

BRITISH GEOLOGICAL SURVEY

Technical Report WE/89/36

Fluid Processes Series

CHEMICAL SPECIATION MODELLING OF GROUNDWATER IN A SHALLOW GLACIAL SAND AQUIFER. Part II: Radionuclide Speciation and Effect of Organics

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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 PECD 7/9/367

DOE/RW/89.071

CEC Contract F1-1W-0064-UK(H)

Bibliographic reference

Quinn, G W, Duffield, J R, Falck, W E and Williams, D R. 1989. Chemical speciation modelling of groundwater in a shallow glacial sand aquifer. Part II: Radionuclide Speciation and Effect of Organics. *British Geological Survey Technical Report WE/89/36.*

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Preface

This study lies within the MIRAGE II research programme (MIgration of RAdionuclides in the GEosphere) set up by the Commission of the European Communities and supported by the UK Department of the Environment. The work forms part of the project entitled "*In situ* determination of the effects of organics on the mobility of radionuclides in controlled conditions of groundwater flow" which is being carried out by the British Geological Survey at Drigg in Cumbria, on land owned by British Nuclear Fuels Plc. The study involves the detailed geochemical and hydrogeological characterisation of a confined aquifer of glacial sand, 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 ^{58}Co and ^{63}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.

The authors are also grateful to British Nuclear Fuels plc for permission to use the Drigg site and the UK Department of the Environment and the Commission of the European Communities for funding the work.

Other reports which relate to tracer tests at Drigg include:-

Williams G M, Alexander L S, Hitchman S P, Hooker P J, Noy D J, Ross C A M, Stuart A, and West J M, 1985. *In situ* radionuclide migration studies in a shallow sand aquifer (Part 1). Report of the British Geological Survey, Fluid Processes Research Group, FLPU 85 - 7.

Williams G M, Alexander L S, Hitchman S P, Hooker P J, Noy D J, Ross C A M, Stuart A, and West J M, 1985. *In situ* radionuclide migration studies in a shallow sand aquifer (Part 2, appendices). Report of the British Geological Survey, Report No. FLPU 85 - 10.

Williams G M, Hooker P J, Ross C A M, Noy D J, Cook A, Hitchman S P, Wealthall G P. 1986. In situ radionuclide migration studies at Drigg April 1985-March 1986. Report of the British Geological Survey, Fluid Processes Research Group FLPU 86 - 4.

Warwick P, Shaw P, Williams G M and Hooker PJ, 1988. Preliminary studies of cobalt complexation in groundwater. British Geological Survey Fluid Processes Research Group Report No.WE/88/12. also in *Radiochemica Acta*, 44/45, 59 - 63.

Peachey D and Williams G M, 1987. Characterisation of humic material for inter-laboratory comparison. British Geological Survey Fluid Processes Research Group Report No. FLPU 87-5. 19pp.

West J M, 1988. The influence of microbial activity on the degradation of acetate and EDTA. British Geological Survey Fluid Processes Research Group Report No.WE/88/40.

Haigh D G, Williams G M, Hooker P J, Ross CAM 1988. The influence of organics on the sorption of cobalt by glacial sand in laboratory batch experiments. British Geological Survey Fluid Processes Research Group Report No.WE/88/20.

Falck W E 1988. Modelling the interaction between natural organic matter and metal cations: a review. British Geological Survey Fluid Processes Research Group Report No.WE/88/49.

Falck W E, Quinn G W, Duffield J R, Williams D R, 1988 Chemical speciation modelling studies on groundwater in a shallow glacial sand aquifer. PART 1: General principles. British Geological Survey Fluid Processes Research Group Report No.WE/88/48.

Haigh D G, Higgs J J W, Williams G M, Ross C A M, Falck W E, Allen M A and Warwick P, 1989. The influence of organics on the sorption of Np, Eu, U, I, Sr, and Cs by glacial sand in laboratory batch experiments. British Geological Survey Fluid Processes Research Group Report No.WE/89/16.

Longworth G, Wilkins M A and Ivanovitch M, 1988. Role of geocolloids in transport of naturally occurring radionuclides. MRS conference proceedings, Berlin, October 1988.

Executive Summary

The aims of the work detailed in this report are to gain understanding of the changes that occur in groundwater chemistry following the addition of a) the radionuclides ^{58}Co and ^{63}Ni , and b) organic complexants.

The analytical data used in these modelling studies is as for the first report in this series, and consists of inductively coupled plasma analyses for total element concentrations of three samples. For reasons that are detailed in the text (section 4.3) only two of the three samples were modelled using the PHREEQE geochemical code in conjunction with the UWCC thermodynamic database. Acetate and EDTA were used as analogues for the weakest and strongest binding expected by the natural organic matter present in the aquifer.

The results show that at the measured pH, the major form of ^{58}Co will be the Co^{2+} ion. In the case of ^{63}Ni , the major aqueous phase species is NiCO_3^0 . The speciation of cobalt is unaltered with changes in the pH or Eh, whereas nickel is pH sensitive. The formation of solid phase cobalt or nickel species is not predicted. The addition of ^{58}Co to the aquifer as a CoH_2EDTA is predicted to result in the dissociation of the complex and consequent formation of the free Co^{2+} and ZnEDTA^{2-} .

Acetate does not perturb either the natural aqueous speciation or the speciation of the added radionuclides. In contrast, using EDTA as an analogue for natural organic matter results in significant perturbations of both the natural speciation and the radionuclide speciation. It was found that 48% of the total iron, 92% of the total cobalt and 99% of the total nickel were complexed by EDTA with an EDTA concentration equivalent to the measured total organic carbon concentration of 3.5 and 2.5 mg dm^{-3} in sample 2 and 3 respectively.

Table of Contents

1. Introduction	1
2. Addition of Radionuclides to the Drigg Test Site	2
3. Rationale for choosing EDTA and Acetate as Analogues for Natural Organic Matter	3
4. Speciation Calculations	4
4.1 Introduction	4
4.2 Aims of Speciation Studies	4
4.3 Analytical Data	5
4.4 Modelling Techniques	5
5. Results	7
5.1 Addition of Co^{2+} to the Natural Groundwater	7
5.2 Addition of Ni^{2+} to the Natural Groundwater	9
5.3 The Use of Acetate as Model for Natural Organic Matter	10
5.4 The Use of EDTA as Model for Natural and Man-Made Organic Matter	15
6. Discussion and Conclusions	22
7. References	26

Appendix A: Speciation Profiles

Appendix B: List of Species Considered and Relevant Thermodynamic Data

Appendix C: Calculation of Carbonate Activities Necessary for Precipitation of Cobalt- and Nickel-Carbonate

1. Introduction

The chemistry of natural groundwater systems and the effect of organic complexants on the migration of radionuclides is being studied within a project entitled "*In-situ* Determination of the Effects of Organics on the Mobility of Radionuclides in Controlled Conditions of Groundwater Flow", being undertaken by the British Geological Survey at a low level radioactive waste repository in Drigg, Cumbria.

This report forms the second of two reports detailing the use of computer assisted geochemical speciation codes in conjunction with a thermodynamic database to investigate the aqueous phase chemical speciation within groundwater at the experimental site. It deals specifically with the introduction of two radionuclides, i.e. cobalt (^{58}Co) and nickel (^{63}Ni), into the aqueous phase of the groundwater system, and their effects on the aqueous speciation.

Cobalt has been shown to form very mobile complexes (often with EDTA) and creates the major radiological problem at many of the U.S. radioactive waste disposal sites. In the UK Co will arise in Magnox sludge and resin wastes and thus could be significant in decommissioning the Magnox stations. The inventory for light water reactor operating wastes ranks Co second in order of calculated activity arising (PINNEN et al., 1984).

Nickel is an important element in the UK ILW radionuclide inventory (HILL et al., 1981). NEWMAN and ROSS (1985) working on heavy metal migration in a range of UK aquifer sediments found that nickel was the most mobile of the metals studied (Ni, Cd, Zn, Cu, Cr, Pb). Generally nickel is the most mobile of the transition metals in groundwater contamination arising from industrial waste disposal (e.g. WILLIAMS et al., 1984). ROSS and FALCK (1987) suggested from their literature review relatively high mobility with a conservative sorption coefficient of only 10.

Part I of this series examined the natural aqueous chemical speciation within the groundwater at the experimental site and the effect of changes in pH and Eh.

