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# CHEMICAL SPECIATION MODELLING OF GROUNDWATER IN A SHALLOW GLACIAL SAND AQUIFER PART I: General Parameters

W E Falck, G W Quinn\*, J R Duffield\* and D R Williams\*

December 1988

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# Department of the Environment : Commissioned research on radioactive waste management 1987/88

Report Title:Chemical speciation modelling of groundwater in ashallow glacial sand aquifer, Part I: general parameters.

DOE Report No: DOE/RW/89.042

Contract Title: In situ determination of the effects of organics on radionuclide migration in controlled conditions of groundwater flow

**DOE Reference :** Contractor's Reference : PECD 7/9/367 WE/88/48 Sector No: 3.3

Author/Affiliations etc :

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Date of submission to DOE: Period covered by report: December 1988 February 1987 - December 1988

#### Abstract :

Speciation calculations employing PHREEQE have been carried out on groundwaters from the BGS in situ migration experiment at Drigg, Cumbria, to help understand the natural chemistry of the system. Groundwater samples were obtained at intervals during a pumping test and analysed. From these, three analyses were selected as representative of waters drawn from different regions of the aquifer in the course of the pumping test. The influence of uncertainties in the measurement of Eh and pH were studied by sensitivity analysis. As expected within the range of Eh studied a change in the dominant aqueous species from  $Fe^{2+}$ to  $Fe(OH)_3$  occurred as Eh became more positive. This implies that there is a likelihood of trace metals co-precipitating with the  $Fe(OH)_3$ . The results of the calculations show that the groundwater samples were undersaturated with respect to calcite and thus co-precipitation of  $Sr^{2+}$  with calcite will not influence tracer tests involving <sup>85</sup>Sr.

Keywords : 125, 124, 111, 48.

The results of this work will be used in the formulation of Government Policy, but views expressed in this report do not necessarily represent Government Policy.

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CHEMICAL SPECIATION MODELLING OF GROUNDWATER IN A SHALLOW GLACIAL SAND AQUIFER PART I: General Parameters

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### BRITISH GEOLOGICAL SURVEY

Technical Report WE/88/48 Fluid Processes Series

## CHEMICAL SPECIATION MODELLING OF GROUNDWATER IN A SHALLOW AQUIFER PART I: General Parameters

# W E Falck, G W Quinn, J R Duffield and D R Williams

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This report describes work carried out for the Department of the Environment (acting on behalf of the Secretaries of State for the Environment, Scotland and Wales) and the Commission of the European Communities as part of their research programme into radioactive waste management. The results will be used in the formulation of Government policy, but at this stage they do not necessarily represent Government policy. DOE Contract No. PECD/7/9/367 DOE Ref. No. DOE/RW/89.042 CEC Contract No. F1-1W-0064-UK(H)

Bibliographic reference

Falck, W E, Quinn, G W, Duffield, J R, and Williams, D R. 1988. Chemical speciation modelling of groundwater in a shallow glacial sand aquifer part I: General parameters. *British Geological Survey Technical Report* WE/88/48.

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### Preface

This study has been carried out as part of the MIRAGE II research programme (MIgration of RAdionuclides in the GEosphere) funded by the Commission of the European Communities (CEC) and the UK Department of the Environment. The specific BGS research project is entitled "In situ determination of the effects of organics on the mobility of radionuclides under controlled conditions of groundwater flow", which is centred around *in situ* radionuclide migration experiments carried out in a remote part of the Drigg Storage Depot, in Cumbria, which is operated by British Nuclear Fuels Plc.

The work involves the detailed geochemical and hydrogeological characterization of a confined glacial sand aquifer, the laboratory scale investigation of radionuclide sorption processes and how these are affected by the presence of natural and anthropogenic organic compounds. Ultimately the results of field hydraulic testing and laboratory studies of radionuclide sorption will be used to predict the outcome of a field tracer experiment using conservative and reactive radionuclide species.

The work presented in this and related reports is aimed at predicting from preliminary groundwater data gathered during a pumping test the behaviour of the radionuclides <sup>58</sup>Co and <sup>63</sup>Ni which are being considered as tracers. The speciation is also modelled for the case where EDTA and acetate (as models for natural organic complexants) are present in groundwater.

The authors express their thanks to G.M. Williams for arranging the funding and many helpful suggestions.

### **Executive Summary**

The aim of the work detailed in this report has been to gain a better understanding of the speciation chemistry controlling the aqueous chemical forms of elements and compounds normally present in groundwaters found at the BGS *in situ* migration experiment at Drigg, Cumbria. This will form the basis of future modelling studies designed to interpret *in situ* tracer experiments using <sup>60</sup>Co in the presence of naturally occurring organic complexants.

Total element concentrations in relevant samples were obtained using Inductively Coupled Plasma Optical Emission Spectroscopy. The aqueous speciation chemistry was modelled using the geochemical code PHREEQE in conjunction with the UWIST thermodynamic database. The natural chemical speciation of each sample was determined as was the sensitivity to changes in chemical parameters such as pH and oxidation-reduction potential (Eh). In addition, the possible solubility limiting phases were determined for elements of interest.

The results show that for all non-transition metal elements, the major aqueous species is the free ion. However, for the transition metal elements, this is not the case. For manganese, the carbonate species is by far the most abundant. This reflects the different complexing abilities of transition elements as compared to other metals.

In the given system, carbonate equilibria are likely to control the calcium solubility. Calculation predict that the precipitation of calcium carbonate (as calcide) from the aqueous phase is unlikely. Hence, it can be concluded that coprecipitation of  $Ba^{2+}$  and  $Sr^{2+}$  will not occur.

The speciation of aqueous iron is very sensitive to changes in pH and Eh. When the Eh is changed by only 110mV (from +227mV to +117mV) the dominant aqueous species is changed from Fe(OH)3<sup>0</sup> to Fe<sup>2+</sup>. The total change in the concentration of Fe(OH)3<sup>0</sup> over this range is an order of magnitude. Fe(OH)3<sup>0</sup> is an aqueous species of potential interest because calculations suggest that species such as this may precipitate and coprecipitate with radionuclide species (e.g. Co, Ni). The formation of iron hydroxide leads to an increase in the number of surface sites available for sorption of charged species and a corresponding reduction in their aqueous concentration. There is also an increased probability of the formation of colloidal particles involving humic and fulvic substances.

Changes in pH and Eh are both possible during the tracer test, where waters of differing compositions are likely to mix within the aquifer as a result of pumping. These will be modelled and presented in part II, along with predictions for the speciation of various radionuclides added to the groundwater.

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#### 1. Introduction

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Groundwater has been pumped from a confined glacial sand aquifer at Drigg in which an array of boreholes has been constructed for radiotracer experiments. During the pumping test, groundwater samples were obtained and analysed (Haigh et al., 1989). This enabled the geochemical speciation code PHREEQE (Parkhurst et al. 1982) to be used to calculate the chemical species that may exist in the groundwater and to identify the geochemical controls on reactive radionuclide species introduced into the system.

The report is in two parts: part I considers the natural speciation chemistry of the groundwater and part 2 considers changes brought about by the introduction of radionuclides and organic species.

#### 2. Description of Drigg Borehole Array

The geology of the experimental site has been described by Wealthall et al. (1988). It consists of a glacial sand interbedded between two clay horizons. The sand is heterogeneous containing lenses of clay, which is reflected in the results of preliminary nonreactive tracer experiments (Sen et al., 1989). A general cross-section outlining the geology and the arrangement of observation and testing wells is given in Figure 1, with a plan-view of the borehole array in Figure 2.

