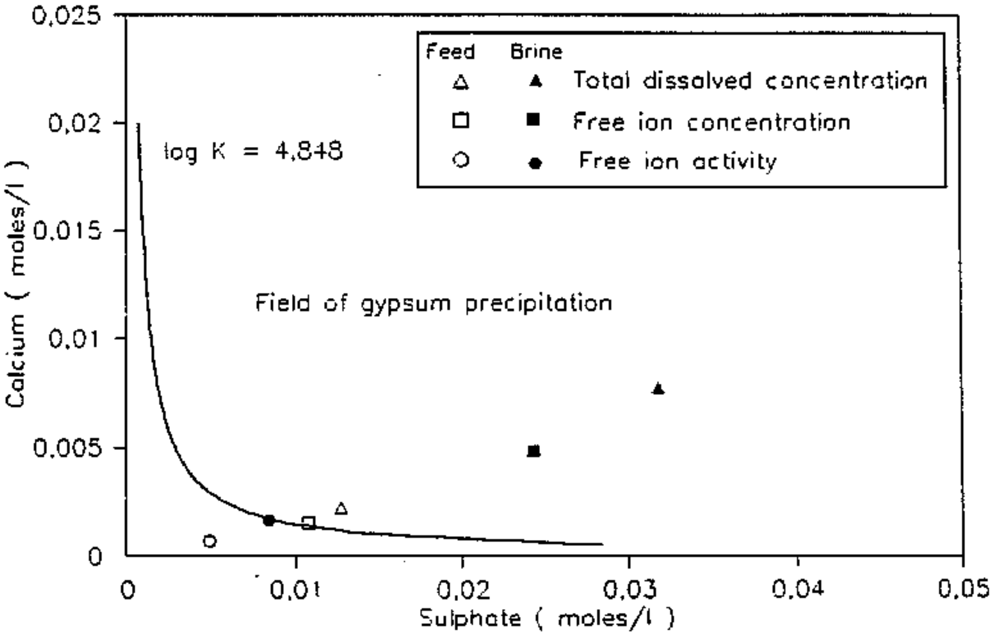

FIGURE 8 : *Position of the EDR feed and brine composition relative to the gypsum saturation curve, plotted as:- the total dissolved concentrations, the free ion concentrations and the free ion activities of calcium and sulphate.*

TABLE 1
Molar concentrations of calcium and sulphate ions in EDR feed and brine, based on:- (a) total dissolved concentrations, (b) free ion concentrations and (c) free ion activity.

	EDR Feed		EDR Brine	
	Ca^{2+}	SO_4^{2-}	Ca^{2+}	SO_4^{2-}
Total dissolved concentration (molar)	$2,2 \times 10^{-3}$	$1,27 \times 10^{-2}$	$7,7 \times 10^{-3}$	$3,18 \times 10^{-2}$
Free ion concentration (molar)	$1,5 \times 10^{-3}$	$1,08 \times 10^{-2}$	$4,8 \times 10^{-3}$	$2,4 \times 10^{-2}$
Free ion activity (molar)	$7,0 \times 10^{-4}$	$4,9 \times 10^{-3}$	$1,6 \times 10^{-3}$	$8,4 \times 10^{-3}$
Ratio of free ion concentration to total ion concentration	0,68	0,85	0,62	0,75
Ratio of free ion activity to total ion concentration	0,32	0,39	0,21	0,26

The saturation state, with respect to gypsum, of seven ERD brines is shown in Figure 9. Three brines are predicted to be supersaturated, plotting just inside the field of gypsum precipitation.

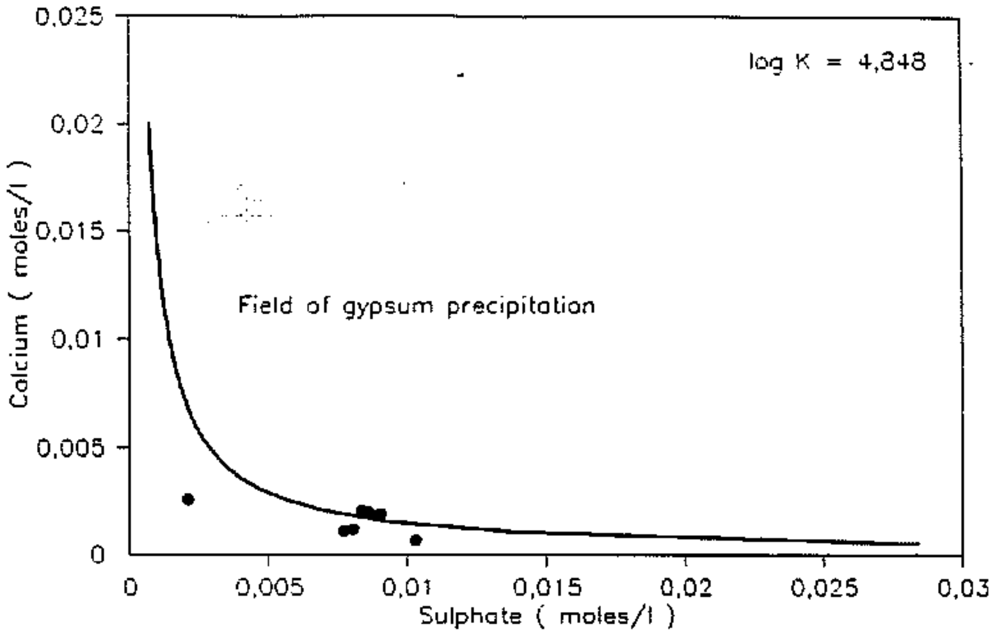

FIGURE 9 : *The relationship between some EDR brine compositions (represented by the molar activity of free calcium and sulphate ions) and the gypsum saturation curve.*

Solution 6 : Construction of a phase diagram indicating the field of precipitation of the mineral concerned. Data should be based on the molar activities of the free ions to take account of the effect of complexation, and the effect of the presence of other ions in solution.

Chemical speciation offers a realistic method for the assessment of the saturation state of a stream with respect to a given mineral.

If process changes were proposed which would result in changes in the feed composition, MINTEQA2 could be used to model the new feed composition. Examination of the list of saturation indices would enable potential foulants to be identified.

Although this example used feed and brine streams to an EDR plant, the methodology is applicable to other concentrating techniques such as reverse osmosis (**Appendix 6**) or evaporators. For these technologies, where a pure water condensate is produced and all salts remain in the brine, projected water compositions at different water recoveries could be modelled. In this way the limiting degree of concentration before precipitation occurred could be established. The use of MINTEQA2 to study this aspect has been incorporated into WRC Project No. 325, *Research on the Modelling of Tubular Reverse Osmosis Systems.*

4.5 The Effect of Temperature on the Solubility and Nature of the Solid Phase

While most salts exhibit increased solubility with increasing temperature, some display inverse solubility. In addition increased temperature may result in a phase change for the solid concerned. MINTEQA2 can be used to examine the effect of temperature on the amount and nature of a precipitated solid. Gypsum is used as an example of this modeling technique.