2. Addition of Radionuclides to the Drigg Test Site

Radionuclides and other chemicals used in tracer experiments at the Drigg test site are introduced into the aquifer by means of a tracer release chamber which is inserted into one of the boreholes of the array (borehole D219, see Figure 2 in Part I of this report). When in place the chamber is flushed by a small submersible pump with groundwater and then shut off. The radionuclides are contained in dissolved form in glass vials which are broken me-

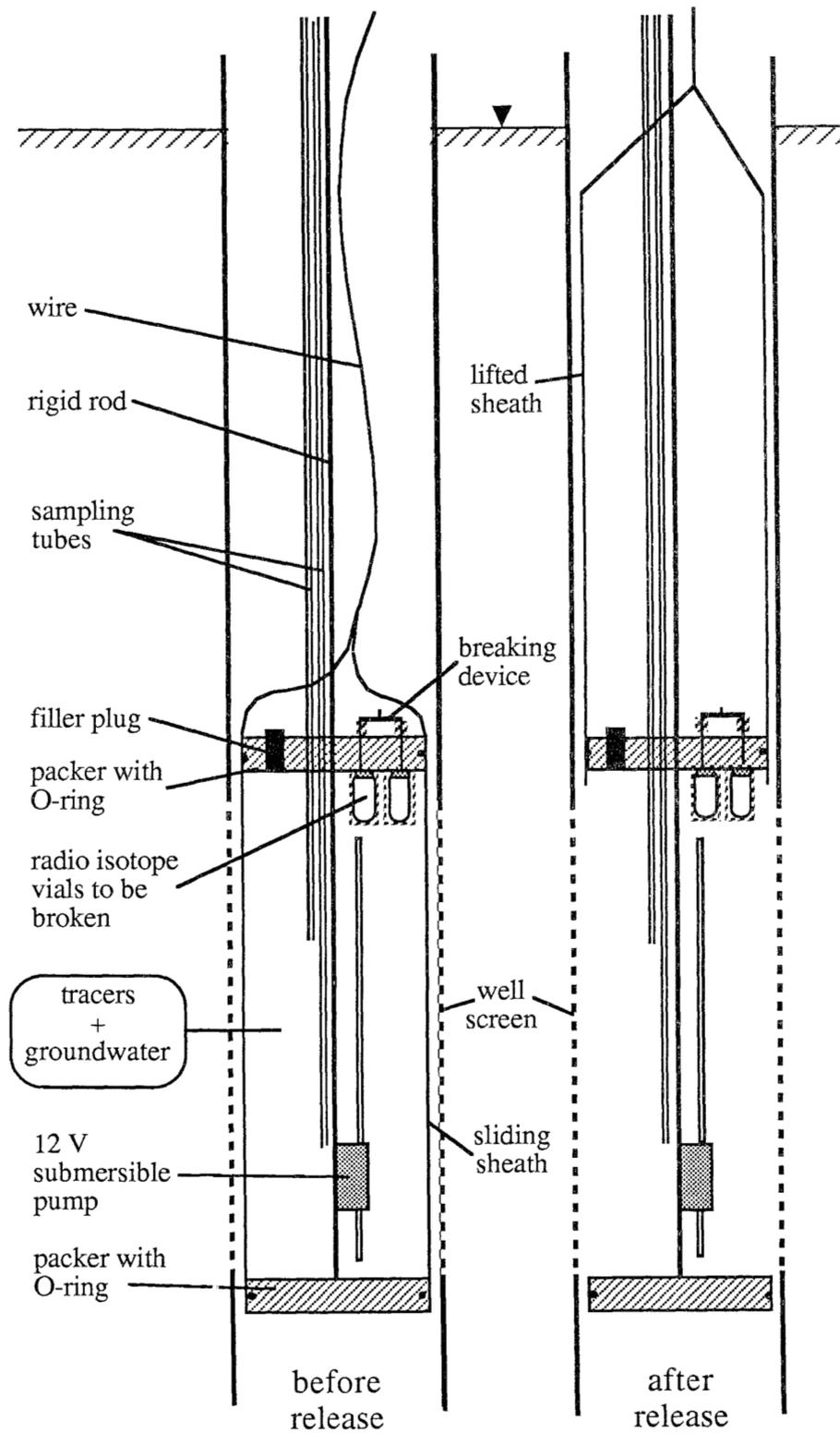


Figure 1: Tracer release chamber before and after release (not to scale).

chanically and mixed with the water volume (approx. 20 l) of the chamber by the submersible pump (Figure 1). After allowing for equilibrium to be attained etc. the sheath of the chamber is lifted out of the borehole, thus releasing a pulse of spiked groundwater uniformly mixed over the length of the chamber.

It was anticipated to release 1.85×10^8 Bq (= 5 mCi) each of ^{58}Co and ^{63}Ni giving pulse concentrations in the chamber volume of 1.36×10^{-10} mol dm^{-3} and 8.76×10^{-8} mol dm^{-3} respectively. For some experiments the radionuclides would be released as preformed complexes with EDTA.

3. Rationale for Choosing EDTA and Acetate as Analogue for Natural Organic Matter

The binding of metal ions to natural organic matter has been shown to facilitate the migration of metal ions (MEANS et al., 1978) and therefore should be a prerequisite of all speciation studies. However, natural organic material is difficult to characterise in sufficient detail to be able to predict metal binding in geochemical codes that are currently available. FALCK (1988) found that the only currently available model directly compatible with speciation models developed so far is the discrete ligand model. Unfortunately this approach does not allow for varying binding behaviour for instance as result of variations in ionic strength. There has been a plethora of papers published in the open literature giving binding constants for metal-fulvate/humate binding, e.g. PITLUCK et al. (1987), but these are all conditional constants and are applicable only over a narrow range of physicochemical conditions. However more sophisticated models are presently being developed.

The properties and binding capacity of the natural organic matter present in the experimental site have been considered by STUART et al. (1988) and WARWICK et al. (1988). The total organic carbon concentration lies between 2.5 and 7.6 ppm. The binding constants for the type of organic molecules found at the experimental site have not been determined, but there is evidence that the binding nature of natural organic matter does not change significantly in material recovered from different environments or sites (BUFFLE, pers. comm.).

In the speciation studies presented here, it was decided to use two simple organic ligands, acetate and ethylenediaminetetraacetate (EDTA), as analogues for soluble organic matter. Acetate is a weak complexant of metal ions, and is widely present in the environment formed

from cellulosic materials; hence it should provide an indication of the lower limit of interactions between metals and natural organic matter. In contrast, ethylenediaminetetraacetate is a strong complexant for transition metal and other divalent ions and should therefore be close to the strongest metal-natural organic matter interactions that will be observed. In the range of calculations performed the organic carbon concentration in the sample is assumed to consist totally of acetate or EDTA, but radionuclide mobility is not necessarily implied by complexation with these ligands.

4. Speciation Calculations

4.1 Introduction

As stated in Part I, the experimental investigation of aqueous chemical speciation in a complex geochemical system is difficult not only because of the many dependent variables in the system, but also because many constituents of interest are present only in trace concentrations. The use of thermodynamic speciation computer codes in conjunction with appropriate databases provides the geochemist with a powerful and time efficient technique for examining chemical speciation occurring in such systems.

The geochemical code that has been used in these speciation studies is PHREEQE (NEA, 1984 version), and a fuller description of the code and its accompanying thermodynamic database can be found in PARKHURST et al. (1980), BALMAN et al. (1988), UWIST (1987) and also Part I of this series.

4.2 Aims of Speciation Studies

The aims of the chemical speciation studies detailed here can be summarized as follows:-

- a) to determine the major aqueous chemical form of the radionuclides that are added, since this will considerably influence their migration behaviour.
- b) to identify any potential problems involving the precipitation of species containing the radionuclide, which will interfere with the results of the tracer tests.
- c) to examine the change in aqueous speciation when metal binding with natural organic matter is considered. Acetate and EDTA are to be used as analogues for the latter.

4.3 Analytical Data

The analytical data used as input to these speciation studies are identical to those used for Part I. Speciation calculations have been carried out on samples 2 and 3 which are representative of the groundwater chemistry during phase II and III of the pumping test (see Part I). These data comprise total analytical concentrations for 26 aqueous components and measurements of Total Inorganic and Total Organic Carbon (TIC and TOC), pH, and oxidation-reduction potential. Further details of the sampling and measuring techniques have been presented by HAIGH et al. (1989) and details of the analytical results, and techniques are presented in Part I.

4.4 Modelling Techniques

Speciation profiles have been used to examine the sensitivity of the radionuclide speciation to changes in the pH and the oxidation-reduction potential. This technique has an advantage over speciation studies conducted solely at the measured values of the system, in that it identifies trends in the aqueous speciation. The profiles were generated by determining the chemical speciation (using PHREEQE) at several points within the range of pH and Eh selected (generally comprising the highest and lowest observed values for pH and Eh).

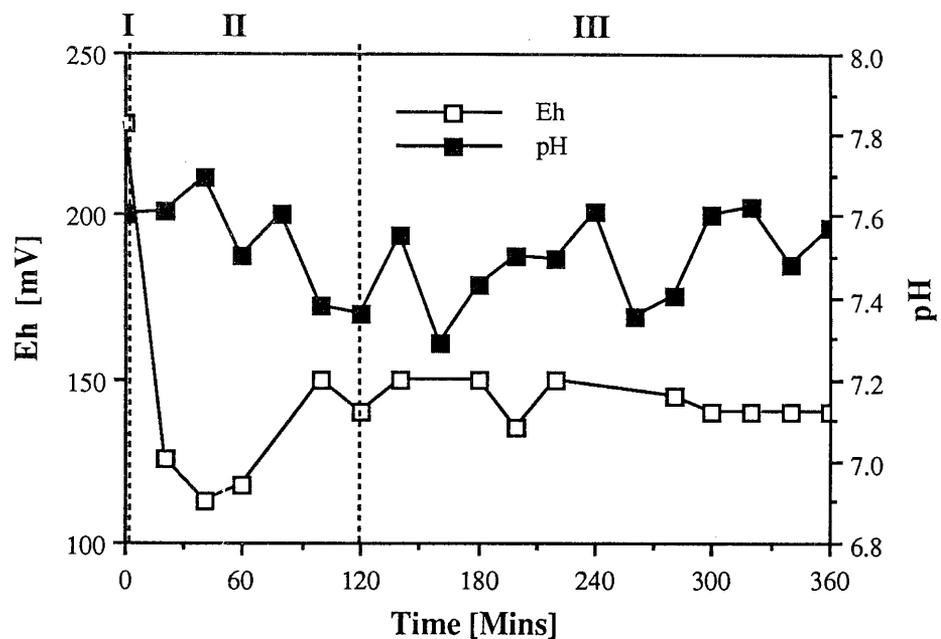


Figure 2: Time versus concentration profile for pH and Eh measurements.