Data on the mineralogy, petrology and cation exchange capacities of the glacial sand have been reported elsewhere (Bloodworth and Inglethorpe, 1988). The aquifer consists mainly of quartz (>60%), together with of various feldspars and clay minerals. In the lower, more silty part of the aquifer some calcite has been found. The organic matter content is around 1-2% by weight. As would be expected in glacial sediments the properties vary considerably throughout the site. Total cation exchange capacities reflect the distribution of the clay content in the profile.

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Figure 1: Cross-section through the experimental array.



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Figure 3: Draw-down response of well D219 during pumping test, 16/09/87, a) plotted on linear time axis; b) plotted on logarithmic time axis.

#### 3. The Pumping Test

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This test was carried out in borehole D219 the position of which is given in Figure 2. Borehole D219 is used as release well during the tracer tests (Sen et al. 1989). The test was run at a pumping rate of 1.2 l/min and lasted for approx. 6 hours. The draw-down response is given in Figure 3a.

The time to empty any significant wellbore storage was calculated to be 23 minutes. After approx. 120 minutes significant vertical leakage occurred. Analysis of the pumping test (Jacob method) yield a transmissivity of  $2.0 \times 10^{-5}$  m<sup>2</sup>/s. The total volume of aquifer sampled was estimated to be 1.6 m<sup>3</sup>. The radial distance sampled around the well assuming no mixing and no dispersion is approx. 1.2 m.

Plotting the drawdown on a log scale time axis (Figure 3b) reveals three different zones. The drawdown from 0 to 23 mins. can be attributed to emptying the wellbore storage. It is suggested that from 23 to 200 mins. the major contribution comes from flow from the aquifer, while after 200 mins. leakage from adjacent strata becomes significant (Brightman et al. 1989).

#### 4. Analytical Procedures

Throughout the pumping test oxidation-reduction potential, pH, temperature and the electrical conductivity were determined through in-line field measurements. Groundwater samples were also taken at 20 min. intervals and analysed, the results are given in detail by Haigh et al. (1989).

Eh was determined in the field using an Orion combination redox electrode (97-78) connected to an Orion meter (407A). pH was determined with an Orion combination electrode (91-05) which had been calibrated with pH 7.0 and pH 10.0 buffers. Electrical conductivity was determined using a pHOX conductivity probe and meter.

Groundwater samples for chemical analyses were filtered after collection using  $0.45\mu m$  filters with glass fibre prefilters. 30 ml of the filtered sample was added to 0.3 ml of ARISTAR concentrated HCl in a Nalgene HPDE bottle. This sample was used for Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis and Total

Organic Carbon (TOC) determination. Another 30 ml filtered sample was added to 0.3 ml of 2M sodium hydroxide solution for analysis of sulphide by ICP-OES. Anions were determined on filtered, unpreserved samples with Ion-Chromatography (IC). Total alkalinity was also determined on filtered, unpreserved samples.

The determination of Ca, Mg, Na, K, total S, Si, Ba, Sr, Mn, Fe, Al, total P, Ni, Mo, Cr, Co, Zn, Cd, Pb and Cu was carried out using a Perkin-Elmer Plasma II Emission Spectrometer. The precision is usually around 1%. Reduced sulphur was also determined using ICP-OES (Cave and Green, 1988). Samples and standard were prepared by pipetting 15 ml of either sample or standard into an autosampler tube, and adding a known volume of 1000 mg/l Sc solution; the ratio of volumes of Sc-solution to sample being no less than 0.4 to 15 ml. Precision is around 5%. The anions Cl<sup>-</sup>, SO4<sup>2-</sup>, Br, NO3<sup>-</sup> and HPO4<sup>2-</sup> were determined with a Dionex 2000i Ion Chromatograph fitted with an AG4A guard column, an AS4A separator column and an AMMS anion micro-membrane suppressor. The precision was 1-3% on 0.7 ml samples, depending on the total concentration. Fluoride was determined with an Ion-Sensitive Electrode (ISE). Total alkalinity was determined in the laboratory titrating a sample with 0.1M sulphuric acid against an end point of pH 4.3, measured with a pH-electrode.

### 5. Changes in Groundwater Chemistry During Pumping

Examination of time versus concentration profiles (Figures 4 and 5) for the 19 samples collected suggests that there are 3 different phases throughout the course of the pumping test (*cf.* Figure 3b).

The initial phase (I) represents emptying of the well, and examination of Table 1 below shows that there is possibly some contamination in this period, e.g. by iron, zinc and/or copper. During the second phase (II) it can be postulated that groundwater is drawn from the aquifer around the borehole, whereas in the third phase (III) it is perhaps originating from an area further away. In comparison to the second phase, the third one has increased concentrations of calcium, chloride and sulphate.

In order to best represent the system, it was decided to model the speciation in three samples, each of which was representative of an individual groundwater composition. Samples for speciation calculations were thus chosen to be from 0, 60 and 340 minutes after the start of the pumping test.



Figure 4: Time versus concentration profile for calcium and iron.



Figure 5: Time versus concentration profile for  $HCO_3^-$  and  $SO_4^{2-}$ .

BGS La	b. Code		729	732	746
Time of	Samplin	ıg [min]	0	60	340
Species	Unit	Method	,		
<u> </u>	<u>г</u> (1)			15.20	
Ca	[mg/l]	I.C.P.	24.06	15.32	17.74
Mg	[mg/l]	I.C.P.	5.27	3.59	4.55
Na	[mg/I]	I.C.P.	24.9	12	12.7
K	[mg/l]	I.C.P.	1.25	<1.0	<1.0
Si	[mg/l]	I.C.P.	3.45	3.06	3.1
Ba	[mg/l]	I.C.P.	0.066	0.044	0.058
Sr	[mg/l]	I.C.P.	0.088	0.063	0.055
Mn	[mg/l]	I.C.P.	0.441	0.22	0.193
Fe	[mg/l]	I.C.P.	1.75	1.21	0.915
Al	[mg/l]	I.C.P.	<0.06	<0.06	<0.06
Р	[mg/l]	I.C.P.	<0.6	<0.6	<0.6
Ni	[mg/l]	I.C.P.	<0.085	<0.085	<0.085
Мо	[mg/l]	I.C.P.	<0.6	<0.6	<0.6
Cr	[mg/l]	I.C.P.	<0.12	<0.12	<0.12
Со	[mg/l]	I. <b>C.</b> P.	<0.035	<0.035	< 0.035
Zn	[mg/l]	I.C.P.	0.946	0.077	0.048
Cd	[mg/l]	I.C.P.	<0.024	<0.024	<0.024
Pb	[mg/l]	I.C.P.	<0.1	<0.1	<0.1
Cu	[mg/l]	I.C.P.	0.04	<0.015	<0.015
S <sup>2-</sup>	[mg/l]	I.C.P.	<0.006	<0.006	<0.006
Cŀ	[mg/l]	I.C.	12	12.1	14.2
SO₄²-	[mg/l]	I.C.	13.7	9.91	11.2
Br	[mg/l]	I.C.	0.15	0.15	0.09
NO3 <sup>-</sup>	[mg/l]	I.C.	0.5	0.34	<0.1
HPO42-	[mg/l]	I.C.	<0.1	<0.1	<0.1
HCO3-	[mg/l]	titr.	123	62.6	61.8
F-	[mg/l]	I.S.E.	0.107	<0.1	<0.1
TIC	[mg/l]		0	0	0
TOC	[mg/l]		7.6	3.5	2.5
pН			7.6	7.5	7.48
Eh	[mV]		228	117	140

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 Table 1: Analytical data for the three samples used in modelling.

Chemical analyses for these three samples obtained using the methods described in the previous section are given below in Table 1. It is apparent from this table, that the majority of the trace metals are present below their appropriate detection limits, and consequently, all analytical values which are preceded by a '<' have been omitted from speciation calculations.