4.5.1 Example 6 : Can temperature be used to prevent precipitation of gypsum in the Tutuka Power Station EDR feed?

The Tutuka ERD feed water, which was known to precipitate gypsum, was speciated using MINTEQA2. The maximum solubility of the system occurs at 47 °C. Successive model runs were undertaken at increasing temperatures (**Appendix 5**). The molar mass of solid precipitated was plotted against temperature. Figure 10 shows that at temperatures up to approximately 47 °C, the solid in equilibrium with the solution is gypsum ($CaSO_4.2H_2O$) and that it displays increased solubility with increasing temperature. Above 47 °C, gypsum is no longer the stable solid phase and is replaced by anhydrite ($CaSO_4$), which exhibits inverse solubility.

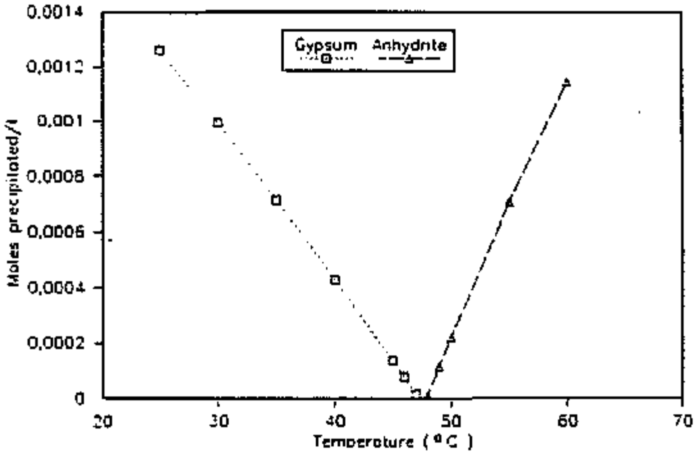

FIGURE 10 : *The effect of temperature on the solubility of gypsum*

Solution 6 : Construction of a phase diagram showing variation in solubility of the mineral of concern with temperature.

The phase change from gypsum to anhydrite with increasing temperature is well known (Krauskopf, 1979), but the modeling technique is applicable to any of the solids included in the MINTEQA2 database. A diagram such as Figure 10 can be used to examine whether potential precipitation could be prevented or minimised by altering a process operating temperature.

4.6 The Effect of Oxidation State on the Distribution of Chemical Species

The measurement of redox potential in natural systems, although seemingly simple, is fraught with difficulties, and is complicated and controversial. Part of the difficulty stems from the fact that some of the reactions that determine redox potential are slow, so that instantaneous readings with a platinum electrode do not give the true equilibrium potential. Figure 11 shows the scatter of Eh measurements for some redox pairs obtained from field measurements plotted against calculated Eh values (Lindberg and Runnells,1984). The spread is so wide that most Eh measurements can only be used in a qualitative sense. Pankow (1991) advocates that Eh measurements should be viewed only as providing guidance as to the direction of reactions within any given system and as to the range of concentration values that are feasible in the system.

Within this framework MINTEQA2 can be used to determine the equilibrium Eh of a solution, provided concentrations of both the reduced and oxidised species are known. Alternatively, if only total concentrations are known, a fixed redox ratio can be imposed and MINTEQA2 will calculate the concentration of species present in the reduced and in the oxidised state. Two examples are given where the redox option in MINTEQA2 has been used (**Appendix 7**).

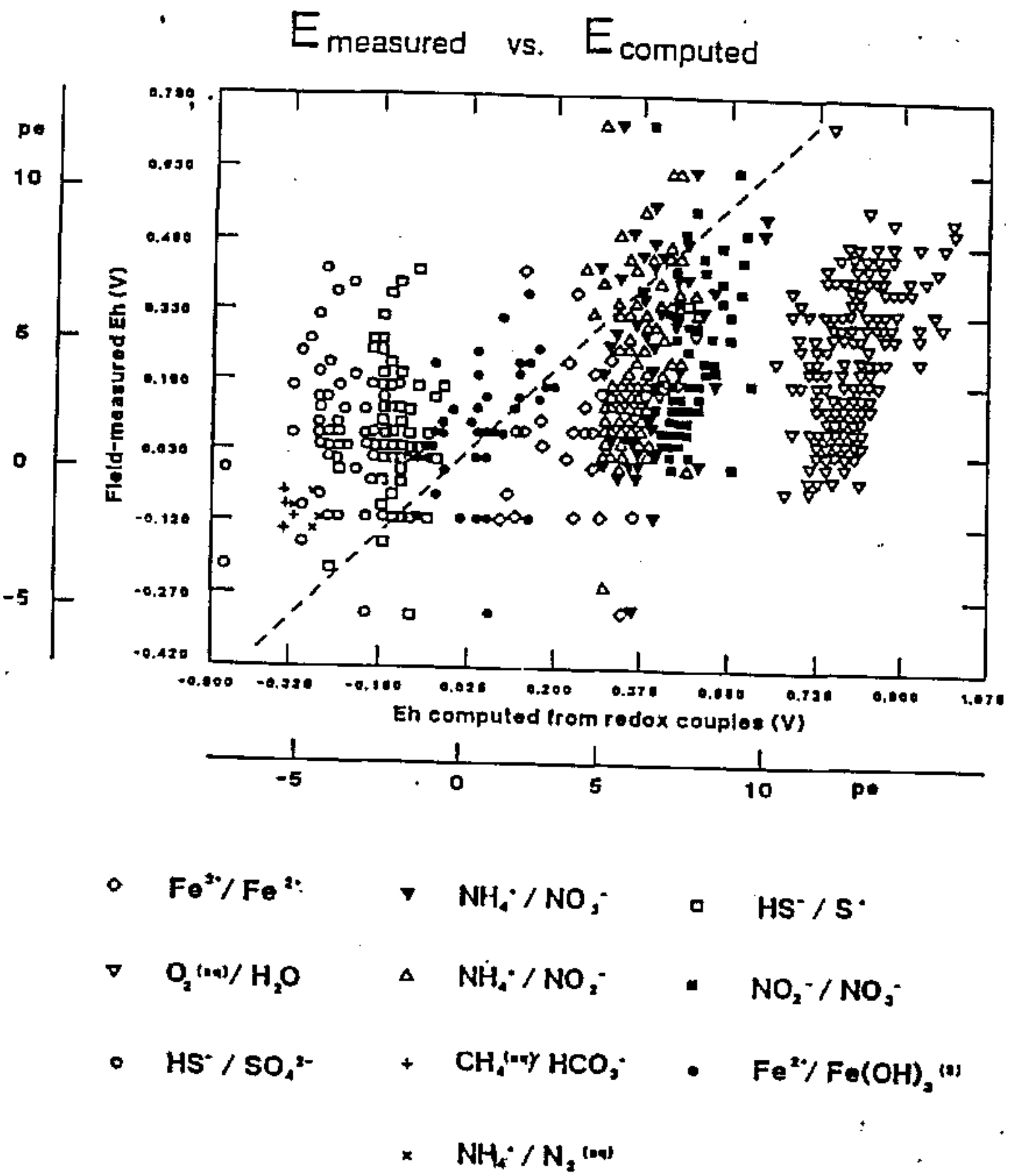

FIGURE 11 : *Scatter of Eh values measured in the field versus Eh values computed from redox couples. For a given computed Eh value, there is a wide scatter of measured values. (after Lindberg & Runnels, 1984)*

4.6.1 Example 7 : Determination of effect of the redox potential of a stream on the distribution of chemical species present when analytical data is unreliable.