It can be seen from Figure 2 that the measured pH and Eh values undergo considerable variation during pumping (see part I of this report). pH was therefore scanned from pH=6.0 to pH=8.0, with an increment of 0.5 pH units and the Eh scanned from -100mV to +200mV with an increment of 50mV.

When considering the addition of simple organic molecules, the concentration of the organic molecule was adjusted to give a Total Organic Carbon concentration similar to that observed in the groundwater. The chemical speciation at the measured pH and Eh of the natural system was calculated for four different conditions, detailed below:-

- 1) the unperturbed natural system
- 2) the natural system with the addition of acetate or EDTA
- 3) the natural system with the addition of Ni or Co
- 4) the natural system with both radionuclides and organic ligands added.

The addition of acetate to the chemical system was accomplished without difficulty. In contrast the addition of EDTA as a sodium salt to the solution by a PHREEQE type reaction (this enabled the correct charge balance to be maintained) encountered considerable difficulties when the concentration of EDTA exceeded 10^{-7} mol dm⁻³. This was due to the convergence routines in PHREEQE becoming unstable, and consequently giving a result that made no chemical sense, or produced a singular matrix (i.e. a determinant equal to 0). Various techniques to overcome these problems were investigated including; the addition of EDTA in small steps, control of the convergence routines and altering the simulation so that two solutions were being mixed. Unfortunately, the same problems were observed in all of these operations, although it became apparent that in some cases, the convergence routines were oscillating between two separate partial solutions.

The technique that proved successful involved building up the experimental solution in steps through the addition of one component at a time, and balancing the charge with neutral ions after each step. Unfortunately, this resulted in considerable drift in the pH, and it was necessary to use a technique described by Parkhurst (pers. comm.) to fix this at the experimentally measured value.

This method to fix the pH at a given value in a simulation is somewhat awkward to set up because initially the program PHREEQE was not designed to handle this situation. It involves the creation of a new 'mineral', which is composed of a proton and a chemically non-active aqueous species. The solution is then equilibrated with this 'mineral', the saturation index of which is set to be the negative of the desired pH value.

5. Results

The results are discussed in the following sections and illustrated with 'speciation profiles' which are presented in Appendix A.

5.1 Addition of Cobalt to the natural groundwater as Co^{2+}

The addition of ^{58}Co to the groundwater was modelled at a concentration of $1.34 \times 10^{-10} \text{ mol dm}^{-3}$ (equalling 0.185 GBq). Speciation calculations revealed that the major aqueous species in the pH and Eh scans was Co^{2+} (=98.2% of the total concentration), with the next most abundant species being CoSO_4 (=1.6%), which has a concentration some two orders of magnitude below that of Co^{2+} .

As explained in Part I, the saturation index for a solid species is a thermodynamic measure of how likely this species is to precipitate or dissolve under a given set of experimental conditions. The solid most likely to precipitate is CoCO_3 which is very insoluble (MOREL, 1983). However, thermodynamic calculations show that within the range of conditions studied, this solid species will not precipitate.

The aqueous speciation of cobalt is essentially invariant with respect to changes in the pH. The formation of small amounts of cobalt hydroxide, $\text{Co}(\text{OH})^+$, with a concentration similar to that of CoSO_4 is observed at the upper limit of the pH range studied here (pH= 8.0). The most abundant aqueous species by a considerable margin is still the hydrated free metal ion. One species that could be expected to form is a carbonato complex, however this species is extremely insoluble and the experimental measurement of reliable thermodynamic data is as yet unaccomplished. This will be discussed further in section 6.

In spite of the formation constant for aqueous cobalt carbonate being difficult to measure experimentally due to solubility constraints, it is possible to arrive at an estimate of the $\lg \beta$ from correlation plots, such as that derived by LANGMUIR (1979) between carbonate and oxalate complexes. This procedure has been undertaken for cobalt carbonate by TURNER et al. (1981), and a formation constant estimated from CdSO_4 for the following reaction:



The suitability of CdSO₄ as an analogue for CoCO₃ is not immediately apparent, and therefore the incorporation of this value into the modelling studies should be undertaken with caution. The inclusion of an aqueous cobalt carbonate complex in the modelling studies, does not however drastically alter the aqueous speciation of cobalt as a function of pH. The major aqueous species throughout the pH range studied is still the free aquated Co²⁺ ion, ([Co²⁺]_{min} = 1.01 x 10⁻¹⁰ mol dm⁻³, [CoCO₃]_{max} = 2.81 x 10⁻¹¹ mol dm⁻³) the concentration of which is still 5 times that of the CoCO_{3(aq)}. A comparison of the aqueous cobalt speciation with and without CoCO₃ is presented in Table 1.

Table 1: Percentage aqueous speciation of cobalt with pH.
[Co]_{tot} = 1.34 x 10⁻¹⁰ mol dm⁻³.

a) no CoCO ₃ ⁰ considered in the aqueous phase.					
pH	6.0	6.5	7.0	7.5	8.0
[Co ²⁺]	98.6	98.6	98.5	98.1	97.0
[Co(OH) ⁺]	0.0	0.1	0.2	0.6	1.8
[CoSO ₄ ⁰]	1.3	1.3	1.3	1.3	1.2

b) CoCO ₃ ⁰ considered in the aqueous phase					
pH	6.0	6.5	7.0	7.5	8.0
[Co ²⁺]	98.4	97.8	95.8	90.1	76.2
[Co(OH) ⁺]	0.0	0.1	0.2	0.5	1.4
[CoCO ₃ ⁰]	0.3	0.9	2.8	8.2	21.3
[CoSO ₄ ⁰]	1.3	1.2	1.2	1.2	1.0

Cobalt can exist in up to seven different oxidation states, of which only three are prevalent in the conditions observed in natural systems. These are Co(0), Co(II) and Co(III). The aqueous couple Co(II) and Co(III) has a standard electrode potential of +1.84V (COTTON and WILKINSON, 1988), ie.



The complexation of cobalt by organic ligands will generally decrease the value of the standard electrode potential. An example of this is the reduction of the standard electrode potential to +0.38V when the cobalt is complexed with ethylenediaminetetraacetic acid (HIN-FAT and HIGGINSON, 1967), ie.



This value is however in excess of measured Eh values in the Drigg experimental array (see Part I of this report and Figure 2), and as a direct consequence of this Co(III) will only be found in extremely low concentrations. The modelling studies presented here support this in that Co(III) is not found in appreciable concentrations ($>10^{-18} \text{ mol dm}^{-3}$). The net result is that the Eh speciation profile is essentially featureless, with the major aqueous species again being the hydrated free Co^{2+} ion, and the next most abundant aqueous species CoSO_4 (=1.6%).

5.2 Addition of Ni^{2+} to the natural groundwater

It was assumed that ^{63}Ni was added to the groundwater to give a concentration of $9.41 \times 10^{-8} \text{ mol dm}^{-3}$ and an activity of 0.185 GBq.

The modelling predicts from the saturation indices, that there will be no precipitation of solid species containing nickel. The most likely nickel species to form a solid phase would be the carbonate species (KELLEY and ANDERSON, 1935):



followed by the nickel hydroxide species (BAES and MESMER, 1976):



Over the range of pH and Eh neither of these species have shown a tendency to precipitate. Indeed, it is possible to show by simple calculations, that the aqueous phase is less than 0.1% saturated with the dominant aqueous nickel species, being nickel carbonate. The aqueous solubility of nickel carbonate is given in a common laboratory reference (CRC Handbook, 1984) as 93 mg dm^{-3} , which is equivalent to $7.95 \times 10^{-4} \text{ mol dm}^{-3}$, a figure some 4 orders of magnitude greater than the calculated activity of nickel carbonate.

Nickel possesses only one oxidation state, Ni(II), that is likely to be observed in natural aqueous systems. Consequently, the oxidation-reduction speciation profile of nickel was not expected to show any changes and this has been supported by the modelling. The major aqueous species throughout the Eh range at the pH of interest is the carbonato complex (NiCO_3^0 , $\approx 88\%$) with the free hydrated metal ion (Ni^{2+} , $\approx 10\%$) being the next most abundant.

In contrast, the speciation of nickel exhibits considerable changes within the pH range studied (Table 2).

Table 2: Percentage distribution of nickel species with pH
 $[\text{Ni}]_{\text{tot}} = 9.41 \times 10^{-8} \text{ mol dm}^{-3}$

pH	6.0	6.5	7.0	7.5	8.0
$[\text{Ni}^{2+}]$	71.3	50.1	25.9	10.3	3.6
$[\text{Ni}(\text{HCO}_3)^+]$	8.2	5.8	3.0	1.2	0.4
$[\text{NiCO}_3^0]$	19.6	43.4	70.7	88.1	95.0

From this table, it is obvious that at low pH values, the major aqueous nickel species is the free hydrated metal ion Ni^{2+} , but at high pH values, the major aqueous nickel species is the carbonato complex, NiCO_3^0 . Hence, from the speciation profile plot, it can be concluded that the aqueous speciation of nickel is pH dependent, with the free nickel ion and the nickel carbonato complex competing to be the major form of nickel in the aqueous phase.

5.3 The use of Acetate as a Model for Natural Organic Matter

The rationale behind the use of acetate as an analogue for soluble organic matter has been previously discussed (see section 3). In these speciation studies acetate was added as the sodium form to the natural groundwater samples and also to those spiked with Co and Ni. The concentration of the added acetate is given in Table 3.

The results which follow are presented in the form of two tables for each sample; the first of these giving a comparison of the natural speciation with that observed when acetate has been added, and the second comparing the speciation of the radio-tracer spiked groundwater to that of a groundwater spiked with radio-tracers and added acetate.

Table 3: Total concentrations [mol dm⁻³] for elements of interest in groundwater samples 2 and 3.