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### 6. Modelling Methodology

#### 6.1 Introduction

The experimental examination of speciation in a complex geochemical system such as that considered by this report is difficult not only because of the many variables present, but also because of the low concentrations of many important constituents. Experimental speciation methods do exist (Aggett et al., 1983) but they are both extremely time and labour intensive. The development of computer assisted geochemical speciation codes has provided the geochemist with not only a viable alternative to the experimental study of these systems, but also an instrument that may help to elucidate areas requiring further study.

Of the large variety of thermodynamic chemical speciation codes available (for a review of those available, see Mangold and Tsang, 1987), the most suitable codes for geochemical speciation are those that have been developed specifically for modelling the geosphere. The computer code that has been used for the study of aqueous speciation in this study is PHREEQE (**pH REdox EQ**uilibrium Equations, Parkhurst et al. 1980; NEA 1984 version).

#### 6.2 Aim of Speciation Studies

The aims of the chemical speciation studies detailed in following sections can be summarized as follows.

- a/ to determine the natural chemical speciation of the system, and the effect of changing various chemical parameters, for example, pH and Eh.
- b/ to determine the solubility limiting phases.

#### 6.3 Thermodynamic Database.

A common feature of all geochemical speciation codes is the use of a thermodynamic database, containing formation constants, solubility products, and if applicable to the code, distribution coefficients. The thermodynamic database used by PHREEQE, contains formation constants ( $\beta$  values) for aqueous species and solubility products (K<sub>sp</sub> values) for

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solid species. All species in the PHREEQE database are defined in terms of a master species, with formation constants for each aqueous species being written in terms of an association reaction:

$$pM + qL + rH \iff M_p L_q H_r$$
 (i)

and those for solid phase species, i.e. solubility constants, being defined in a similar manner, but written in terms of a dissociation reaction:

$$MX_{(s)} \iff M^{n+} + X^{N-} \qquad \qquad (ii)$$

The thermodynamic database in use at UWIST (UWIST, 1987) undergoes continual reevaluation and expansion through the incorporation of formation constants and solubility products which have been experimentally measured by various workers in this field. All the formation constants and solubility products incorporated in the UWIST thermodynamic database have been taken from the open literature which has of course been subject to peer review. These constants represent the best thermodynamic data currently available. In many cases ionic strength corrections to these constants are required because the thermodynamic constants used by PHREEQE are required to be under set standard conditions, i.e. at a temperature of 25°C, and an ionic strength of I= 0.0. The method of correction currently in use is the Davies equation, the application of which is well understood, and enables the correction of formation constants in an ionic strength range of I= 0.0 to I= 0.3 mol dm<sup>-3</sup>.

#### 6.4 Speciation Calculations

#### 6.4.1 Overview

The speciation calculations detailed in Part I of this report can be divided into two classes. The first of these comprises simple speciation calculations considering aqueous components only, and allow for no mass transfer between the aqueous and solid phase. These calculations have been undertaken in order to establish the natural aqueous chemical speciations of the groundwaters before they are perturbed by the tracer tests, and to gain a better understanding of the systems response to changes in chemical parameters. The other class involves precipitation-dissolution reactions which consider the response of the system to equilibration with solids. The solids for these calculations were chosen after considering their saturation state (calculated previously), and the geochemical likelihood of their presence in the aquifer. For some of the solids, e.g. iron hydroxides, no experimental corroboration is available since the mineralogical studies (Bloodworth and Inglethorpe, 1988) analysed only the bulk mineral content and not the surface.

Mineralogical analysis to validate thermodynamic geochemical speciation findings is anticipated in the future.

#### 6.4.2 pH and Eh Scans

As can be seen from the experimental concentration versus time profiles (see Figure 6), some variability is observed in the measured pH and Eh values.



Figure 6: Time versus concentration profile for pH and Eh measurements.

The variability of Eh analytical values has led various workers in this field (Lindberg et al. 1984, Nordstrom 1986) to believe that the oxidation-reduction couples commonly found in groundwaters are not in equilibrium. Indeed, Nordstrom has found that the oxidation-reduction chemistry of the groundwater under study was most likely to be dominated by sulphide, organic carbon and iron. Furthermore, Brownlow (1979) has concluded that:-

"... The major controls on Eh and pH are:- (1) the organic process of photosynthesis, respiration, and decay; (2) oxidation-reduction reactions involving iron, sulfur, and carbon; and (3) the balance between dissolved CO<sub>2</sub> and calcium carbonate in natural waters ..."

In the groundwater samples considered in this report, it is most likely that the oxidationreduction potential of the system is determined by either sulphur or iron oxidation-reduction reactions.

In order to investigate the behaviour of the system at different pH and Eh values, and to avoid the scenario of basing geochemical conclusions on speciation calculations that were too restrictive, it was decided to scan the pH (or Eh) over the experimentally observed range. This technique has the added advantage of providing a means of observing trends in the system with changes in a single chemical parameter.

The technique used to carry out these scans, involved setting the pH or the Eh to the lowest desirable value (determined from the field measurements) and increasing the appropriate chemical parameter by a set increment to an upper limit (also determined from the field measurements) whilst carrying out speciation calculations using PHREEQE at each step. The output from the PHREEQE computer code is then converted into tabular form and presented as a plot of species concentration *versus* pH or (Eh). The following ranges were used:-

pH scan:	pH 5.5	to	pH 8.0,	increments of 0.5 pH units.
Eh scan:	Eh = -100  mV	to	+200 mV,	increments of 50 mV.

#### 6.4.3 Mass Transfer Calculations

Mass transfer calculations were carried out using the PHREEQE computer code to equilibrate the aqueous system with a designated mineral, and comparing the initial and final

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concentrations of all elements considered in the calculations. As previously stated, the minerals were chosen according to the following:-

- a) the saturation state of the mineral calculated previously
- b) the geochemical likelihood of the mineral being present in the sediment.

The minerals chosen for this study were drawn from the following list:-

Fe(OH)<sub>3</sub> amorphous, Fe(OH)<sub>3</sub> crystalline, Fe<sub>3</sub>(OH)<sub>8</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>S<sub>4</sub>, goethite, haematite, magnetite and siderite.

#### 7. Results

#### 7.1 Introduction

This section summarizes the results from the speciation plots presented in Appendix B. Some of these plots (Figures 7 to 12) are duplicated in this section purely to emphasize salient points.

The speciation profiles presented in Appendix B can be divided into three representing the different groundwater analyses adopted. Further subdivision gives five sub-sectors, corresponding to individual elemental groups (i.e. calcium, carbonates, iron, solid phases and sulphur) which have been chosen for this study. This results in the following speciation plots for each sample (1, 2, 3):-

pH scan
pH scan
pH scan
Eh scan at $pH = 7.0$
Eh scan at $pH = 7.5$
pH scan
Eh scan at $pH = 7.0$
Eh scan at $pH = 7.5$
pH scan
Eh scan at $pH = 7.0$
Eh scan at $pH = 7.5$

The Eh scans for calcium and carbonate speciation plots are not included as no changes were observed in the dominant aqueous species throughout the Eh range scanned (-100 to +200mV). One example of a carbonate Eh scan is presented in Appendix B (*cf.* Figure 8).

In addition to the Eh scans detailed above, oxidation-reduction speciation calculations for samples 2 and 3 were carried out at pH 7.2. However the majority of information portrayed on these plots was redundant when compared to the speciation plot obtained at pH 7.0.

A full list of the species considered in the modelling is given in Appendix A, with the species that are included on the speciation plots having a molality greater than  $10^{-12}$  mol dm<sup>-3</sup>.

#### 7.2 Calcium

The calcium speciation plots presented in Appendix B, show that over the range of pH values considered, the dominant aqueous form of calcium is the free  $Ca^{2+}$  ion. Calcium carbonate,  $CaCO_3^0$ , of which the corresponding solid phase calcite has been observed in the sediments, is not a significant form of calcium, only forming approximately 0.36%.  $(Ca^{2+}=96\%, CaSO4^0 = 1.8\%, CaHCO3^+ = 1.5\%)$ . As expected, the concentration of  $CaCO3^0$  increases with increasing pH, but examination of the relevant saturation index graphs reveals that the precipitation of calcium carbonate as the mineral calcite in this system is unlikely.