A mine effluent in the Witbank region had a pH value of 2,5. The available chemical analysis was limited and the oxidation state of iron in the water was not indicated. A general treatment was being sought which would make the water more suitable for further treatment or for use as a source of low grade water. Because the chemical data was inexact, a general approach to the chemical speciation of the water was adopted. In a preliminary investigation, MINTEQA2 was used to examine iron speciation in the effluent by initially assuming that all iron was present in the ferrous state and then assuming that all iron was present in the ferric state. These two model scenarios gave the limiting conditions for iron speciation. Model predictions (Table 2) indicated that a possible treatment route would be to aerate the water, to ensure that all iron was in the oxidised state. Under these conditions 99 % of iron would be removed from solution as the solid phase, hematite. Saturation of the solution with lime, would result in the precipitation of several metal hydroxides, leaving a treated water consisting largely of sodium, potassium and chloride ions together with smaller amounts of calcium and sulphate ions. The high pH of the treated water could be adjusted with sulphuric acid, resulting in the precipitation of gypsum and removing further calcium and sulphate ions from the water.

TABLE 2

Predicted chemical composition of acid mine water under different modeling conditions. The data indicates that a possible treatment method would be aeration and and saturation.with lime, $Ca(OH)_2$. The TDS of the treated water is reduced.

	Untreated acid mine water (mg/ℓ)	Acid mine water, all iron as Fe^{2+} (mg/ℓ)	Acid mine water, all iron as Fe^{3+} (mg/ℓ)	Acid mine water, aerated (mg/ℓ)	Acid mine water, aerated and saturated with lime
Al	308	186	308	308	308
Ca	191	191	191	191	804
Total Fe	661				
Fe^{2+}		661	-	0	0
Fe^{3+}		-	0	0	0
PO_4	0,2	0,2	0,2	0,2	0
SO_4	4 345	3 888	4 345	4 345	918
pH	2,5	2,5	1,7	1,9	12,5
Eh (mv)	-	-	-	1 105	1 105
TDS (mg/ℓ)	5 866	5 287	5 205	5 205	2 010

4.6.2 Example 8 : Use of MINTEQA2 to aid interpretation of a corrosion experiment.

The corrosion behaviour of copper metal in an aerated acetic acid solution was examined in a laboratory experiment. Over an exposure period of six days, the corrosion rate of the copper strips decreased. The aerated acid solution turned blue and a black precipitate formed on the surface of the copper.

MINTEQA2 was used to model possible chemical interactions occurring in the experiment, to predict the nature of any precipitate and to aid interpretation of the results.

The predicted undersaturated state of the solution did not fit experimental observations that a black precipitate (tenorite?) was formed on the surface of some copper strips. An additional MINTEQA2 run predicted that tenorite would be in equilibrium with a solution containing 2,095x10^{-2} M/ℓ of cupric ions. This concentration is approximately four times that of the concentration of cupric ions in the experimental solution. The increase in molar activity required to initiate precipitation of tenorite is only threefold. It is not unreasonable, that due to poor mixing in the experimental tank, such an increase in concentration could occur at the metal /liquid interface, leading to precipitation of tenorite on the metal surface. This speculation was supported by observations that a copper strip placed directly in the stream of air bubbles did not develop a passivation coating and showed the highest corrosion rate.

4.7 The Effect of Organic Material on Metal Complexation

It is generally accepted that the presence of organic material, particularly humic substances, in an aqueous system can influence the distribution of the inorganic species present. Reviews on this subject have been presented by Canabiss et al (1984); Perdue et al (1988) and others. The organic material may be dissolved or particulate. Either of these categories offers different mechanisms of interaction with the inorganic ions present in the water, for example, dissolved organic material may form ionic complexes or ion pairs with inorganic ions, while particulate organic material may offer electrostatic adsorption surfaces on which the inorganic ions may bind. The nature of the organic material will depend on the environment of the water, for example, the organic material found in a lake water will be different from that in an esturine water, and even within a given body of water there may be seasonal or depth variations in the nature of the organic material present. Reviews of natural organic material found in different ecosystems are given by Bowen (1979); Duursma and Dawson (1981); Schnitzer and Khan (1987); and Wetzel (1975).

This complexity of natural systems, is compounded by the analytical difficulties of identifying all the organic compounds present. Thus waters whether natural or process streams are rarely well characterised in terms of their organic content. As a result there are few thermodynamic data available for naturally occurring organic compounds. The lack of thermodynamic data restricts the use of chemical speciation computer models in studying the effect of organic complexation on the distribution of inorganic species.

Two approaches have been taken in attempts to resolve this difficulty;

(i) the use of *recipes* representing common sources of organic material

(ii) the use of *composite organic ligands*, for which the complexing affinity with some metals has been determined.

Use of recipes representing common sources of organic material

A number of recipes for the organic component of several waters have been developed to enable the effect of the organic material on metal complexation to be considered. These include, a recipe representing the organic content of sewage, (Morel et al, 1975), a recipe representing the organic content of sludge derived soil leachate, (Mattigod and Sposito, 1978), and a recipe representing the organic composition of seawater, (Stumm and Brauner, 1975). These recipes, given in Table 3, consist of organic acids whose proton dissociation constants fall into the same ranges observed for organic material in natural systems and which are expected to be present or to simulate closely the organic acids present in each system. The measured stability constants for trace metal complexes with these organic compounds are assumed to be good approximations to the unknown stability constants and are available in the MINTEQA2 database. This approach has been questioned (Perdue, 1983) but Mattigod and Sposito (1978), referring to contaminated soil solutions, consider that the dangers in this approach *are not considered to be as serious as completely neglecting the organic speciation of trace metals in a soil solution.*

TABLE 3

Recipes developed to represent organic ligands present in sewage, sludge-derived soil leachate and seawater.

Recipe for Sewage		Recipe for sludge-derived soil leachate		Recipe for seawater	
Ligand	Conc (mM)	Ligand	Conc (μM)	Ligand	Conc (mM)
Acetate	0,500	Benzenesulphonate	54	Acetate	0,007
Glycinate	0,500	Salicylate	54	Citrate	0,007
Tartrate	0,250	Phthalate	107	Tartrate	0,007
Glutamate	0,200	Citrate	72	Glycinate	0,007
Salicylate	0,155	Maleate	107	Glutamate	0,007
Phthalate	0,125	Ornithine	44	Phthalate	0,007
		Lysine	44		
		Valine	44		
		Arginine	32		
TOTAL	6,0 mM carbon		2,2 mmol/g ΔH^+		2,3 mg/ℓ carbon

Use of composite organic ligands, for which the complexing affinity with some metals has been determined.

A recent addition to the MINTEQA2 database, (December 1991), is a composite ligand, DOM, representing natural dissolved organic matter from the Suwannee River. Details of the nature of, and the thermodynamic constants relevant to this composite ligand are given in Appendix 7.

4.7.1 Example 9 : Is the return of sewage effluent to the Lethabo Power Station cooling water circuit affecting the distribution of the major inorganic species in the water?