Component	Sample 2	Sample 3
Acetate	4.27 x 10 ⁻⁵	2.84 x 10 ⁻⁵
Calcium	3.19 x 10 ⁻⁴	3.69 x 10 ⁻⁴
Iron	2.17 x 10 ⁻⁵	1.64 x 10 ⁻⁵
Magnesium	1.48 x 10 ⁻⁴	1.87 x 10 ⁻⁴
Inorganic C	1.03 x 10 ⁻³	1.01 x 10 ⁻³
Cobalt	1.34 x 10 ⁻¹⁰	1.34 x 10 ⁻¹⁰
Nickel	9.41 x 10 ⁻⁸	9.41 x 10 ⁻⁸

Table 4: The effect of added acetate on sample 2 with no radionuclides. pH = 7.5, E_h = 117 mV, [Acetate] = 4.27 x 10⁻⁵ mol dm⁻³

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.11 x 10 ⁻⁴	97.61	3.11 x 10 ⁻⁴	97.61
	CaCO ₃ ⁰	5.12 x 10 ⁻⁷	0.16	5.12 x 10 ⁻⁷	0.16
	CaHCO ₃ ⁺	2.65 x 10 ⁻⁶	0.83	2.60 x 10 ⁻⁶	0.82
	CaSO ₄ ⁰	4.34 x 10 ⁻⁶	1.36	4.20 x 10 ⁻⁶	1.32
	Ca(Ac) ⁺			1.41 x 10 ⁻⁷	0.04
Iron	Fe ²⁺	1.68 x 10 ⁻⁵	77.51	1.68 x 10 ⁻⁵	77.51
	Fe(OH) ⁺	1.44 x 10 ⁻⁷	0.67	1.44 x 10 ⁻⁷	0.67
	Fe(OH) ₂ ⁺	2.88 x 10 ⁻⁷	1.33	2.88 x 10 ⁻⁷	1.33
	Fe(OH) ₃ ⁰	4.05 x 10 ⁻⁶	18.68	4.05 x 10 ⁻⁶	18.68
	Fe(OH) ₄ ⁻	3.38 x 10 ⁻⁸	0.16	3.38 x 10 ⁻⁸	0.16
	FeSO ₄ ⁰	1.77 x 10 ⁻⁷	0.82	1.77 x 10 ⁻⁷	0.82
	FeHCO ₃ ⁺	1.74 x 10 ⁻⁷	0.80	1.74 x 10 ⁻⁷	0.80
	Fe(Ac) ⁺			1.47 x 10 ⁻⁸	0.07
Carbon	CO ₃ ²⁻	1.73 x 10 ⁻⁶	0.16	1.73 x 10 ⁻⁶	0.16
	HCO ₃ ⁻	1.00 x 10 ⁻³	92.79	1.00 x 10 ⁻³	92.79
	H ₂ CO ₃ ⁰	6.77 x 10 ⁻⁵	6.25	6.77 x 10 ⁻⁵	6.25
Acetate	Ac ⁻			4.27 x 10 ⁻⁵	99.20
	HAc			7.37 x 10 ⁻⁸	0.17
	Ca(Ac) ⁺			1.41 x 10 ⁻⁷	0.33
	Mg(Ac) ⁺			9.54 x 10 ⁻⁸	0.22
	Fe(Ac) ⁺			1.47 x 10 ⁻⁸	0.04

Table 5: The effect of acetate on sample 2 with added radionuclides.
pH = 7.5, $E_h = 117 \text{ mV}$, $[\text{Co}]_{\text{tot}} = 1.34 \times 10^{-10} \text{ mol dm}^{-3}$,
 $[\text{Ni}]_{\text{tot}} = 9.41 \times 10^{-8} \text{ mol dm}^{-3}$, $[\text{Acetate}]_{\text{tot}} = 4.27 \times 10^{-5} \text{ mol dm}^{-3}$.

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.11 x 10 ⁻⁴	97.61	3.11 x 10 ⁻⁴	97.61
	CaCO ₃ ⁰	5.12 x 10 ⁻⁷	0.16	5.12 x 10 ⁻⁷	0.16
	CaHCO ₃ ⁺	2.65 x 10 ⁻⁶	0.83	2.60 x 10 ⁻⁶	0.82
	CaSO ₄ ⁰	4.34 x 10 ⁻⁶	1.36	4.20 x 10 ⁻⁶	1.32
	Ca(Ac) ⁺			1.41 x 10 ⁻⁷	0.04
Iron	Fe ²⁺	1.68 x 10 ⁻⁵	77.49	1.68 x 10 ⁻⁵	77.49
	Fe(OH) ⁺	1.44 x 10 ⁻⁷	0.67	1.44 x 10 ⁻⁷	0.67
	Fe(OH) ₂ ⁺	2.88 x 10 ⁻⁷	1.33	2.88 x 10 ⁻⁷	1.33
	Fe(OH) ₃ ⁰	4.05 x 10 ⁻⁶	18.68	4.05 x 10 ⁻⁶	18.68
	Fe(OH) ₄ ⁻	3.38 x 10 ⁻⁸	0.16	3.38 x 10 ⁻⁸	0.16
	FeSO ₄ ⁰	1.77 x 10 ⁻⁷	0.82	1.77 x 10 ⁻⁷	0.82
	FeHCO ₃ ⁺	1.74 x 10 ⁻⁷	0.80	1.74 x 10 ⁻⁷	0.80
	Fe(Ac) ⁺			1.47 x 10 ⁻⁸	0.07
Cobalt	Co ²⁺	1.31 x 10 ⁻¹⁰	97.76	1.31 x 10 ⁻¹⁰	97.76
	Co(OH) ⁺	7.98 x 10 ⁻¹³	0.60	7.97 x 10 ⁻¹³	0.60
	CoSO ₄ ⁰	1.91 x 10 ⁻¹²	1.42	1.88 x 10 ⁻¹²	1.40
	Co(Ac) ⁺			7.92 x 10 ⁻¹⁴	0.06
Nickel	Ni ²⁺	9.68 x 10 ⁻⁹	10.30	9.72 x 10 ⁻⁹	10.34
	NiHCO ₃ ⁺	1.10 x 10 ⁻⁹	1.17	1.10 x 10 ⁻⁹	1.17
	NiCO ₃ ⁰	8.28 x 10 ⁻⁸	88.09	8.28 x 10 ⁻⁸	88.04
	Ni(CO ₃) ₂ ²⁻	2.49 x 10 ⁻¹⁰	0.27	2.49 x 10 ⁻¹⁰	0.27
	NiSO ₄ ⁰	1.26 x 10 ⁻¹⁰	0.13	1.24 x 10 ⁻¹⁰	0.13
Carbon	CO ₃ ²⁻	1.73 x 10 ⁻⁶	0.16	1.73 x 10 ⁻⁶	0.16
	HCO ₃ ⁻	1.00 x 10 ⁻³	92.79	1.00 x 10 ⁻³	92.79
	H ₂ CO ₃ ⁰	6.77 x 10 ⁻⁵	6.25	6.77 x 10 ⁻⁵	6.25
Acetate	Ac ⁻			4.27 x 10 ⁻⁵	99.21
	HAc			7.37 x 10 ⁻⁸	0.17
	Na(Ac)			1.43 x 10 ⁻⁸	0.03
	Ca(Ac) ⁺			1.41 x 10 ⁻⁷	0.33
	Mg(Ac) ⁺			9.54 x 10 ⁻⁸	0.22
	Fe(Ac) ⁺			1.47 x 10 ⁻⁸	0.04

Table 6: The effect of added acetate on sample 3 with no radionuclides.
pH = 7.5, $E_h = 140$ mV, $[\text{Acetate}]_{\text{tot}} = 2.84 \times 10^{-5} \text{ mol dm}^{-3}$

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.60 x 10 ⁻⁴	97.56	3.60 x 10 ⁻⁴	97.56
	CaCO ₃ ⁰	5.52 x 10 ⁻⁷	0.15	5.52 x 10 ⁻⁷	0.15
	CaHCO ₃ ⁺	3.00 x 10 ⁻⁶	0.81	3.00 x 10 ⁻⁶	0.80
	CaSO ₄ ⁰	5.74 x 10 ⁻⁶	1.55	5.55 x 10 ⁻⁶	1.50
Iron	Fe ²⁺	1.04 x 10 ⁻⁵	63.16	1.04 x 10 ⁻⁵	63.16
	Fe(OH) ⁺	8.42 x 10 ⁻⁸	0.51	8.42 x 10 ⁻⁸	0.51
	Fe(OH) ₂ ⁺	3.94 x 10 ⁻⁷	2.41	3.94 x 10 ⁻⁷	2.41
	Fe(OH) ₃ ⁰	5.28 x 10 ⁻⁶	32.20	5.28 x 10 ⁻⁶	32.20
	Fe(OH) ₄ ⁻	4.23 x 10 ⁻⁸	0.26	4.23 x 10 ⁻⁸	0.26
	FeSO ₄ ⁰	1.25 x 10 ⁻⁷	0.76	1.25 x 10 ⁻⁷	0.76
	FeHCO ₃ ⁺	1.05 x 10 ⁻⁷	0.64	1.05 x 10 ⁻⁷	0.64
	Fe(Ac) ⁺			5.82 x 10 ⁻⁹	0.04
Carbon	CO ₃ ²⁻	1.64 x 10 ⁻⁶	0.15	1.64 x 10 ⁻⁶	0.15
	HCO ₃ ⁻	9.91 x 10 ⁻⁴	92.53	9.91 x 10 ⁻⁴	92.53
	H ₂ CO ₃ ⁰	6.98 x 10 ⁻⁵	6.51	6.98 x 10 ⁻⁵	6.51
Acetate	Ac ⁻			2.78 x 10 ⁻⁵	99.11
	HAc			5.01 x 10 ⁻⁸	0.17
	Na(Ac)			6.52 x 10 ⁻⁹	0.03
	Ca(Ac) ⁺			1.05 x 10 ⁻⁷	0.38
	Mg(Ac) ⁺			7.80 x 10 ⁻⁸	0.28
	Fe(Ac) ⁺			5.82 x 10 ⁻⁹	0.02