#### 7.3 Carbonate

The carbonate pH speciation plots (see Figure 7) for all samples show that the major aqueous species is either  $H_2CO_3^0$ , or  $HCO_3^-$  (depending on the pH). The  $H_2CO_3^0$  species dominates at pH values below 6.25, with the bicarbonate species being the predominant aqueous species above this value. This speciation is the same as that expected from a study of the appropriate pK<sub>a</sub> values ( $CO_3^{2-}$ ,  $HCO_3^-$ ,  $H_2CO_3^0$ ). At pH = 7.5, the relative aqueous distribution of the carbonates can be summarized as follows:-

CO <sub>3</sub> <sup>2-</sup>	0.2%
HCO3 <sup>-</sup>	92,1%
H <sub>2</sub> CO <sub>3</sub> <sup>0</sup>	6.1%
Others	1.6%

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The combined metal carbonates, car be seen to constitute only 1.6% of the aqueous carbon, and hence do not have any major influence on carbonate speciation.

It was previously suspected that changes in the redox potential could alter the aqueous carbonate speciation through changes in the aqueous sulphur speciation. It was postulated that altering the oxidation-reduction potential would effect the sulphide concentration as per equation (iii)

$$S^{2-} + 4 H_2O \iff SO_4^{2-} + 8 H^+ + 8 e^-$$
 (iii)

which would change the aqueous calcium speciation via equation (iv)

$$Ca^{2+} + SO_4^{2-} \iff CaSO_4^0$$
 (iv)

and alter the equilibrium concentration of carbonate via equations (v), (vi), (vii)

$Ca^{2+} + CO_3^{2-}$	⇔	CaCO <sub>3</sub> <sup>0</sup>	(v)
$H^{+} + CO_{3}^{2-}$	⇔	HCO3-	(vi)
H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	⇔	H <sub>2</sub> CO <sub>3</sub> <sup>0</sup>	(vii)

The modelling studies have however revealed that sulphide is not a major species and hence there is no 'feedback' from the sulphur oxidation-reduction system into the calcium system.

The carbonate versus Eh plot presented for sample 1 (see Figure 8), demonstrates overwhelmingly that there is no feedback via sulphur into the carbonate system from changes in the redox potential of the system. The major species throughout the Eh range scanned is  $HCO_3^-$ , which accounts for ca. 94% of the total.



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Figure 7: Selected carbonate species versus pH. Data from sample 1.



Figure 8: Selected carbonate species versus Eh. Data from sample 1.

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7.4 Iron

Two species of iron are dominant within the range of the conditions examined. The first of these,  $Fe^{2+}$ , is dominant at pH below 7.0 and below an Eh of 110mV, whilst the iron(III) hydroxide  $Fe(OH)_{3^0}$  is the major species above these values. The appearance of  $Fe(OH)_{3^0}$  as a dominant species at high pH or Eh values is important, because it implies that the chemistry of the iron system is no longer being controlled by iron(II) reactions, but instead by those of iron(III).

Examination of the iron pH scans shows that Eh as well as pH affect the formation of  $Fe(OH)_3^0$ , (Figure 9). As the Eh increases (e.g. sample 1) the iron(III) hydroxide species  $(Fe(OH)_3^0)$  becomes dominant at correspondingly lower pH values (*cf.* sample 2). A similar effect can be seen in pH dependency of this species in the Eh scans.

At pH = 8.0,  $Fe(OH)_3^0$  is the dominant species, and the next most important species are also hydroxides,  $Fe(OH)_2^+$  and  $Fe(OH)_4^-$ .







Figure 10: pH effect on iron speciation *versus* Eh, at pH 7.0 (top) and pH 7.5 (bottom), species with concentrations less than 10<sup>-12</sup> molar omitted, data from sample 2.

The iron Eh scans similarly show iron(III) to be the major redox state at high Eh values. The pH dependence of the iron(II) and iron(III) relationship is emphasized in the speciation plots for sample 2 (Figure 10). When the Eh scan was run at the lower pH, i.e. pH=7.0 at an Eh of +200 mV, Fe<sub>2</sub><sup>+</sup> is found to be the major aqueous form of iron, whilst at pH=7.5and the same Eh value, Fe(OH)<sub>3</sub><sup>0</sup> is the primary iron species in solution.

#### 7.5 Sulphur

The sulphur speciation plots all show the major aqueous form of sulphur to be the free sulphate ion  $SO_4^{2-}$ . This species remains the most abundant form of aqueous sulphur throughout a variety of conditions (see Appendix B and also Figure 11), i.e. from pH = 5.5 to 8.0 and Eh = -100mV to +200mV, hence it can be concluded that the influence of varying pH and Eh on the sulphur system is negligible within the boundaries of interest here.





Figure 11: Major sulphur species versus pH, data from sample 1.

#### 7.6 Solid Phases

The saturation index of a solid phase, which is defined as

$$SI = \log (IAP / K_{sp})$$

#### where IAP is the ion activity product

provides an indication whether a particular solid phase will precipitate or remain in solution. It can also be used to predict if the dissolution of a solid phase will occur depending on its value. The following shows possible values for log  $(IAP/K_{sp})$ :

SI	<	0	phase is undersaturated
SI	=	0	phase is in equilibrium
SI	>	0	phase in supersaturated

Examination of the saturation index plots in Appendix B reveals that the profiles of many minerals do cross the "zero" line i.e.  $\log (IAP/K_{sp}) = 0$ , and hence will have a tendency to precipitate. It must be remembered that these plots only predict whether it is thermo-dynamically possible for a certain species to precipitate or dissolve, and that they give no information about the aqueous concentration of the solid phase precursor. Of the various minerals detailed on the plots, the only ones that are liable to be present in the system in appreciable amounts are goethite, calcite and the iron hydroxides. Aqueous FeCO<sub>3</sub> is only found in concentrations of less than  $10^{-12}$  mol dm<sup>-3</sup>, and so is unlikely to precipitate as siderite. The other iron oxides are found in similar concentrations well below saturation.

It can be seen from the graphs (see Appendix B and also Figure 12), that calcite is unlikely to precipitate under all conditions. Calcite has been responsible for the co-precipitation of certain doubly charged cations of a smaller ionic radius (Pingitore 1986), which is a situation that is unlikely to occur in this system.

In contrast, the iron hydroxide minerals are near saturation. The iron(III) hydroxide species  $(Fe(OH)_3^0)$  is dominant in the alkaline and oxidizing (>110mV) regions examined, and the saturation index plots reveal that the precipitation of both the amorphous and crystalline forms of Fe(OH)<sub>3</sub> is possible. It must be emphasized that the formation of crystalline Fe(OH)<sub>3</sub> in preference to amorphous Fe(OH)<sub>3</sub> is unlikely. The initial precipitate of amorphous Fe(OH)<sub>3</sub> will then undergo ageing and crystallisation.



Figure 12: Saturation index of selected solids versus pH, data from sample 3.

### 7.7 Precipitation-Dissolution Reactions

The precipitation-dissolution calculations presented in Appendix C suggest that the equilibration of the aqueous phase with solid phase iron containing minerals results in the removal of iron from the aqueous phase. This is supported by comparison with the solid phase speciation plots (see above) and the aqueous iron speciation profiles, which show in many cases, that insoluble iron species are super-saturated by at least one order of magnitude.