Sewage effluent was returned as make-up water to a cooling water circuit at the Lethabo Power Station. MINTEQA2 was used to examine whether the presence of dissolved organic matter had a significant effect on the chemical speciation of the major cations in the cooling water (**Appendix 7**). The recipe approach was used.

In order to model this type of scenario a total carbon and inorganic carbon analysis of the water is required. By subtraction, the dissolved organic carbon concentration can be determined. This value is required to adjust the sewage recipe to match the organic carbon concentration of the cooling water.

Of the various organic ligands contained in the sewage recipe, only acetate and phthalate showed any affinity to complex with the calcium, magnesium and sodium ions of the cooling water. The overall effect of the formation of these complexes is negligible at the organic carbon concentration modelled. The amount of calcium carbonate precipitated is predicted to be reduced by 1 mg/ℓ (to 61,7 mg/ℓ) due to the formation of the soluble calcium acetate and calcium phthalate complexes. Increasing the concentration of the sewage components up to a total carbon concentration of 6 mM/ℓ (approximating raw sewage), reduced the amount of calcium carbonate precipitated by 2 mg/ℓ.

Using the sewage recipe to model the impact of returning sewage effluent to the cooling water circuit, suggests that the effect on the major ions in the water appears negligible. The reduced volume of calcium carbonate sludge produced, and hence the increased calcium concentration of the cooling water, could however be significant where large volumes of water are treated to remove hardness ions.

4.7.2 Example 10 : The effect of dissolved organic matter (DOM) on the distribution of chemical species in a cooling water

The Lethabo Power Station cooling water discussed in Example 9 was modelled with increasing amounts of dissolved organic material, represented by the composite organic ligand, DOM.

Of the cations present in the water, only calcium and magnesium form soluble metal-organic complexes. Figure 12 shows the changing percentage distribution of calcium species with increasing concentration of dissolved organic matter. As the concentration of dissolved organic matter increases, the metal-organic complex increases at the expense of all other calcium species, including the equilibrium solid phase, calcium carbonate. At organic concentrations greater than approximately 4,0 mM, the calcium-organic complex becomes the dominant calcium species present. The affinity of the dissolved organic material for calcium is sufficiently strong to compete with the precipitation process.

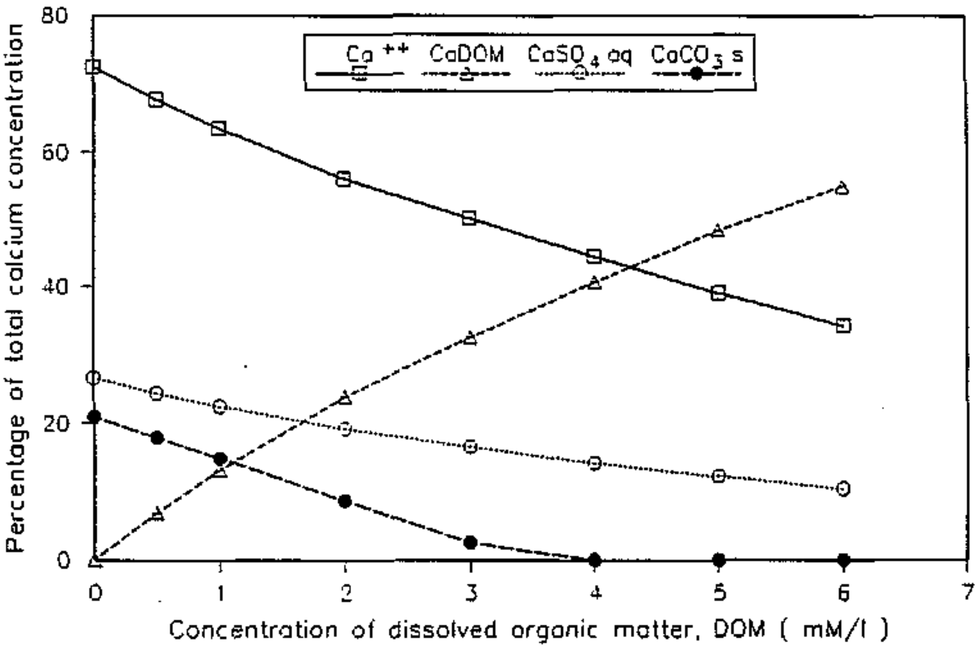

FIGURE 12 : *Variation in the percentage distribution of calcium species with increasing concentration of dissolved organic matter. The concentration of the soluble calcium-organic complex increases at the expense of all other calcium species present, including the equilibrium solid phase, calcium carbonate.*

The formation of a calcium-organic complex, has implication for the efficient operation of any flocculation/clarification or water softening process used to treat this cooling water, and would result in less calcium being removed from the water than expected. This conclusion is similar to that reached when the cooling water was modelled with the sewage recipe, but in this case, the model predicts that the amount of calcium carbonate precipitated would be reduced by 55 mg/ℓ, compared to a reduction of only 1 mg/ℓ when the sewage recipe was used.

4.8 Effect of Adsorption on Species Distribution

In many aqueous environments, the fate or distribution of metal ions is regulated by adsorption/desorption reactions occurring at the interface between the aqueous solution and colloidal or particulate matter such as mineral particles, organic matter or living cells. These reactions occur because the surface of the solid particle possesses an electrical charge which may be positive or negative. Stumm et al. (1976) showed that these surface reactions can be considered as analogous to the corresponding reactions in solution and that the same co-ordination chemistry principles were applicable.

When adsorption onto the surface of natural sediment particles is considered, as would be the case in modeling environmental problems, there is evidence that the complexing capacity of sediments is determined largely by amorphous ferric oxide which forms a coating on the inorganic "support" particles (Luoma and Davies, 1983).

MINTEQA2 utilise this fact and a thermodynamic database for adsorption onto an amorphous iron oxide substrate is included for use with the Diffuse Layer Adsorption Model.

4.8.1 Example 11 :- What is the extent of adsorption of phosphate species (onto an iron oxide surface) and how does adsorption effect the distribution of phosphate species.

The chemical speciation of phosphate in a fresh water impoundment (Inanda Dam) was examined to give greater understanding of the interactions occurring between phosphate and other chemical species in the water. Model runs with MINTEQA2 established that the summer surface water was in equilibrium with the partial pressure of carbon dioxide and oxygen in the atmosphere. MINTEQA2 predicted that 99,3 % of phosphate would be precipitated and be present in the solid phase hydrapatite, or if fluoride were included in the water chemistry, as flouroapatite. No site sediment data was available, consequently adsorption modeling onto an iron oxide surface was undertaken using two sets of sediment data provided by the EPA. The availability of two sets of sediment data, provided an opportunity to examine the effect of different surface characteristics on the predicted extent of adsorption. Details of the surface characteristics calculated from the two sets of sediment data are given in **Appendix 7**. The distribution of species adsorbed onto each separate iron oxide surface is given in Table 4. The Diffuse Layer Adsorption Model was used. On each adsorbing surface, designated as Set A and Set B, two sites were defined; a high energy site (Type 1) and a low energy site (Type 2). The concentration of Type 1 sites is 2,5 % that of the Type 2 sites in the Diffuse Layer Model.