Table 7: The effect of acetate on sample 3 with added radionuclides.
pH = 7.5, $E_h = 140$ mV, $[Co]_{tot} = 1.34 \times 10^{-10}$ mol dm⁻³,
 $[Ni]_{tot} = 9.41 \times 10^{-8}$ mol dm⁻³, $[Acetate]_{tot} = 2.84 \times 10^{-5}$ mol dm⁻³

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.60 x 10 ⁻⁴	97.56	3.60 x 10 ⁻⁴	97.56
	CaCO ₃ ⁰	5.52 x 10 ⁻⁷	0.15	5.52 x 10 ⁻⁷	0.15
	CaHCO ₃ ⁺	3.00 x 10 ⁻⁶	0.81	3.00 x 10 ⁻⁶	0.80
	CaSO ₄ ⁰	5.74 x 10 ⁻⁶	1.55	5.55 x 10 ⁻⁶	1.50
	Ca(Ac) ⁺			1.05 x 10 ⁻⁷	0.03
Iron	Fe ²⁺	1.03 x 10 ⁻⁵	63.17	1.03 x 10 ⁻⁵	63.17
	Fe(OH) ⁺	8.42 x 10 ⁻⁸	0.51	8.42 x 10 ⁻⁸	0.51
	Fe(OH) ₂ ⁺	3.94 x 10 ⁻⁷	2.41	3.94 x 10 ⁻⁷	2.41
	Fe(OH) ₃ ⁰	5.28 x 10 ⁻⁶	32.21	5.28 x 10 ⁻⁶	32.21
	Fe(OH) ₄ ⁻	4.23 x 10 ⁻⁸	0.26	4.23 x 10 ⁻⁸	0.26
	FeSO ₄ ⁰	1.25 x 10 ⁻⁷	0.76	1.23 x 10 ⁻⁷	0.75
	FeHCO ₃ ⁺	1.05 x 10 ⁻⁷	0.64	1.05 x 10 ⁻⁷	0.64
Cobalt	Co ²⁺	1.31 x 10 ⁻¹⁰	97.76	1.31 x 10 ⁻¹⁰	97.76
	Co(OH) ⁺	7.56 x 10 ⁻¹³	0.56	7.54 x 10 ⁻¹³	0.56
	CoSO ₄ ⁰	2.18 x 10 ⁻¹²	1.63	2.14 x 10 ⁻¹²	1.60
	Co(Ac) ⁺			5.10 x 10 ⁻¹⁴	0.04
Nickel	Ni ²⁺	1.03 x 10 ⁻⁸	10.97	1.04 x 10 ⁻⁸	11.01
	NiHCO ₃ ⁺	1.14 x 10 ⁻⁹	1.22	1.14 x 10 ⁻⁹	1.21
	NiCO ₃ ⁰	8.21 x 10 ⁻⁸	87.32	8.22 x 10 ⁻⁸	87.32
	Ni(CO ₃) ₂ ²⁻	2.35 x 10 ⁻¹⁰	0.25	2.35 x 10 ⁻¹⁰	0.25
	NiSO ₄ ⁰	1.53 x 10 ⁻¹⁰	0.16	1.51 x 10 ⁻¹⁰	0.16
Carbon	CO ₃ ²⁻	1.64 x 10 ⁻⁶	0.15	1.64 x 10 ⁻⁶	0.15
	HCO ₃ ⁻	9.91 x 10 ⁻⁴	92.53	9.91 x 10 ⁻⁴	92.53
	H ₂ CO ₃ ⁰	6.98 x 10 ⁻⁵	6.51	6.98 x 10 ⁻⁵	6.51
Acetate	Ac ⁻			2.78 x 10 ⁻⁵	99.11
	HAc			5.01 x 10 ⁻⁸	0.18
	Ca(Ac) ⁺			1.05 x 10 ⁻⁷	0.38
	Mg(Ac) ⁺			7.80 x 10 ⁻⁸	0.28

It can be seen from the preceding tables, that the addition of acetate to either the natural or the radio-tracer spiked groundwater has little influence on the speciation of the aqueous system. The major aqueous form of acetate is the free aquated acetate ion, CH_3COO^- , with minor contributions from the protonated form and also the calcium and magnesium complexes.

5.4 The Use of EDTA as a Model for Man-Made and Natural Organic Matter

It is generally thought that natural and artificial complexing agents enhance the mobility of metal ions by the formation of neutral or negatively charged complexes which are not retarded as strongly as positively charged metal ions. Anthropogenic complexing agents may be released together with radionuclides from a repository. To simulate this situation, it was proposed to release a precomplexed CoH_2EDTA complex into the experimental test site. It was anticipated that the Co-EDTA species would not dissociate during the time scale of the tracer test, and therefore a chemically reactive tracer (Co^{2+}) would be transformed into a conservative tracer which had enhanced mobility.

Table 8: Percentage distribution of total cobalt with pH.
 $[\text{EDTA}]_{\text{tot}} = 1.34 \times 10^{-10} \text{ mol dm}^{-3}$

pH	6.0	6.5	7.0	7.5	8.0
Co^{2+}	98.3	98.3	98.1	97.7	96.4
$\text{Co}(\text{OH})^+$	0.0	0.1	0.2	0.6	1.8
$\text{Co}(\text{OH})_2^0$	0.0	0.0	0.0	0.0	0.1
CoSO_4^0	1.6	1.6	1.6	1.6	1.6
CoEDTA^{2-}	0.01	0.01	0.01	0.02	0.02

The thermodynamic modelling studies have however predicted that the addition of a radio-labelled CoH_2EDTA complex to the aquifer at the experimental site will dissociate (via reaction vi),



and consequently, the aqueous cobalt speciation will be extremely similar to that observed in section 5.1. In these low concentrations ($1.34 \times 10^{-10} \text{ mol dm}^{-3}$), the EDTA once dissociated, will form aqueous complexes with zinc, manganese and calcium. Tables 8 and 9

which are presented below, show that over a range from pH 6.0 to pH 8.0, less than 0.1% of the total Co and less than 0.1% of total EDTA is present as an EDTA complex.

Table 9: Percentage distribution of EDTA species with pH.
 $[\text{EDTA}]_{\text{tot}} = 1.34 \times 10^{-10} \text{ mol dm}^{-3}$

pH	6.0	6.5	7.0	7.5	8.0
CaEDTA ²⁻	0.1	0.1	0.1	0.1	0.1
MnEDTA ²⁻	1.0	0.9	0.6	0.3	0.3
ZnEDTA ²⁻	98.6	98.9	99.3	99.5	99.6
ZnHEDTA ⁻	0.2	0.1	0.0	0.0	0.0
CoEDTA ²⁻	0.01	0.01	0.01	0.02	0.02

An invaluable feature of computer assisted modelling is the ability to ask 'what-if?' type questions, and obtain results on a reasonable time scale. In this case, the effect on the system of increasing the EDTA concentration was investigated, with the ultimate aim of ensuring formation of a Co-EDTA complex.

Table 10: The effect of different concentrations [mol dm⁻³] of EDTA on the natural speciation in the aquifer.

[EDTA]	1.34×10^{-10}	1.0×10^{-5}
Species	%	%
Co ²⁺	97.7	6.3
CoSO ₄ ⁰	1.6	0.1
Co-EDTA	0.0	93.0
Zn ²⁺	77.8	4.2
Zn(OH) ⁺	2.3	0.1
ZnCO ₃ ⁰	17.4	0.9
Zn-EDTA	0.0	94.6
Fe ²⁺	78.0	46.3
Fe(OH) ⁺	1.3	0.8
Fe(OH) ₃ ⁰	18.3	10.9
Fe-EDTA	0.0	40.6

Figures given are metal percentage abundances. The figures given for % EDTA are a summation of the concentrations of all the relevant EDTA species.

The computer modelling studies, show that in order to complex over 90% of the added cobalt, the EDTA concentration has to be at least 10^{-5} mol dm⁻³. The effect that this has on the speciation is summarized in Table 10. It can be seen that the addition of 10^{-5} mol dm⁻³ of EDTA to the natural groundwater has some dramatic effects, for example, the abundance of free Fe²⁺ drops by 30% and that of free Zn²⁺ by 73%. Obviously, this concentration of EDTA has a significant effect upon the chemical speciation in the groundwater.

However, taking into account dilution effects due to hydrodynamic dispersion, a much higher initial EDTA concentration would be required in order to maintain Co in the complexed form over longer distances. A quantitative account of this process could only be given with a coupled model which considers thermodynamic and kinetic as well as hydrodynamic effects.

If EDTA is to be used as an analogue for strong binding by natural organic matter, then an EDTA concentration of 1.21×10^{-5} mol dm⁻³ and 8.67×10^{-6} mol dm⁻³ is required for the total organic carbon level to be equivalent of that measured in samples 2 and 3 respectively.

Addition of EDTA as the sodium salt to both the natural groundwater samples and those spiked with Co and Ni was modelled. The total concentrations of elements of interest are given in Table 11. The results for this study are presented in Tables 12 to 15, with the format being the same as that of the section 5.3.

Table 11: Total concentrations [mol dm⁻³] for elements of interest in groundwater samples 2 and 3.