The geochemically most important minerals to consider are the amorphous and crystalline forms of Fe(OH)<sub>3</sub> because the aqueous precursors of other minerals are present in concentrations of less than  $10^{-12}$  mol dm<sup>-3</sup>. The equilibration of the aqueous system with iron(III) hydroxides (Fe(OH)<sub>3</sub> *amorphous* and *crystalline*) reveals that a substantial proportion of iron is removed from the aqueous phase and transferred into the solid phase, possibly as surface bound hydroxides which will not be observed in mineralogical analyses of the bulk solid phase.

#### 8. Discussion and Conclusions

1

The speciation calculations reported here have described the natural state speciation of each element identified in groundwater from the experimental array. This speciation is summarized in Table 2 where a listing is given of percentage abundance of major aqueous species likely to exist in each of the 3 groundwater compositions considered.

It can be seen from Table 2, that for all the non-transition metal elements the major aqueous species is the ionized 'uncomplexed' element; i.e. the free ion. For example, the major form of calcium is  $Ca^{2+}$ . However, for the transition metal elements; i.e. manganese, iron and zinc, the major aqueous species is not the free metal ion. Indeed, for manganese, the carbonate species is by far the most abundant. This difference in aqueous speciation reflects the different complexing abilities of elements in the transition metal block as compared to those in other parts of the periodic table.

The speciation calculations to date, have shown that the speciation of aqueous iron is very sensitive to changes in pH and oxidation-reduction potential (see section 7.4). This is emphasized by comparison of the aqueous iron speciation for samples 1 and 2, where the oxidation-reduction potential has changed by only 110mV, from +227mV to +117mV and the dominant aqueous species has changed from Fe(OH)<sub>3</sub><sup>0</sup> to Fe<sup>2+</sup>. The total change in the concentration of Fe(OH)<sub>3</sub><sup>0</sup>, over this range of oxidation-reduction potential is from 2.8 x 10<sup>-5</sup> mol kg<sup>-1</sup> to 4.1 x 10<sup>-6</sup> mol kg<sup>-1</sup>, i.e. by an order of magnitude. The formation of Fe(OH)<sub>3</sub><sup>0</sup> as a dominant aqueous species under oxidizing conditions is important because the calculations (see section 8.6) suggest that species such as this may precipitate.

A consequence of the formation and precipitation of iron hydroxides in the unperturbed aqueous system is that a significant proportion of the iron is predicted to transfer from the aqueous into the solid phase. The analyses of the aqueous phases suggests that in reality this does not occur, implying the presence of solubilising matter, e.g. natural organic matter. Furthermore the predicted formation of iron hydroxides would lead to an increase in the number of surface sites available for sorption of charged species and a corresponding reduction in their aqueous concentration. There is also an increased probability of the formation of colloidal particles involving humic and fulvic substances. Indeed, it has been shown (Theng 1976, 1979) that divalent and higher valence cations form bridges between polyanionic humic substances and negatively charged inorganic colloids such as iron hydroxides. This in turn reduces the concentration of other cations in the aqueous system.

measured pH measured Eh [mV]		7.60 +227	7.50 +117	7.48 +140
Element	Species	Sample 1 % abundance	Sample 2 % abundance	Sample 3 % abundance
Calcium	Ca <sup>2+</sup>	96.2	97.6	97.4
	CaHCO <sub>3</sub> ⁺	1.5	< 0.1	< 0.1
	CaSO₄⁰	1.9	1.4	1.6
Magnesium	Mg <sup>2+</sup>	96.4	97.6	97.7
	MgHCO <sub>3</sub> +	1.7	< 0.1	< 0.1
Sodium	Na⁺	99.8	99.9	99.9
Zinc	Zn <sup>2+</sup>	58.7	75.5	no zinc
	ZnOH⁺	2.1	2.3	present
	ZnCO <sub>3</sub> <sup>0</sup>	31.2	17.4	
Iron	Fe <sup>2+</sup>	2.7	77.5	63.2
	Fe(OH) <sub>2</sub> <sup>+</sup>	5.2	1.3	2.4
	Fe(OH) <sub>3</sub> <sup>0</sup>	91.0	18.7	32.2
Manganese	Mn <sup>2+</sup>	10.5	21.4	22.6
	MnCO <sub>3</sub> <sup>0</sup>	89.0	78.0	76.7
Silicon	H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup>	99.5	99.6	99.6
Chlorine	Cl <sup>-</sup>	99.9	99.9	99.9
Bromine	Br	99.9	99.9	99.9
Fluorine	F	98.4	no fluorine	no fluorine
	MgF⁺	1.2	present	present
Sulphur	SO4 <sup>2+</sup>	91.0	93.9	93.1
	CaSO₄ <sup>0</sup>	6.8	4.1	4.6
	MgSO4 <sup>0</sup>	2.0	1.5	1.9
Carbon	HCO3 <sup>-</sup>	93.7	92.8	92.5
(inorganic)	H <sub>2</sub> CO <sub>3</sub> <sup>0</sup>	4.9	6.3	6.5
Nitrogen (inorganic)	NO3 <sup>-</sup>	99.7	99.9	no nitrogen present

1.14

 Table 2: Percentage molar abundance of major species for each sample

A further reduction in the aqueous concentration of cations may be induced through the formation of mixed hydroxy polymeric species with iron. Quantitative modelling of such systems is not possible at the present time due to lack of thermodynamic data relating to the formation of even simple polymers.

As previously stated (see section 7.6), modelling studies predict that the precipitation of calcium carbonate (as calcite) from the aqueous phase is unlikely. This can be seen from the calculated saturation index, which does not exceed zero. Calcite, has however been observed in the mineralogical analyses (Bloodworth et al., 1988) and this may be a source of calcium carbonate via dissolution.

A consequence of the calcium carbonate not being supersaturated in solution and thus not being likely to precipitate is that the co-precipitation of other doubly charged cations (e.g.  $Ba^{2+}$  and  $Sr^{2+}$  is concluded not to occur. This is particularly important, as in the past it was surmised that strontium which was a radionuclide of interest in previous tests (Williams et al., 1985) might have been removed from the aqueous phase by co-precipitation with calcium carbonate.

The measured pH of these groundwater samples is slightly alkaline, and their aqueous iron chemistry is very sensitive to shifts in both the pH and the oxidation-reduction potential of the system as a whole. One possible process which will alter either of these parameters is the pumping of oxygenated water into the system as quantified by equation (viii)

$$H_2O \Leftrightarrow O_2(g) + 4 H^+ + 4 e^-$$
 (viii)

This process might occur in the tracer test if groundwater of differing redox states are mixed as a result of pumping. It would be valuable to model, this process since formation or dissolution of solid phase iron complexes is likely to have a profound effect on tracemetal chemistry. Part II of this report will consider this process in more detail, along with results of speciation modelling the groundwater system following the introduction of radionuclides tracer

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## Appendix A.

This appendix gives a list of all the aqueous species that have been considered in the computer assisted modelling calculations.