TABLE 4

Surface water in Inanda Dam, December, 1990; a comparison of the predicted percentage distribution of dissolved, adsorbed and precipitated phosphate, calcium, sulphate, nickel and boron species, with and without adsorption modeling. Two separate amorphous iron oxide surfaces were defined by sediment data Set A and sediment data Set B.

	Dissolved			Adsorbed			Precipitated		
	No adsorption modeling	Set A	Set B	No adsorption modeling	Set A	Set B	No adsorption modeling	Set A	Set B
PO_4	0,7	0,0	0,1	-	100,0	99,9	99,3	0,0	0,0
Ca	91,4	0,9	13,4	-	99,1	78,8	8,6	0,0	7,8
SO_4	100,0	92,7	98,2	-	7,3	1,0	0,0	0,0	0,0
Ni	100,0	0,0	0,4	-	100,0	99,6	0,0	0,0	0,0
H_3BO_3	100,0	89,2	97,8	-	10,8	2,2	0,0	0,0	0,0

Table 4 indicates that five species, (phosphate, calcium, sulphate, nickel and boron) would be adsorbed on to particulate matter coated with amorphous iron oxide. For the strongly adsorbed species, phosphate and nickel, the different characteristics of the iron oxide surfaces did not affect the distribution of these species significantly. For calcium, modeling with the adsorption surface defined by sediment data Set B, decreased the amount of adsorbed calcium and increased the amount of calcium predicted to be present in a solid precipitated phase.

The most striking feature of the results is the impact of the adsorption routine on the distribution of the phosphate species. Without adsorption modeling, 99,3 % of the total phosphate concentration was predicted to be present as a calcium phosphate solid (either hydrapatite or fluorapatite). This would effectively mean that unless water conditions changed, causing the solid to redissolve, that phosphate would be immobilised in the environment. However, modeling with an adsorption routine indicated that phosphate would be present as an adsorbed phase. Circumstances which could lead to desorption have not been investigated but could include change in the pH value, or an increase in the calcium concentration of the water.

The effect of different iron oxide surfaces on the extent of adsorption, is significantly less than the effect of not including the possibility of adsorption in the model parameters.

4.9 Modeling Environmental Problems

Modeling environmental problems presents difficulties in that site specific data is frequently lacking. In natural systems, adsorption and metal complexation with organic material are likely to exert important influences on the distribution of chemical species. Examples 10 and 11 illustrate that useful information can be obtained by making reasonable assumptions and by making use of hypothetical or composite ligands, even when site specific data is lacking.

South Africa is fortunate in that environmental degradation due to industrial activity has not reached the levels found in some other industrial countries and that remedial clean-up activities on the scale of the Superfund sites found in the USA have not been necessary. MINTEQA2 has been used in the USA as a tool for assessing the risks associated with trace or heavy metal contamination, and to indicate or delimit the remedial action required. The following example is an illustration of the way in which MINTEQA2 can be used to give greater insight into the chemical parameters which might control metal behaviour in a contaminated site. Details are given in **Appendix 7**.

4.9.1 Example 12 : What is the predicted distribution of zinc species in a contaminated site? Will soil clean-up measures need to be implemented?

Figure 13 shows the results obtained for the distribution of zinc species in a contaminated soil. It was assumed that organic complexing and adsorption were mechanisms likely to influence the distribution of zinc species. The soil water was modelled using the DOM composite ligand and the Diffuse Layer Model for adsorption onto an iron oxide surface.

Figure 13 has been compiled from data presented by researchers at the U.S. EPA Environmental Research Laboratory, Athens, Georgia. Model runs were conducted at a pH value of 7.

A series of computer simulations were undertaken with varying total concentrations of zinc. In this way, the variation in the species distribution with total concentration was determined. Limits of acceptable concentrations of zinc were demarcated. Site data was compared to the computer predictions and areas of concurrence sought.

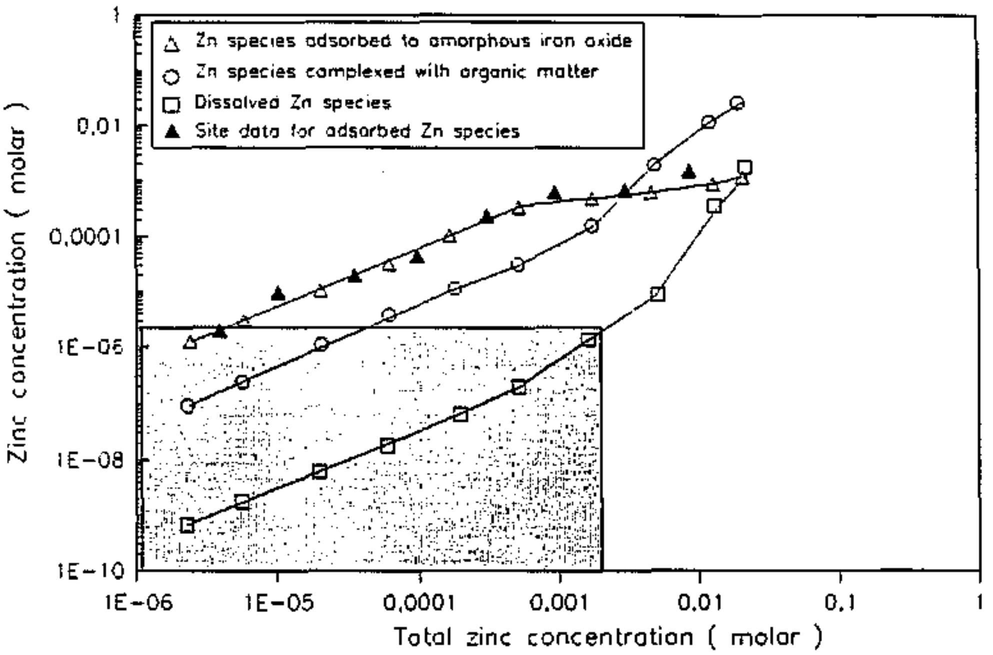

FIGURE 13 : *Predicted distribution of zinc between dissolved species, zinc adsorbed on soil, and zinc complexed with dissolved organic matter, over a range of total zinc concentrations. The stippled area indicates the acceptable zinc concentration area, based on acute fresh water criteria.* **Solid symbols indicate site data.**

The figure shows that for a given total zinc concentration, MINTEQA2 predicts that zinc will be distributed between (in decreasing molar concentrations), species adsorbed on soil particles (amorphous iron oxide surfaces), species associated with organic matter, and dissolved species. This situation holds even for low total concentrations of zinc. Site specific data closely matched the predicted equilibrium species distribution. The implication was that soil clean up measures would need to be implemented, as the boundaries of the stippled box indicate the zone of acceptable zinc concentration, based on fresh water acute criteria.

Solution 12 : **Determination of the variation in species distribution with total concentration of zinc. Select acceptable concentration criteria. Evaluate species distribution relative to acceptable limits to indicate areas of clean-up activity.**

4.10 Prediction of Osmotic Pressure

The activity of water in a solution is a fundamental thermodynamic property. One particular use is in the prediction of the osmotic pressure of a solution. The osmotic pressure was required in Water Research Commission Project No. 325, *Research on the Modelling of Tubular Reverse Osmosis Systems*, in order to predict the formation of precipitates in tubular reverse osmosis plants. One of the calculated parameters from MINTEQA2 is the activity of water. It was found that the MINTEQA2 calculation was in error leading to incorrect values for the osmotic pressure.