Component	Sample 2	Sample 3
EDTA	1.21×10^{-5}	8.67×10^{-6}
Calcium	3.19×10^{-4}	3.69×10^{-4}
Iron	2.17×10^{-5}	1.64×10^{-5}
Manganese	4.04×10^{-6}	3.51×10^{-6}
Carbonate	1.03×10^{-3}	1.01×10^{-3}
Cobalt	1.34×10^{-10}	1.34×10^{-10}
Nickel	9.41×10^{-8}	9.41×10^{-8}

From these tables, it can be seen that the addition of EDTA to the natural groundwater has a significant influence on the aqueous speciation. The main aqueous component which is effected is iron, with approximately 48% of the aqueous iron being complexed with EDTA which in is equivalent to $\approx 90\%$ of the total EDTA.

When the groundwater is spiked with cobalt and/or nickel (see Tables 13 and 15), again approximately 48% of the iron is present as an EDTA complex. Furthermore, at least 91% of the total concentration of the appropriate radionuclide is present as an EDTA complex.

Table 12: The effect of EDTA on sample 2 with no radionuclides.
pH = 7.5, $E_h = 117$ mV, $[\text{EDTA}]_{\text{tot}} = 1.21 \times 10^{-5}$ mol dm⁻³

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.11 x 10 ⁻⁴	97.61	3.13 x 10 ⁻⁴	98.24
	CaCO ₃ ⁰	5.12 x 10 ⁻⁷	0.16	4.32 x 10 ⁻⁷	0.13
	CaHCO ₃ ⁺	2.65 x 10 ⁻⁶	0.83	2.29 x 10 ⁻⁶	0.72
	CaSO ₄ ⁰	4.34 x 10 ⁻⁶	1.36	3.71 x 10 ⁻⁶	1.16
Iron	Fe ²⁺	1.68 x 10 ⁻⁵	77.51	8.54 x 10 ⁻⁶	39.41
	Fe(OH) ⁺	1.44 x 10 ⁻⁷	0.67	6.93 x 10 ⁻⁸	0.32
	Fe(OH) ₂ ⁺	2.88 x 10 ⁻⁷	1.33	1.37 x 10 ⁻⁷	0.63
	Fe(OH) ₃ ⁰	4.05 x 10 ⁻⁶	18.68	1.88 x 10 ⁻⁶	8.68
	Fe(OH) ₄ ⁻	3.38 x 10 ⁻⁸	0.16	1.59 x 10 ⁻⁸	0.07
	FeSO ₄ ⁰	1.77 x 10 ⁻⁷	0.82	7.86 x 10 ⁻⁸	0.36
	FeHCO ₃ ⁺	1.74 x 10 ⁻⁷	0.80	7.79 x 10 ⁻⁸	0.35
	FeEDTA ²⁻			2.15 x 10 ⁻⁶	9.92
	FeEDTA ⁻			5.45 x 10 ⁻⁶	25.15
FeEDTA(OH) ²⁻			3.24 x 10 ⁻⁶	14.95	
Carbon	CO ₃ ²⁻	1.64 x 10 ⁻⁶	0.15	1.75 x 10 ⁻⁶	0.17
	HCO ₃ ⁻	9.91 x 10 ⁻⁴	92.53	9.54 x 10 ⁻⁴	93.07
	H ₂ CO ₃ ⁰	6.98 x 10 ⁻⁵	6.51	6.32 x 10 ⁻⁵	6.17
EDTA	CaEDTA ²⁻			2.22 x 10 ⁻⁸	0.18
	FeEDTA ²⁻			2.15 x 10 ⁻⁶	17.77
	FeEDTA ⁻			5.45 x 10 ⁻⁶	45.04
	FeEDTA(OH) ²⁻			3.24 x 10 ⁻⁶	26.78
	MnEDTA ²⁻			7.41 x 10 ⁻⁸	0.61
	ZnEDTA ²⁻			1.14 x 10 ⁻⁶	9.42

Table 13: The effect of EDTA on sample 2 with added radionuclides.
pH = 7.5, $E_h = 117$ mV, $[Co]_{tot} = 1.34 \times 10^{-10}$ mol dm⁻³,
 $[Ni]_{tot} = 9.41 \times 10^{-8}$ mol dm⁻³, $[EDTA]_{tot} = 1.21 \times 10^{-5}$ mol dm⁻³.

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	%element	[mol dm ⁻³]	%element
Calcium	Ca ²⁺	3.11 x 10 ⁻⁴	97.61	3.13 x 10 ⁻⁴	98.24
	CaCO ₃ ⁰	5.12 x 10 ⁻⁷	0.16	4.32 x 10 ⁻⁷	0.13
	CaHCO ₃ ⁺	2.65 x 10 ⁻⁶	0.83	2.29 x 10 ⁻⁶	0.72
	CaSO ₄ ⁰	4.34 x 10 ⁻⁶	1.36	3.71 x 10 ⁻⁶	1.16
Iron	Fe ²⁺	1.68 x 10 ⁻⁵	77.51	8.61 x 10 ⁻⁶	39.73
	Fe(OH) ⁺	1.44 x 10 ⁻⁷	0.67	6.99 x 10 ⁻⁸	0.32
	Fe(OH) ₂ ⁺	2.88 x 10 ⁻⁷	1.33	1.38 x 10 ⁻⁷	0.63
	Fe(OH) ₃ ⁰	4.05 x 10 ⁻⁶	18.68	1.90 x 10 ⁻⁶	8.77
	Fe(OH) ₄ ⁻	3.38 x 10 ⁻⁸	0.16	1.61 x 10 ⁻⁸	0.07
	FeSO ₄ ⁰	1.77 x 10 ⁻⁷	0.82	7.93 x 10 ⁻⁸	0.37
	FeHCO ₃ ⁺	1.74 x 10 ⁻⁷	0.80	7.86 x 10 ⁻⁸	0.36
	FeEDTA ²⁻			2.14 x 10 ⁻⁶	9.88
	FeEDTA ⁻			5.40 x 10 ⁻⁶	24.92
FeEDTA(OH) ²⁻			3.21 x 10 ⁻⁶	14.81	
Cobalt	Co ²⁺	1.31 x 10 ⁻¹⁰	97.93	5.92 x 10 ⁻¹²	4.34
	Co(OH) ⁺	7.98 x 10 ⁻¹³	0.60	3.40 x 10 ⁻¹⁴	0.03
	CoSO ₄ ⁰	1.91 x 10 ⁻¹²	1.42	7.52 x 10 ⁻¹⁴	0.06
	CoEDTA ²⁻			1.28 x 10 ⁻¹⁰	95.52
	CoEDTA ⁻			7.58 x 10 ⁻¹⁴	0.06
Nickel	Ni ²⁺	9.68 x 10 ⁻⁹	10.30	1.61 x 10 ⁻¹¹	0.02
	NiHCO ₃ ⁺	1.10 x 10 ⁻⁹	1.17	1.61 x 10 ⁻¹²	0.00
	NiCO ₃ ⁰	8.28 x 10 ⁻⁸	88.09	1.18 x 10 ⁻¹⁰	0.13
	Ni(CO ₃) ₂ ²⁻	2.49 x 10 ⁻¹⁰	0.27	3.52 x 10 ⁻¹³	0.00
	NiSO ₄ ⁰	1.26 x 10 ⁻¹⁰	0.13	1.82 x 10 ⁻¹³	0.00
	NiEDTA ²⁻			9.33 x 10 ⁻⁸	99.26
NiEDTA ⁻			5.09 x 10 ⁻¹⁰	0.54	
Carbon	CO ₃ ²⁻	1.73 x 10 ⁻⁶	0.16	1.75 x 10 ⁻⁶	0.16
	HCO ₃ ⁻	1.00 x 10 ⁻³	92.79	9.54 x 10 ⁻⁴	93.07
	H ₂ CO ₃ ⁰	6.77 x 10 ⁻⁵	6.25	6.32 x 10 ⁻⁵	6.17
EDTA	CaEDTA ²⁻			2.18 x 10 ⁻⁸	0.18
	FeEDTA ²⁻			2.14 x 10 ⁻⁶	17.69
	FeEDTA ⁻			5.40 x 10 ⁻⁶	44.63
	FeEDTA(OH) ²⁻			3.21 x 10 ⁻⁶	26.53
	MnEDTA ²⁻			7.29 x 10 ⁻⁸	0.60
	ZnEDTA ²⁻			1.14 x 10 ⁻⁶	9.42
	NiEDTA ²⁻			5.09 x 10 ⁻¹⁰	0.00
	NiHEDTA ⁻			9.33 x 10 ⁻⁸	0.77
	CoEDTA ²⁻			1.28 x 10 ⁻¹⁰	0.00

Table 14: The effect of added EDTA on sample 3 with no radionuclides.
pH = 7.5, $E_h = 140$ mV, $[\text{EDTA}]_{\text{tot}} = 8.67 \times 10^{-6}$ mol dm⁻³.