AC = Acetate						
H⁺	SiO4	Ba(NO <sub>3</sub> ) <sub>3</sub> .	FeCl,	ZnNO <sub>3</sub> +	Mn(OH) <sub>3</sub>	H <sub>2</sub> EDTA <sup>2</sup>
C.	SiF <sub>6</sub> <sup>2</sup>	$Ba(NO_3)_4^2$	FcSO₄⁺	$Zn(NO_3)_2$	MnCl*	H <sub>3</sub> EDIA <sup>-</sup>
H <sub>2</sub> O	CaOH⁺	BaSO₄ ►	FcSO <sub>4</sub> <sup>2-</sup>	$Zn(NO_3)_3$	MnCl <sub>2</sub>	HEDTA
Ca²+	CaCO,	$Ba(SO_4)_2^{2}$	FcF <sup>2+</sup>	Cu(OH)*	MnCl <sub>3</sub>	H <sub>5</sub> EDIA <sup>+</sup>
Mg <sup>2+</sup>	CaHCO <sub>3</sub> *	ВаНСО,	FcF <sub>2</sub> <sup>+</sup>	Cu(OH) <sub>2</sub>	MnHCO <sub>3</sub> *	H <sub>6</sub> EDIA"
Na*	CaSO4	BaCO <sub>3</sub>	FcF,	Cu(OH),	MnSO <sub>4</sub>	
K⁺	CaF <sup>+</sup>	Co(OH)⁺	FcCl₄	HCuO <sub>2</sub>	$Mn(NO_3)_2$	
Fe <sup>2+</sup>	CaCl <sup>+</sup>	Co(OH) <sub>2</sub>	FeBr <sup>2+</sup>	Cu(OH) <sub>4</sub> <sup>2</sup>	MnF <sup>+</sup>	MgEDIA
Mn <sup>2+</sup>	CaH <sub>2</sub> SiO <sub>4</sub>	Co(OH),	FcBr <sub>2</sub> *	$Cu_{2}(OH)_{2}^{2+}$	Mn <sup>3+</sup>	MGHEDIA
Ba <sup>2+</sup>	CaH <sub>3</sub> SiO <sub>4</sub> +	Co(OH) <sub>4</sub> <sup>2</sup>	FcH <sub>3</sub> SiO₄	CuO <sub>2</sub> <sup>2</sup>	MnO <sub>4</sub> <sup>2</sup>	NaEDIA <sup>3</sup>
Sr <sup>2+</sup>	$Ca(H_3SiO_4)_2$	CoF <sup>+</sup>	FcNO <sub>3</sub> <sup>2+</sup>	CuSO₄	MnO <sub>4</sub> .	Nahedi A <sup>2</sup>
H₄SiO₄	CaNO,*	CoCl <sup>+</sup>	FcOH <sub>4</sub> <sup>2</sup>	CuF <sup>+</sup>	Mn <sub>2</sub> (OH) <sup>3+</sup>	Na <sub>2</sub> EDIA <sup>2</sup>
Cl	Ca(NO <sub>3</sub> ) <sub>2</sub>	CoCl <sub>2</sub>	FcHCO <sub>3</sub> +	SrOH⁺	Mn <sub>2</sub> (OH) <sub>3</sub> <sup>+</sup>	KEDIA <sup>2</sup>
CO, 2.	MgOH <sup>+</sup>	CoCl,	FcCl <sup>+</sup>	Sr(OH) <sub>2</sub>	Mn(OH) <sub>4</sub> <sup>2</sup>	KHEDIA"
SO <sup>2</sup> .	MgCO,	CoCl <sub>4</sub> <sup>2</sup>	FeCl <sub>2</sub>	$Sr(NO_3)_2$	MnCO <sub>3</sub>	FeEDTA <sup>®</sup>
NO,	MgHCO,*	CoBr <sup>+</sup>	FeF <sup>+</sup>	SrCO <sub>3</sub>	MnBr*	Fehedia
F	MgSO	CoBr <sub>2</sub>	Zn(OH)⁺	SrHCO <sub>3</sub> +	MnNO <sub>3</sub> *	FeH_EDTA
Co <sup>2+</sup>	MgF <sup>+</sup>	CoNO,*	Zn(OH) <sub>2</sub>	SrSO	MnCl <sup>2+</sup>	FeEDTAOH <sup>2</sup>
Br	Mg <sub>4</sub> (OH) <sub>4</sub>	$Co(NO_3)_2$	Zn(OH)	SrCl <sup>+</sup>	HAC	FeEDTOH <sub>2</sub> +
ŀ	MgC1*	CoSO	HZnO <sub>2</sub> .	SrCl <sub>2</sub>	CaAC*	FeEDTA
Zn <sup>2+</sup>	MgBr⁺	$Co(SO_4)_2^2$	Zn(OH) <sub>4</sub> 2	SrF <sup>+</sup>	MgAC*	FeHEDTA
Cu <sup>2+</sup>	MgH,SiO,	Co <sup>3+</sup>	Zn,(OH) <sup>3+</sup>	SrF <sub>2</sub>	NaAC	FeEDTA(OH) <sup>2</sup>
AC	MgH,SiO,	Co(OH) <sup>2+</sup>	Zn <sub>2</sub> (OH) <sub>6</sub> <sup>2</sup>	SrNO,*	FeAC <sup>+</sup>	FeEDTA(OH) <sub>2</sub> <sup>5</sup>
EDTA⁴-	Mg(H,SiO,),	CoCl <sup>2+</sup>	ZnCO,	CuF,	FcAC <sup>2+</sup>	FeEDTA(OH)2+
HSO,	NaCO,	Co <sub>4</sub> (OH) <sub>4</sub> <sup>4+</sup>	$Zn(CO_{3})^{2}$	CuNO,*	FeAC <sub>2</sub> <sup>+</sup>	MnEDTA <sup>2</sup>
H,SO,	NaHCO,	Co,(OH)3+	ZnHCO,	Cu(NO,)	FeAC <sub>3</sub>	MnHEDTA <sup>-</sup>
S <sup>2.</sup>	NaSO	FeOH⁺	ZnSO	Cu(NO <sub>1</sub> ),	MnAC <sup>+</sup>	MnEDTA <sup>-</sup>
HS <sup>.</sup>	NaOH	FeOH,	$Zn(SO_{4})^{2}$	CuCl <sup>+</sup>	BaAC⁺	BaEDTA <sup>2</sup>
H	Na,SO,	FeOH	Zn(SO),4	CuCl,	SrAC <sup>+</sup>	BaHEDIA
О́Н <sup>.</sup>	NaCl	FeSO	Zn(SO)	CuCl	CoAC*	SrEDIA
0,	NaF	Fe(HS),	ZnCl <sup>+</sup>	CuCl <sup>2</sup>	CoAC <sub>2</sub>	STHEDTA
H,	NaNO,	Fe(HS),	ZnCl,	CuBr <sup>+</sup>	CoAC,	COEDTA
HNO.	KSO,	Fe <sup>3+</sup>	ZnCl	CuCO,	ZnAC <sup>+</sup>	CoHEDTA
HF	кон	FeOH <sup>2+</sup>	ZnCI(OH)	Cu(CO,),2	ZnAC <sub>2</sub>	COEDTA
HF	KCI	FeOH,⁺	ZnF⁺	CuHCO,	ZnAC <sub>3</sub> <sup>-</sup>	CoHEDTA
HCÍ	KNO,	FeOH	ZnBr⁺	Cu <sup>+</sup>	ZnAC <sup>2</sup>	ZnEDTA <sup>2</sup>
HCO.	BaOH⁺	FeOH	ZnBr,	CuCl,	CuAC <sup>+</sup>	ZnHEDTA <sup>.</sup>
H,CO.	BaF⁺	Fe,(OH),⁴	ZnBr,	CuCl <sup>2</sup>	CuAC <sub>2</sub>	ZnHEDTA
H,SiO.	BaCl <sup>+</sup>	Fe,(OH),5+	ZnS	CuBr	CuAC <sub>3</sub>	CuEDTA <sup>2</sup>
H,SiO.2	Ba(NO.)⁺	FeCl <sup>2+</sup>	Zn(HS),	CuBr,	CuAC <sup>2</sup>	CuHEDTA <sup>.</sup>
HSiO	Ba(NO,),	FeCl <sub>2</sub> <sup>+</sup>	Zn(HS),	Mn(OH)⁺	HEDTA <sup>3</sup>	CuEDTA(OH) <sup>3</sup>
#### Appendix B

This appendix contains all the speciation profiles that have been produced from the computer modelling studies. All the species that are listed in Appendix A have been considered in these studies, but only species that have a concentration greater than 10<sup>12</sup> mol dm<sup>-3</sup> have been presented on the following plots.