The cause of the error was identified and an improved calculation procedure for the prediction of osmotic pressure was developed (Kerr, 1992). The enhanced equation was reported to the US EPA who indicated that they would incorporate the change in the next release of MINTEQA2. Further improvements have subsequently been made (Brouckaert et al., 1993) (**Appendix 8**).

The co-operation between Water Research Commission Projects Nos 325 and 309, resulted in Pollution Research Group personnel contributing to a recently published book entitled *Reverse Osmosis : Membrane Technology, Water Chemistry, and Industrial Applications*. The relevant chapter is given in **Appendix 9**

CHAPTER 5

METHODS OF MONITORING THE DEGREE OF SATURATION

Although the use of chemical speciation programs has provides a means to tackle precipitation problems with greater insight, there remains a need for a practical methods to monitor the degree of saturation of concentrating solutions, with respect to common scaling minerals. Some small scale laboratory tests have been developed which help determine the fouling potential of streams undergoing reverse osmosis or ultrafiltration.

For rapid assessment of the fouling potential of an effluent, accelerated fouling tests can be conducted. These involve evaporating the effluent under vacuum, at a temperature similar to that which would be encountered in a treatment situation. Filtration of the effluent at different water recoveries allows any precipitated solids to be identified. The onset of precipitation indicates a crude limit to the degree to which the effluent can be concentrated. The identification of the solid precipitated can yield useful information about the chemical nature of the effluent which might not have been apparent from the available chemical analysis, for example, the first mineral to exceed its solubility limit might involve a cation present only in trace amounts and which was not reported in the routine chemical analysis of the effluent.

The results of accelerated fouling tests should be verified by bench scale membrane tests. For these a membrane test rig, such as a PCI 3-cell test rig is used. After initial characterisation of membranes and determination of operating parameters, total recycle and batch concentration experiments are conducted. From total recycle experiments, where all permeate is returned to the feed tank so that the composition of the feed is constant, information on species rejection and permeate flux is obtained. A decline in permeate flux could indicate membrane fouling. This can be investigated further by undertaking batch concentration experiments where the permeate is removed from the system and the feed thus concentrated. If the fouling is concentration dependent, filtering the concentrate at successive water recoveries, will enable the onset of solid precipitation and associated water recovery to be identified. Details of these experiments are given in **Appendix 10**.

While laboratory tests are useful, an on-line method to detect the proximity to saturation, with respect to a particular mineral, would be of considerable benefit to industry. A patent entitled *Precipitation Control Method and Apparatus*, lodged in the name of the Water Research Commission, was accepted by the Register of Patents in October 1992 (**Appendix 11**). The patent describes an apparatus which will indicated the degree of saturation of a solution, with respect to a set of chosen scaling minerals, through the measurement of conductivity. The apparatus is suitable for use with desalination equipment such as evaporators, seeded slurry evaporators, electrodialysis, or reverse osmosis.

The principle behind the apparatus is that the conductance of a solution will change when salts are added or removed, due to an increase or decrease in the number of ions present, their relative mobilities, and the distribution of chemical species. By comparing the electrical resistance of the concentrating stream to a control stream, an indication can be gained of the saturation state of the solution.

Experimental work to refine the apparatus and to evaluate the sensitivity of conductivity measurements as an indicator of saturation, is continuing.

CHAPTER 6
SOURCES OF INFORMATION

For general background to a problem or for specific information on water related problems, the Waterlit database has proved invaluable. Although the database only extends back to 1975, all papers referenced are housed in South Africa and are thus readily available. Once hard copy of a reference has been obtained, the reference list in that paper can be used to find older reference material, if necessary.

The computer programs used have associated databases of equilibrium constants. MINTEQA2 has the most comprehensive thermodynamic database, containing equilibrium constants for the formation of over 1 500 chemical species. This database is adequate for solving a broad range of problems without the need for additional user-supplied equilibrium constants. If the standard database is found to be incomplete or inadequate for a particular problem, additional data can be added to it.

Finding the required thermodynamic data to make additions to a database can be a time consuming and laborious task for those not familiar with the literature. The following compilation of data sources should provide adequate coverage of equilibrium information for most problems. A bibliography supplied by Prof J.C. Westall, Department of Chemistry, Oregon State University, Corvallis, Oregon, is acknowledged. Useful text books which cover the basic principles of aquatic chemistry and some mineralogical reference texts have been included.

6.1 Aquatic Chemistry Text Books

The following books are useful for those whose knowledge of aquatic chemistry needs to be upgraded or for those whose who need a refresher course.

James F. Pankow. Aquatic Chemistry Concepts, Lewis Publishers. Inc. Michigan, 1991, ISBN 0-87371-150-5.

Snoeyink, V.L. and Jenkins, D. Water Chemistry, John Wiley & Sons, Inc., USA, 1980, ISBN 0-471-01596-9.

Stumm, W. and Morgan, J.J. Aquatic Chemistry, 1981, Wiley-Interscience, New York.

Of these texts, that by Pankow is most suited to beginners, while Stumm and Morgan is more suited to those with a background in physical chemistry.

6.2 Mineralogical Text Books

A mineralogical text book is a useful companion when modeling problems involving solids in MINTEQA2. The database relevant to solid phases, is based on a database compiled by the U.S. Geological Survey (WATEQ3), for naturally occurring minerals. As a result solid phases are identified by their mineralogical names rather than by chemical names or chemical formulae. For those with little or no exposure to mineralogy, this can be a source of confusion and frustration. A mineralogical text also aids in assessing which solids are realistic for the system being studied. Particularly for silicate minerals, users should be careful to assess whether it is likely that some minerals would ever precipitate from an aqueous solution. For example, the mineral kyanite, Al_2SiO_5, is contained in the database because it could be dissolved by natural waters. Its precipitation from an aqueous phase is however unlikely, since its formation is dependent on a combination of correct bulk rock composition (aluminium rich clays), high pressures (3 to 5 kbars), medium temperatures (500 °C) and geological time. Similar arguments can be made for other silicate and anhydrous minerals. Most mineralogical textbooks give the locality and the rock type in which a mineral is found. In general, minerals found in sedimentary rocks, hydrothermal deposits or very low grade metamorphic rocks are more likely to be a possible precipitate from an aqueous solution than minerals formed in igneous or metamorphic rocks. Some suitable reference texts are :

Dana's Textbook of Mineralogy. John Wiley and Son's Inc. London 1922.

Kostov, I. Mineralogy Oliver & Boyd, Edinburgh. 1st English Edition 1968. ISBN 05 001667 9.

Deer, W.A., Howie R.A. and Zussman J. Rock Forming Minerals, Volume 1 to 5. Longmans, London.

There are several geochemistry books which bridge the disciplines of pure chemistry and geology. These books are useful when dealing with natural systems as opposed to laboratory solutions. If environmental problems are being modelled these books should give a good indication of whether model predictions fall within the spectrum found in nature. They are :

Krauskopf, K.B. Introduction to Geochemistry, 2nd Edition. 1979. McGraw-Hill International Series in the Earth and Planetary Sciences, ISBN 0-07-035447-2.