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.60 x 10 ⁻⁴	97.45	3.62 x 10 ⁻⁴	97.96
	CaCO ₃ ⁰	5.52 x 10 ⁻⁷	0.15	5.02 x 10 ⁻⁷	0.14
	CaHCO ₃ ⁺	3.00 x 10 ⁻⁶	0.81	2.66 x 10 ⁻⁶	0.72
	CaSO ₄ ⁰	5.74 x 10 ⁻⁶	1.55	5.17 x 10 ⁻⁶	1.40
Iron	Fe ²⁺	1.03 x 10 ⁻⁵	63.17	5.21 x 10 ⁻⁶	31.82
	Fe(OH) ⁺	8.42 x 10 ⁻⁸	0.51	4.27 x 10 ⁻⁸	0.26
	Fe(OH) ₂ ⁺	3.94 x 10 ⁻⁷	2.41	2.08 x 10 ⁻⁷	1.27
	Fe(OH) ₃ ⁰	5.28 x 10 ⁻⁶	32.21	2.86 x 10 ⁻⁶	17.44
	Fe(OH) ₄ ⁻	4.23 x 10 ⁻⁸	0.26	2.41 x 10 ⁻⁸	0.15
	FeSO ₄ ⁰	1.25 x 10 ⁻⁷	0.76	5.77 x 10 ⁻⁸	0.35
	FeHCO ₃ ⁺	1.05 x 10 ⁻⁷	0.64	4.76 x 10 ⁻⁸	0.29
	FeEDTA ²⁻			7.23 x 10 ⁻⁷	4.41
	FeEDTA ⁻			4.53 x 10 ⁻⁶	27.66
	FeEDTA(OH) ²⁻			2.67 x 10 ⁻⁶	16.30
Carbon	CO ₃ ²⁻	1.64 x 10 ⁻⁶	0.15	1.71 x 10 ⁻⁶	0.16
	HCO ₃ ⁻	9.91 x 10 ⁻⁴	92.53	9.43 x 10 ⁻⁴	86.51
	H ₂ CO ₃ ⁰	6.98 x 10 ⁻⁵	6.51	6.27 x 10 ⁻⁵	5.75
EDTA	CaEDTA ²⁻			1.41 x 10 ⁻⁸	0.18
	FeEDTA ²⁻			7.23 x 10 ⁻⁷	8.34
	FeEDTA ⁻			4.53 x 10 ⁻⁶	52.25
	FeEDTA(OH) ²⁻			2.67 x 10 ⁻⁶	30.80
	MnEDTA ²⁻			3.56 x 10 ⁻⁸	0.41
	ZnEDTA ²⁻			6.87 x 10 ⁻⁷	7.92

Table 15: The effect of EDTA on sample 3 with added radionuclides.
pH = 7.5, $E_h = 140$ mV, $[Co]_{tot} = 1.34 \times 10^{-10}$ mol dm⁻³,
 $[Ni]_{tot} = 9.41 \times 10^{-8}$ mol dm⁻³, $[EDTA]_{tot} = 8.67 \times 10^{-6}$ mol dm⁻³.

Element	Species	No organics present		Organics present	
		[mol dm ⁻³]	% _{element}	[mol dm ⁻³]	% _{element}
Calcium	Ca ²⁺	3.60 x 10 ⁻⁴	97.45	3.62 x 10 ⁻⁴	98.10
	CaCO ₃ ⁰	5.52 x 10 ⁻⁷	0.15	5.02 x 10 ⁻⁷	0.14
	CaHCO ₃ ⁺	3.00 x 10 ⁻⁶	0.81	2.66 x 10 ⁻⁶	0.72
	CaSO ₄ ⁰	5.74 x 10 ⁻⁶	1.55	5.17 x 10 ⁻⁶	1.40
Iron	Fe ²⁺	1.03 x 10 ⁻⁵	63.17	5.27 x 10 ⁻⁶	32.17
	Fe(OH) ⁺	8.42 x 10 ⁻⁸	0.51	4.31 x 10 ⁻⁸	0.26
	Fe(OH) ₂ ⁺	3.94 x 10 ⁻⁷	2.41	2.10 x 10 ⁻⁷	1.28
	Fe(OH) ₃ ⁰	5.28 x 10 ⁻⁶	32.21	2.89 x 10 ⁻⁶	17.58
	Fe(OH) ₄ ⁻	4.23 x 10 ⁻⁸	0.26	2.43 x 10 ⁻⁸	0.15
	FeSO ₄ ⁰	1.25 x 10 ⁻⁷	0.76	5.84 x 10 ⁻⁸	0.36
	FeHCO ₃ ⁺	1.05 x 10 ⁻⁷	0.64	4.81 x 10 ⁻⁸	0.29
	FeEDTA ²⁻			7.15 x 10 ⁻⁷	4.37
	FeEDTA ⁻			4.48 x 10 ⁻⁶	27.35
FeEDTA(OH) ²⁻			2.64 x 10 ⁻⁶	16.12	
Cobalt	Co ²⁺	1.31 x 10 ⁻¹⁰	97.76	1.04 x 10 ⁻¹¹	7.76
	Co(OH) ⁺	7.56 x 10 ⁻¹³	0.56	6.04 x 10 ⁻¹⁴	0.05
	CoSO ₄ ⁰	2.18 x 10 ⁻¹²	1.63	1.60 x 10 ⁻¹²	0.12
	CoEDTA ²⁻			1.23 x 10 ⁻¹⁰	91.79
	CoEDTA ⁻			1.81 x 10 ⁻¹³	0.09
Nickel	Ni ²⁺	1.03 x 10 ⁻⁸	10.97	1.04 x 10 ⁻⁸	11.01
	NiHCO ₃ ⁺	1.14 x 10 ⁻⁹	1.22	1.14 x 10 ⁻⁹	1.21
	NiCO ₃ ⁰	8.21 x 10 ⁻⁸	87.32	8.22 x 10 ⁻⁸	87.32
	Ni(CO ₃) ₂ ²⁻	2.35 x 10 ⁻¹⁰	0.25	2.35 x 10 ⁻¹⁰	0.25
	NiSO ₄ ⁰	1.53 x 10 ⁻¹⁰	0.16	1.51 x 10 ⁻¹⁰	0.16
	NiEDTA ²⁻			5.13 x 10 ⁻⁸	99.15
	NiHEDTA ⁻			5.13 x 10 ⁻¹⁰	0.55
Carbon	CO ₃ ²⁻	1.64 x 10 ⁻⁶	0.15	1.71 x 10 ⁻⁶	0.16
	HCO ₃ ⁻	9.91 x 10 ⁻⁴	92.53	9.43 x 10 ⁻⁴	93.10
	H ₂ CO ₃ ⁰	6.98 x 10 ⁻⁵	6.51	6.27 x 10 ⁻⁵	6.19
EDTA	CaEDTA ²⁻			1.38 x 10 ⁻⁸	0.16
	FeEDTA ²⁻			7.15 x 10 ⁻⁷	8.16
	FeEDTA ⁻			4.48 x 10 ⁻⁶	51.14
	FeEDTA(OH) ²⁻			2.64 x 10 ⁻⁶	30.14
	MnEDTA ²⁻			3.49 x 10 ⁻⁸	0.40
	ZnEDTA ²⁻			6.86 x 10 ⁻⁷	7.83
	NiEDTA ²⁻			9.32 x 10 ⁻⁸	1.06
	NiHEDTA ⁻			5.13 x 10 ⁻¹⁰	0.01
	CoEDTA ²⁻			1.23 x 10 ⁻¹⁰	0.00

6. Discussion and Conclusions

The modelling studies have shown that the speciation of ^{58}Co and ^{63}Ni is invariant with changes in the oxidation-reduction potential of the system. For cobalt, this is hardly surprising, as the magnitude of the Co(II)/Co(III) redox couple (equation [ii]) considerably exceeds any measured values that have been observed at the experimental site. In contrast to cobalt, nickel has only one oxidation state likely to be observed in aqueous systems.

The low concentration ($[\text{Co}]_{\text{tot}} = 1.34 \times 10^{-10} \text{ mol dm}^{-3}$, $[\text{Ni}]_{\text{tot}} = 1.34 \times 10^{-8} \text{ mol dm}^{-3}$) of the radionuclides that are added to the groundwater implies that there will be little or no precipitation of solid species containing them. Indeed, for the least soluble species, the metal carbonates, to precipitate, the activity of the carbonate ion

$$a_{\text{CO}_3^{2-}} = \gamma_{\text{CO}_3^{2-}} \cdot [\text{CO}_3^{2-}] \quad \text{[vii]}$$

would need to exceed 0.78 for cobalt and 1.42 for nickel. (see Appendix C for calculations.) The corresponding carbonate concentration is far in excess of that measured at the experimental site, hence it can be concluded that the precipitation of any solid species containing Ni or Co is unlikely.

The aqueous speciation of cobalt is relatively insensitive to changes in the pH. When the possibility of formation of an aqueous cobalt carbonate species was excluded from the modelling calculations, the speciation profile vs. pH was essentially invariant, with the aquated free metal ion accounting for at least 97% (see Table 1) of the total cobalt in the system. When aqueous cobalt carbonate formation was included in the calculations, this species became the second most abundant cobalt species accounting for a maximum of 21% of the total cobalt. It should be stressed, that the concentration of the free metal ion is still 5 times that of the carbonate species, therefore the aqueous chemistry of cobalt will be dominated by the free hydrated metal ion.

The formation constant of cobalt carbonate has only been estimated by one group of workers (TURNER et al., 1981), and this value has been derived using correlation techniques and extrapolated from the formation constant of CdSO_4 . The major pitfall in this technique is that the formation constant has not been measured experimentally, but calculated using numerical approximations, and so is at best only an estimate. As such, large errors are liable to be incorporated in the value of this constant. The primary reason for the paucity of thermodynamic data for cobalt carbonate is its low solubility, indeed a common laboratory

reference work, the CRC Handbook states that CoCO_3 is insoluble in both hot and cold water. This low solubility has made the measurement of accurate values for the formation constant extremely difficult, and hence the only commonly available formation constant for CoCO_3 in the chemical literature is a numerical estimate.