### Calcium speciation Vs pH, Drigg sample 1

Temperature =  $25^{\circ}$ C, Eh = +228 mV



# Calcium speciation Vs pH, Drigg sample 2

Temperature =  $25^{\circ}$ C, Eh = +117mV



рΗ

## Calcium speciation Vs pH, Drigg sample 3

Temperature =  $25^{\circ}$ C, Eh = +141 mV



### Carbonate speciation Vs pH, Drigg sample 1

Temperature =  $25^{\circ}$ C, Eh = +228 mV





### Carbonate speciation Vs pH, Drigg sample 3

Temperature =  $25^{\circ}$ C, Eh = + 141 mV





## Iron speciation Vs pH, Drigg sample 1

Temperature = 25°C, Eh = +228 mV







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•



Eh ( /mV )



### Iron speciation Vs Eh, Drigg sample 3

Temperature = 25°C, pH = 7.0



. .



Temperature =  $25^{\circ}$ C, Eh = +228 mV



• Temperature =  $25^{\circ}$ C, Eh = +117 mV





Temperature = 25°C, pH = 7.6



Temperature =  $25^{\circ}$ C, pH = 7.0





Temperature = 25°C, pH = 7.5



Temperature =  $25^{\circ}$ C, pH = 7.48



Eh ( /mV )

•••



рН

#### Saturation Index Vs pH, Drigg sample 2 Temperature = 25 °C, Eh = 116mV ▲ BaCO<sub>3</sub> Calcite 7. Fe(OH)<sub>3</sub>a -Fe(OH)<sub>3</sub>cry -Fe<sub>3</sub>(OH)<sub>8</sub> 5 o-Fe<sub>3</sub>O<sub>4</sub> - Siderite Lg ( IAP/KT ) -Goethite 3 1 O -1 -3 <del>|</del> 5.0 7.5 8.0 6.5 7.0 6.0 8.5 5.5 рΗ



рΗ

### Saturation Index Vs Eh, Drigg sample 1

Temperature = 25 °C, pH = 7.6







Saturation Index Vs Eh, Drigg sample 2

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## Saturation Index Vs Eh, Drigg sample 3

Temperature = 25°C, pH = 7.5



### Appendix C

This appendix contains the results of the mass transfer calculations.

### 1 Sample 1

### 1.1 FeOH<sub>3</sub> amorphous

Equilibrated Mineral : FeOH, amorphous

	Initial	Final
pH Eh (/mV)	7.60 228	7.59 83
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca Mg Na K Fe Mn Ba Sr Si Cl Cl C S N F Br Zn	$\begin{array}{c} 602.99\\ 216.83\\ 108.31\\ 319.70\\ 31.34\\ 0.80\\ 0.48\\ 1.00\\ 122.84\\ 338.50\\ 2070.0\\ 168.43\\ 8.06\\ 5.63\\ 1.88\\ 14.47\\ 922\end{array}$	$\begin{array}{c} 602.99\\ 216.83\\ 108.31\\ 319.70\\ 0.77\\ 0.80\\ 0.48\\ 1.00\\ 122.84\\ 338.50\\ 2070.0\\ 168.43\\ 8.06\\ 5.63\\ 1.88\\ 14.47\\ 14.47\end{array}$

### **1.2** FeOH<sub>3</sub> crystalline

**Equilibrated Mineral :** FeOH<sub>3</sub> crystalline

	Initial	Final
pH Eh (/mV)	7.60 228	7.59 5
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca Mg Na K Fe Mn Ba Sr Si Cl Cl C S S N F Br Zn	$\begin{array}{c} 602.99\\ 216.83\\ 108.31\\ 319.70\\ 31.34\\ 0.80\\ 0.48\\ 1.00\\ 122.84\\ 338.50\\ 2070.0\\ 168.43\\ 8.06\\ 5.63\\ 1.88\\ 14.47 \end{array}$	$\begin{array}{c} 602.99\\ 216.83\\ 108.31\\ 319.70\\ 0.31\\ 0.80\\ 0.48\\ 1.00\\ 122.84\\ 338.50\\ 2070.0\\ 168.43\\ 8.06\\ 5.63\\ 1.88\\ 14.47 \end{array}$
Zn Cu	14.47 0.63	14.47 0.63

## 2 Sample 2

## 2.1 FeOH<sub>3</sub> amorphous

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Equilibrated Mineral : FeOH<sub>3</sub> amorphous

	Initial	Final
pH	7.50	7.49
Êh (/mV)	117	17
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca	318.64	318.64
Mg	147.70	147.70
Na	521.97	521.97
Fe	21.67	17.52
Mn	4.04	4.04
Ba	320.37	320.37
Sr	0.72	0.72
Si	108.95	108.95
Cl	341.30	341.30
C .	1025.02	1025.02
S	106.05	106.05
N	5.48	5.48
Br	1.88	1.88
Zn	1.20	1.20

## 2.2 FeOH<sub>3</sub> crystalline

Equilibrated Mineral	l :	FeOH <sub>3</sub>	crystalline
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	Initial	Final
рН	7.50	7.49
Eh (/mV)	117 -	-84
Total Concentrations (/µmol dm <sup>-3</sup> )		
Са	318.64	318.64
Mg	147.70	147.70
Na	521.97	521.97
Fe	21.67	17.40
Mn	4.04	4.04
Ba	320.37	320.37
Sr	0.72	0.72
Si	108.95	108.95
C1	341.30	341.30
С	1025.02	1025.02
S	106.05	106.05
N	5.48	5.48
Br	1.88	1.88
Zn	1.20	1.20

## 2.3 Magnetite

Equilibrated Minera	1:	Magnetite	$(Fe_3O_4)$	)
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	Initial	Final
pH Eh (/mV)	7.50 117	7.33 119
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca Mg Na Fe Mn Ba Sr Si Cl Cl C S S N Br Zn	$\begin{array}{c} 318.64\\ 147.70\\ 521.97\\ 21.67\\ 4.04\\ 320.37\\ 0.72\\ 108.95\\ 341.30\\ 1025.02\\ 106.05\\ 5.48\\ 1.88\\ 1.20\\ \end{array}$	$\begin{array}{c} 318.64\\ 147.70\\ 521.97\\ 1.42\\ 4.04\\ 320.37\\ 0.72\\ 108.95\\ 341.30\\ 1025.02\\ 106.05\\ 5.48\\ 1.88\\ 1.20\\ \end{array}$

### 2.4 Fe<sub>3</sub>OH<sub>8</sub>

Equilibrated Mineral :  $Fe_3OH_8$ 

	Initial	Final
pH	7.50	7.47
En (/mv)	117	37
Total Concentrations (/µmol dm³)		
Ca	318.64	318.64
Mg	147.70	147.70
Na	521.97	521.97
Fe	21.67	15.46
Mn	4.04	4.04
Ba	320.37	320.37
Sr	0.72	0.72
Si	108.95	108.95
C1	341.30	341.30
C	1025.02	1025.02
S	106.05	106.05
N	5.48	5.48
Br	1.88	1.88
Zn	1.20	1.20
## 2.5 Fe<sub>3</sub>S<sub>4</sub>

#### **Equilibrated Mineral :** Fe<sub>3</sub>S<sub>4</sub>

	Initial	Final
pH	7.50	7.52
Eh (/mV)	117	-113
Total Concentrations (/µmol dm <sup>-3</sup> )		
Са	318.64	318.64
Mg	147.70	147.70
Na	521.97	521.97
Fe	21.67	22.54
Mn	4.04	4.04
Ba	320.37	320.37
Sr	0.72	0.72
Si	108.95	108.95
Cl	341.30	341.30
C	1025.02	1025.02
S	106.05	107.20
N	5.48	5.48
Br	1.88	1.88
Zn	1.20	1.20

#### 2.6 Goethite

Equilibrated Mineral : Goethite (FeO(OH))