Garrels, R.M. and Christ, C.L. Minerals, Solutions and Equilibria. 1965. Harper and Row, Publishers, Incorporated, New York.

Garrels and Christ present a mathematical handling of equilibrium constants for geologically important reactions. Krauskopf provides the background, setting and mathematically less rigourous treatment of naturally occurring reactions.

6.3 Tables of Thermodynamic Constants

6.3.1 Metal-ion complexes

The original IUPAC project on stability constants resulted in two books :

J. Bjerrum, G. Schwarzenbach, L.G. Sillen, Stability Constants of Metal-Ion Complexes, Part I, Organic Ligands, Special Publication No. 6, The Chemical Society, London, 1957.

J. Bjerrum, G. Schwarzenbach, L.G. Sillen, Stability Constants of Metal-Ion Complexes, Part II, Inorganic Ligands, Special Publication No. 7, The Chemical Society, London, 1958.

These two volumes have been superseded by :

L.G. Sillen and A.E. Martell, Stability Constants of Metal-Ion Complexes, Special Publication No. 17, The Chemical Society, London, 1964.

and three supplements :

L.G. Sillen and A.E. Martell, Stability Constants of Metal-Ion Complexes, Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971.

E. Hogfeldt, Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands, IUPAC Chemical Data Series, No. 21, Pergamon Press, Oxford, 1982.

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6.3.3 Inorganic acids and bases

D.D. Perrin, Dissociation Constants of Inorganic Acids and Bases in Aqueous Solutions, Butterworths, London, 1969. (IUPAC Chemical Data Series, No. 19, Pergamon Press, Oxford, 1969).

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D.D. Perrin, Ionisation Constants of Inorganic Acids and Bases in Aqueous Solutions, 2nd Edition, IUPAC Chemical Data Series, No. 29, Pergamon Press, Oxford 1982.

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G. Kortuem, W. Vogel and K. Andrussow, Dissociation Constants of Organic Acids In Aqueous Solutions, Butterworths, London, 1961.

This book has been superseded by :

E.P. Serjeant and B. Dempsey, Ionisation Constants of Organic Acids in Aqueous Solution, IUPAC Chemical Data Series, No. 23, Pergamon Press, Oxford, 1982.

6.3.5 Organic bases

D.D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solutions, London, Butterworths, 1965.

D.D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solutions: Supplement, London, Butterworths, 1972. (IUPAC Chemical Data Series No. 12, Pergamon, Oxford, 1972).

6.3.6 Solubilities

An extensive collection of solubility data was compiled by the USSR Academy of Sciences and translated into English :

H. Stephen and T. Stephen, Solubilities of Inorganic and Organic Compounds, Volume 1, Binary Systems, Parts I and II, Pergamon, Oxford, 1963.

Another series of solubilities is based on the classic work of Seidell :

A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Third Edition, Volume 1, Van Nostrand, New York, 1940.

A. Seidell, Solubilities of Organic Compounds, Third Edition, Volume 2, Van Nostrand, New York, 1941.

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The Seidell series was updated by Linke :

W.F. Linke, Solubilities of Inorganic and Metal-Organic Compounds, Fourth Edition, Volume 1, A-Ir, Van Nostrand, Princeton, 1958.

W.F. Linke, Solubilities of Inorganic and Metal-Organic Compounds, Fourth Edition, Volume 2, K-Z, American Chemical Society, Washington, 1965.

6.3.7 Thermodynamic compilations

A compilation of thermodynamic data from the perspective of electrochemistry is available in two works :

W.M. Latimer, Oxidation Potentials, Prentice-Hall, New York, 1952.

The information in Latimer is now available in :

A.J. Bard, R. Parsons and J. Jordan, Eds. Standard Potentials in aqueous Solutions, IUPAC, Marcel Dekker, Inc. New York, 1985.

The National Bureau of Standards published a compilation based on energies of formation :

E.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine, I. Jaffe, Selected Values of Chemical Thermodynamic Properties: NBS Circular 550, U.S. Department of Commerce, Washington, 1952.

This publication has been updated and superseded by a series of publications from 1968 to 1981 (Part 3 supersedes Parts 1 and 2) :

Wagman et al. Selected Values of Chemical Thermodynamic Properties: NBS Technical Note 270, Parts 3-8, U.S. National Bureau of Standards, U.S. Department of Commerce, Washington, 1968-1981.

The latest revision in this series was published in 1982. It supersedes all other versions :

D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall. The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. J. Phys. Chem. Ref. Data, Supplement No. 2 to Volume 11, 1982, pp. 394.

A geochemist's version of essentially some of the same data that's in Latimer and Rossini et al. is :

R.M. Garrels and C.L. Christ. Solutions, Minerals, and Equilibria. Freeman, Cooper and Co., San Francisco, 1965.

A comprehensive table of data on materials of geochemical interest is :

R.A. Robie, B.S. Hemingway, J.R. Fisher, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar Pressure and at Higher Temperatures. U.S. Geological Survey Bulletin 1425, U.S. Government Printing Office, 1978.

Another series of thermodynamic data is the JANAF Tables. These tables are geared more towards completeness of the dataset and $T > 298$ K, as opposed to critical data at $273\text{ K} < T < 298\text{ K}$. The second edition was published as :

D.R. Stull and H. Prophet, JANAF Thermochemical Tables: National Standard Reference Data Series No. 37, U.S. National Bureau of Standards, 1971. 1141 pp.

M.W. Chase, J.L. Curnutt, A.T. Hu, H. Prophet, A.N. Syverud and L.C. Walker. JANAF Thermochemical Tables, 1974 Supplement. J. Phys. Chem. Ref. Data, 3, 311-480, (1974).

M.W. Chase, J.L. Curnutt, H. Prophet, R.A. McDonald and A.N. Syverud. JANAF Thermochemical Tables, 1975 Supplement. J. Phys. Chem. Ref. Data, 4, 1-176, (1975).

M.W. Chase, J.L Curnutt, R.A. McDonald and A.N. Syverud. JANAF Thermochemical Tables, 1978 Supplement. J. Phys. Chem. Ref. Data, 7, 793-940, (1978).

The third edition of the JANAF Tables supersedes the second edition listed above :

M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald and A.N. Syverud. The JANAF Thermochemical Tables, 3rd Edition, J. Phys. Chem. Ref. Data, Supplement No. 1 to Volume 14, 1985. American Chemical Society, Washington, D.C. 2 Volumes, 1896 pages.

Other Useful References

C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations. Wiley, New York, 1976.

6.3.8 Redox equilibria

The classic treatise for reactions involving redox equilibria is:

> M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, 1966.

Diagrams are drawn in great detail and unless one is familiar with the methodology of interpreting Eh-pH diagrams in their various forms, this is not a book from which information can be gained easily. Simplified version of the more important redox systems can be found in Garrels and Christ or Krauskopf.

6.3.9 Criteria for selection of constants

The array of data available can be confusing and frustrating, particularly when published figures differ by significant amounts. The following questions are presented as a guide to help determine which figures may be the most reliable.

(i) Is the author recognised as an expert in the field? An indication of this might be the breadth of data published by the same author.

(ii) Are experimental conditions, for example, ionic strength of solutions, temperature etc., outlined in detail? This could indicate rigour of scientific method.

(iii) Is the work published in a reputable international journal, where the work will have undergone peer review prior to publication, or is it published in an obscure journal?

(iv) Where was the work undertaken? Work produced at a recognised institute may be more reliable than that undertaken at an unknown venue.

(v) What is the date of publication of the data? Older data may have been most carefully obtained, but improvements and advances in analytical techniques may have allowed greater precision and accuracy in experimental work.

6.3.10 Standard notation for reactions and equilibrium constants

An additional source of confusion can be the format in which the data is presented. The following list provides the standard notation for presenting equilibrium equations and constants. Published data should be inspected carefully to ensure that it is presented in the standard format otherwise conversion may be necessary.

In the list provided :

M refers to the metal (or H^+)
L refers to the ligand
HL refers to the protonated ligand
ML refers to the complex.

(i) Stepwise formation constant

$M + L \Leftrightarrow ML$ K_1

$ML_{n-1} + L \Leftrightarrow ML_n$ K_n

(ii) Overall formation constant

$M + nL \Leftrightarrow ML_n$ β_n

(iii) Stepwise formation constant for protonated ligand

$M + HL \Leftrightarrow ML + H$ K^*_1

$ML_{n-1} + HL \Leftrightarrow ML_n + nH^+$ K^*_n

(iv) Overall formation constant for protonated ligand

$M + nHL \Leftrightarrow ML_n + nH^+$ β^*_n

(v) Solubility product or solubility constant

$ML(s) \Leftrightarrow M + L$ K_{sp}

$ML(s) \Leftrightarrow M + L$ K_{s0} .

CHAPTER 7
CONCLUSIONS

The aim of this project was to assist in the more efficient operation of desalination equipment so that scaling and fouling problems would be eliminated or ameliorated. This objective has been achieved, not by producing diagrams for site specific cases, but by investigating the applicability of chemical speciation computer programs to precipitation problems. These programs, especially MINTEQA2, have been shown to be a suitable tool, not only for the study of precipitation, but also for other aspects of aqueous chemistry such as ionic and organic complexation and adsorption phenomena, all of which have a direct bearing on the precipitation process. MINTEQA2 is a tool which will enable operators and managers to understand the chemistry of their particular system and this will enable them to solve their site specific cases. The examples presented in this report, are illustrations of how MINTEQA2 and other programs can be used to tackle site specific problems. Personnel from individual plants and factories are the people best suited to solve site specific problems. A key aspect in any modeling is model verification. Factory personnel are familiar with their chemical systems and can appreciate the interactions between different areas of the plant and are in a better position to critically evaluate the computer predictions.

For physical chemists, the use of chemical speciation is an established technique. However, they have mainly used it for well defined systems. The recent availability of computer programs with extensive databases has provided a powerful tool to aid the understanding of chemical interactions within a given aqueous chemical system. An awareness of the complexity of aqueous systems is imparted through a knowledge of the chemical speciation of a system. The use of chemical equilibrium speciation programs offers access to speciation data, to engineering and water scientists who traditionally would not have used this technique.

Of the chemical speciation programs examined, MINTEQA2 has proved to be the most suitable for general speciation problems. Results obtained from using this program are encouraging. Interest in the program has been considerable. Introductory courses in the use of MINTEQA2 have been given to groups of postgraduate students and to Eskom research personnel. Copies of the program have been distributed to academics, research personnel at Rand Mines, Umgeni Water and the Institute of Groundwater Studies, University of the Orange Free State. Requests for further instructional courses have been received.

Publications resulting from work undertaken during the course of this project have included, 2 published papers and 4 presentations at local conferences.

The full impact of this project will not become apparent for some time. People to whom MINTEQA2 has been introduced are still learning the capabilities of the program. They are working in isolation and chemical speciation has not yet become part of their routine work tools. Future acceptance of the program will indicate the success of this project.

Copies of MINTEQA2, together with the User's Manual, can be obtained from :

Pollution Research Group
Department of Chemical Engineering
University of Natal
King George V Avenue
DURBAN
4001

Tel : (031) 816 3375

The program is distributed free of charge by the U.S. EPA, through the Centre for Exposure Assessment Modeling (CEAM), Environmental Research Laboratory, Athens, Georgia.

CHAPTER 8
RECOMMENDATIONS

MINTEQA2 has been applied to a variety of water related problems. Some of these have been studied in depth, other problems have been used as a means of developing computer modeling skills. Arising from this work a number of suggestions and recommendations are made concerning the future direction of computer modeling based studies, and in particular, areas where the use of MINTEQA2 could be of benefit.

Recommendations arising from this project are :

(i) chemical speciation as a technique to analyse aqueous systems should be encouraged. It is a technique which is applicable to all fields of water related activities.

(ii) the use of chemical speciation computer programs, particularly MINTEQA2, should be promoted. Target groups of potential users should be identified and provided with information on the use of MINTEQA2. This could be achieved by holding introductory workshops and seminars. In this way a base of new users could be established. Presentations at conferences, including subject areas not initially targeted, would disseminate information about the program. The growing field of environmental science, where multimedia research teams or task groups have been established, is a possible new target group.

(iii) advanced workshops for MINTEQA2 users should be held regularly to ensure that new skills, approaches and information about new areas of applicability are disseminated throughout the user body.

(iv) the formation of a MINTEQA2 User's Group should be considered. This could initially function as an informal grouping of MINTEQA2 users, with a self-help function. With current uncertainties over the future level of assistance that the EPA will be able to provide for MINTEQA2 users, such a User's Group could have a crucial role to play in providing back-up to novice users. Communication could take several forms depending on the preference of the majority of users, but could include, the regular distribution of a broadsheet indicating program developments, new areas of applications, and specific modeling problems, or establishment of a communication network via electronic mail. This would be a rapid, convenient, and cost effective means of conveying information. If demand indicated, the group could be formalised through association with an international organisation such as IAWQ.

(v) close contact with the US EPA should be maintained.

(vi) new areas of application for MINTEQA2 should be investigated. Possible areas for research within the field of dilute solution chemistry, are; investigation of the applicability of MINTEQA2 to corrosion chemistry and concrete chemistry. In extending the fields of applicability of MINTEQA2, co-operative research with physical chemists will be necessary. The computational procedures for speciation are well established. The thermodynamic constants are the area of greatest uncertainty. The involvement of physical chemists to determine operational formation constants (as opposed to pure thermodynamic data) for a particular system, would enable the database to be extended or tailored for site specific cases or South African conditions. The concept of operational formation constants has been established for dissolved organic material from the Suwannee river sediments and for amorphous iron oxide coatings. This approach should be extended to complex systems such as :

power station or petrochemical water circuits,
sewage treatment processes,
eutrophic impoundments,
leachates.

Co-operation with physical chemists should be encouraged in order to extend the database into specific areas of interest.

(vii) investigation into extending the use of MINTEQA2 into the field of high salinity waters should be investigated. The activity corrections made by MINTEQA2 are valid only for solutions with ionic strengths up to 0,5 M. New or revised correction coefficients would have to be developed for high ionic strength solutions. This would need the co-operation of specialist chemists and thermodynamists.

(viii) Clean technologies, waste minimisation and pollution prevention techniques should be encouraged as the first consideration in solving precipitation problems.

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