7.50 117	7.33 -122
$\begin{array}{c} 318.64\\ 147.70\\ 521.97\\ 21.67\\ 4.04\\ 320.37\\ 0.72\\ 108.95\\ 341.30\\ 1025.02\\ 106.05\\ 5.48\\ 1.88\\ \end{array}$	$\begin{array}{c} 318.64\\ 147.70\\ 521.97\\ 0.52\\ 4.04\\ 320.37\\ 0.72\\ 108.95\\ 341.30\\ 1025.02\\ 106.05\\ 5.48\\ 1.88\\ \end{array}$
	$\begin{array}{c} 7.50 \\ 117 \\ \hline \\ 318.64 \\ 147.70 \\ 521.97 \\ 21.67 \\ 4.04 \\ 320.37 \\ 0.72 \\ 108.95 \\ 341.30 \\ 1025.02 \\ 106.05 \\ 5.48 \\ 1.88 \\ 1.20 \\ \end{array}$

#### 2.7 Hematite

	Initial	Final
pH	7.50	7.32
Eh (/mV)	117	-122
Total Concentrations (/µmol dm <sup>3</sup> )		
Ca	318.64	318.64
Mg	147.70	147.70
Na	521.97	521.97
Fe	21.67	0.37
Mn	4.04	4.04
Ba	320.37	320.37
Sr	0.72	0.72
Si	108.95	108.95
Cl	341.30	341.30
C	1025.02	1025.02
S	106.05	106.05
N	5.48	5.48
Br	1.88	1.88
Zn	1.20	1.20

Equilibrated Mineral : Hematite (  $Fe_2O_3$ )

### 2.8 Siderite

Equilibrated	Mineral:	Siderite	(FeCO.)
		0.40.100	$(1000_3)$

	Initial	Final
pH Fh (/mV)	7.50	7.51
	117	111
Total Concentrations (/µmol dm³)		
Са	318.64	318.64
Mg	147.70	147.70
Na	521.97	521.97
Fe	21.67	23.85
Mn	4.04	4.04
Ba	320.37	320.37
Sr	0.72	0.72
Si	108.95	108.95
Cl	341.30	341.30
C	1025.02	1027.20
S	106.05	106.05
N N	5.48	5.48
Br	1.88	1.88
Zn	1.20	1.20

## 3 Sample 3

## 3.1 FeOH<sub>3</sub> amorphous

Equilibrated Mineral : FeOH<sub>3</sub> amorphous

	Initial	Final
pH Eh (/mV)	7.48 140	7.48 32
Total Concentrations (/µmol dm <sup>3</sup> )		
Ca Mg Na Fe Mn Ba Sr Si Cl Cl	$\begin{array}{c} 369.00 \\ 187.20 \\ 552.40 \\ 16.38 \\ 3.51 \\ 0.42 \\ 0.63 \\ 110.40 \\ 400.50 \\ 1013.00 \end{array}$	$\begin{array}{c} 369.00 \\ 187.20 \\ 552.40 \\ 10.75 \\ 3.51 \\ 0.42 \\ 0.63 \\ 110.40 \\ 400.50 \\ 1013.00 \end{array}$
S Br Zn	124.80 1.13 0.73	124.80 1.13 0.73

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## **3.2 FeOH**<sub>3</sub> crystalline

Equilibrated	Mineral	:	FeOH,	crystalline
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	Initial	Final
pH Eh (/mV)	7.48 140	7.48 68
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca Mg Na Fe Mn Ba Sr Si Cl C C S Br Zn	369.00 187.20 552.40 16.38 3.51 0.42 0.63 110.40 400.50 1013.00 124.80 1.13 0.73	$\begin{array}{c} 369.00\\ 187.20\\ 552.40\\ 10.67\\ 3.51\\ 0.42\\ 0.63\\ 110.40\\ 400.50\\ 1013.00\\ 124.80\\ 1.13\\ 0.73\\ \end{array}$

# 3.3 Magnetite

Equilibrated Mineral	l:	Magnetite (	[Fe <sub>3</sub> O <sub>4</sub> ]	
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	Initial	Final
pH Eh (/mV)	7.48 140	7.36 120
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca Mg Na Fe Mn Ba Sr Si Cl	369.00 187.20 552.40 16.38 3.51 0.42 0.63 110.40 400.50	$\begin{array}{r} 369.00\\ 187.20\\ 552.40\\ 1.12\\ 3.51\\ 0.42\\ 0.63\\ 110.40\\ 400.50\end{array}$
C S Br Zn	1013.00 124.80 1.13 0.73	1013.00 124.80 1.13 0.73

# 3.4 Fe<sub>3</sub>OH<sub>8</sub>

Equilibrated Mineral : Fe<sub>3</sub>OH<sub>8</sub>

	Initial	Final
pH Fb (/mV)	7.48	7.44 67
	140	
Total Concentrations (/µmol dm <sup>-3</sup> )		
Са	369.00	369.00
Mg	187.20	187.20
Na	552.40	552.40
Fe	16.38	8.11
Mn	3.51	3.51
Ba	0.42	0.42
Sr	0.63	0.63
Si	110.40	110.40
Cl	400.50	400.50
C .	1013.00	1013.00
S	124.80	124.80
Br	1.13	1.13
Zn	0.73	0.73

## 3.5 Fe<sub>3</sub>S<sub>4</sub>

#### Equilibrated Mineral : $Fe_3S_4$

	Initial	Final
pH	7.48	7.56
Eh (/mV)	140	-133
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca	369.00	369.00
Mg	187.20	187.20
Na	552.40	552.40
Fe	16.38	17.31
Mn	3.51	3.51
Ba	0.42	0.42
Sr	0.63	0.63
Si	110.40	110.40
Cl	400.50	400.50
Cl	1013.00	1013.00
S	124.80	126.04
Br	1.13	1.13
Zn	0.73	0.73

#### 3.6 Goethite

Equilibrated Mineral : Goethite (FeO(OH))

	Initial	Final
pH	7.48	7.37
Êh (/mV)	140	-123
Total Concentrations (/µmol dm <sup>-3</sup> )		
Ca	369.00	369.00
Mg	187.20	187.20
Na	552.40	, 552.40
Fe	16.38	0.41
Mn	3.51	3.51
Ba	0.42	0.42
Sr	0.63	0.63
Si	110.40	110.40
Cl	400.50	400.50
Ċ	1013.00	1013.00
S	124.80	124.80
Br	1.13	1.13
Zn	0.73	0.73

#### 3.7 Hematite

Initial	Final
7.48 140	7.36 -124
369.00 187.20 552.40 16.38 3.51 0.42 0.63 110.40 400.50 1013.00 124.80 1.13	$\begin{array}{c} 369.00\\ 187.20\\ 552.40\\ 0.29\\ 3.51\\ 0.42\\ 0.63\\ 110.40\\ 400.50\\ 1013.00\\ 124.80\\ 1.13 \end{array}$
	Initial 7.48 140 369.00 187.20 552.40 16.38 3.51 0.42 0.63 110.40 400.50 1013.00 124.80 1.13 0.73

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Equilibrated Mineral : Hematite (Fe<sub>2</sub>O<sub>3</sub>)

#### 3.8 Siderite

**Equilibrated Mineral :** Siderite (FeCO<sub>3</sub>)

	Initial	Final
pH	7.48	7.54
	140	117
Total Concentrations (/µmol dm <sup>-3</sup> )		κ.
Са	369.00	369.00
Mg	187.20	187.20
Na	552.40	552.40
Fe	16.38	24.10
Mn	3.51	3.51
Ba	0.42	0.42
Sr	0.63	0.63
Si	110.40	110.40
Cl	400.50	400.50
С	1013.00	1021.00
S	124.80	124.80
Br	1.13	1.13
Zn	0.73	0.73