In contrast to the speciation profile of cobalt with pH, the aqueous distribution of nickel species alters markedly with pH. At the upper end of the pH range (pH= 8.0), the most abundant aqueous nickel species is the carbonato complex, while the free aquated metal ion dominates at lower pH values (see Table 2). The difference between nickel and cobalt can be attributed to the more favourable formation constant for the aqueous and the higher solubility of the nickel carbonate (UWIST, 1987, KELLY and ANDERSON, 1935) species;



Indeed, at the measured pH of the groundwater, the aqueous chemistry of nickel will be dominated by the neutral carbonate species. The dominance of the nickel carbonate species in solution and the paucity of thermodynamic data currently available for both cobalt and nickel carbonate suggest that this area in particular should be singled out for further study. The starting point for this would be a critical review of the available thermodynamic literature. This study could then be expanded to evaluate the sensitivity of the metal carbonate species to changes in the formation constants, and ultimately the measurement of formation constants for these species.

When a radionuclide present mainly as the positively charged free metal ion is introduced into the aqueous phase, a series of electrostatic and possibly ion exchange reactions will occur with the aquifer. These interactions will involve negatively charged silicates, iron colloids, natural organic macromolecules and also the natural organic colloids (THENG, 1979). In contrast, by complexing the radionuclide with a ligand (man-made or naturally occurring) so that the charge on the complex is either neutral or negative, these electrostatic and ion exchange interactions will be vastly reduced, or perhaps even eliminated, considerably enhancing migration of the radionuclide.

The use of acetate to simulate the binding of natural organic matter did not perturb either the natural aqueous speciation, or the speciation of the radionuclides when they were added to the aquifer (see section 5.3). It was found that the major form of acetate in the aqueous phase

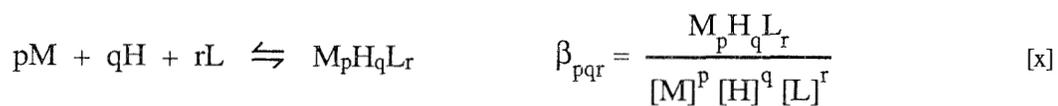
was as the free ion, CH_3COO^- , with less than 1% of the acetate present as other forms. These results reflect the weak binding capacity of the acetate ion in general. Indeed, in an attempt to simulate the binding of metals by fulvic acids using a simple discrete ligand model, DUFFIELD et al. (1988) produced a close fit to that experimentally observed by WARWICK et al. (1988) with 6 ligands. In this 6 ligand model (acetate, citrate, glycinate, oxalate, phthalate and tartrate), the extent of metal-acetate binding was very small. It should be emphasized that this model in no way attempted to give information about the structure or the binding modes of soluble organic matter, but instead concentrated on fitting experimentally observed results with a well characterized simple system.

To simulate the release of organically bound Co from a repository it was proposed to add the cobalt to the experimental aquifer as an inner-sphere complex. However, thermodynamic calculations predict that the addition of cobalt to the experimental site as a CoH_2EDTA complex will be unsuccessful, due to dissociation of the complex (see equation [vi]) giving free Co^{2+} , and the subsequent formation of zinc-EDTA complexes. In order to maintain the cobalt as an EDTA complex ($[\text{CoEDTA}^{2-}] = 93\%$ of Co_{tot}) upon addition to the groundwater, it has been found necessary to increase the concentration of added EDTA to 10^{-5} mol dm^{-3} . The effect of this high concentration is to complex all the zinc and 40% of the total iron as aqueous EDTA species, which will significantly effect both the solid and aqueous phases of the aquifer. In addition, it should be remembered, that as the CoEDTA^{2-} species migrates through the aquifer, dilution effects will occur and consequently, even with this high initial concentration of EDTA, the CoEDTA^{2-} species will have a limited lifetime before dissociation occurs.

EDTA was used as an analogue for natural organic matter as well, substituting all DOC for EDTA. This was expected to give an intimation of the strongest metal–natural organic matter interactions in the aquifer. The results from section 5.4 show that the use of EDTA significantly alters the aqueous speciation of the aquifer whether Co and Ni are present or not. When EDTA is added to the natural groundwater, 48% of the total aqueous iron is complexed, this will also influence the extent of the colloidal and solid phase iron species that are formed. The addition of Co or Ni to the natural groundwater in the presence of EDTA results in significant proportions of these metals ($\approx 99\%$ of Ni_{tot} and $> 92\%$ Co_{tot}) being complexed with EDTA. This will obviously have effects on the mobility of these radio-tracers if used in the experimental site.

The use of acetate and EDTA as analogues for natural organic matter has been instructive. If natural organic matter complexes metals with similar binding strength to that of acetate, then

the migration characteristics of Co and Ni will not be altered appreciably. In contrast to this, if the metal–natural organic matter binding strength is comparable to that of EDTA, then both nickel and cobalt will exhibit markedly different aqueous speciation profiles and consequently different migration characteristics. Examination of some conditional nickel–fulvate formation constants and comparison between these and nickel–acetate, nickel–EDTA constants reveals that the truth may indeed lie in between these two extremes. That is, for the equation:



The following formation constants have been measured:

nickel acetate	$\beta_{101} = 10^{1.29}$	(UWIST, 1988)
nickel EDTA	$\beta_{101} = 10^{20.37}$	(UWIST, 1988)
nickel fulvate	$\beta_{101} = 10^{4.6}$	(PITLUCK et al., 1987)

It can be seen that the formation constant for the nickel-fulvate species lies between that of the nickel-acetate and the nickel-EDTA species, which implies that a significant proportion of the added radionuclides may be complexed, but the migration characteristics of cobalt and nickel may not be altered as drastically as for EDTA.

7. References

- BAES, C.F. and MESMER, R.E. (1976) *The Hydrolysis of Cations*, 483 p., John Wiley and Sons, N.Y.
- BALMAN, J.A., DUFFIELD, J.R. and WILLIAMS, D.R. (April 1988) *Modelling Chemical Speciation in Groundwaters Containing Organic Ligands*, Contr. F3CR05/a1/85/04.
- BRIGHTMAN, M. A., COOK, A. and WEALTHALL, G. P. (1989) *Hydraulics of the Drigg Array*, Rep. Fluid Processes Res. Group, Br. Geol. Surv., (in preparation).
- COTTON, F.A. and WILKINSON, G. (1988⁵) *Advanced Inorganic Chemistry*, 1455 p., Wiley Interscience.
- CRC Press (1984) *Handbook of Chemistry and Physics*, ed. by R.C. Weast.
- DUFFIELD, J.R., QUINN, G.W. and WILLIAMS, D.R. (1988), unpublished results.
- FALCK, W.E (1988) *Modelling the Interaction between Natural Organic Matter and Metal Cations: A Review*, Rep. Fluid Processes Res. Group, Br. Geol. Surv., **WE/88/49**, Report to the UK DoE/CEC (in press).
- FALCK, W.E., QUINN, G.W., DUFFIELD, J.R and WILLIAMS, D.R. (1988): *Chemical Speciation Modelling of Groundwaters in a Shallow Glacial Sand Aquifer, Part I: General Parameters*, Rep. Fluid Processes Res. Group, Br. Geol. Surv., **WE/88/48**, Report to UK DoE/CEC, (submitted).
- HAIGH, D., HITCHMAN, S. P., BLOODWORTH, A. J. and MILODOWSKI, A. (1989): *Chemistry and Mineralogy of the Drigg Array*, Rep. Fluid Processes Res. Group, Br. Geol. Surv., (in preparation).
- HILL, M.D., MOBBS, WHITE, I.F. (1981) *An Assessment of the Radiological Consequences of Disposal of Intermediate Level Wastes in Argillaceous Rock Formations.*- National Radiological Protection Board, **NRPB-R126**.
- HIN-FAT, L. and HIGGINSON, W.C.E. (1967) *Some Observations Concerning Trioxalato-cobaltate*, J. Chem. Soc. (A), 298-301.
- KELLEY, K.K. and ANDERSON, C.T. (1935) *Contributions to the Data on Theoretical Metallurgy. IV Metal Carbonates - Correlations and Applications of Thermodynamic Properties*, Bull. U.S. Bur. Mines, **384**, 78.
- LANGMUIR, D. (1979) *Techniques of Estimating Thermodynamic Properties for Some Aqueous Complexes of Geochemical Interest*, in: JENNE, E.A. [Ed.] *Chemical Modelling in Aqueous Systems*, Amer. Chem. Soc. Symp. Ser., **83**, 353-87.
- MEANS, J.L., CRERAR, D.A. and DUGUID, J.O. (1978): *Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents*, Science, **200**, 1477-81.
- MOREL, F.M.M. (1983): *Principles of Aquatic Chemistry*, 446 p., John Wiley, N.Y.

- NEWMAN, J.R. and ROSS, C.A.M. (1985) Mineralogical and Geochemical Controls on Heavy Metal Pollution in Monolith Lysimeters, Rep. Fluid Processes Res. Group, Br. Geol. Surv., **FLPU 85-5**, 128 p.
- PARKHURST, D. L., THORSTENSON, D. C. and PLUMMER, N. L. (1980): PHREEQE - A computer program for geochemical calculations, U.S. Geol. Survey, **USGS/WRI-80-96**.
- PINNER, A.V., HEMMING, C.R., HILL, M.D. (1984) An Assessment of the Radiological Protection Aspects of Shallow Land Burial of Radioactive Waste, National Radiological Protection Board, **NRPB-R161**, 81 p.
- PITLUCK, M.R., POLLARD, B.D. and HAWORTH, D.T. (1987): Conditional Stability Constant Determination of Metal-Fulvic Acid Complexes, *J. Liq. Chromatogr.*, **10**(10), 2081-103.
- ROSS, C.A.M. & FALCK, W.E. (1987) Argillaceous Sediment Sorption Coefficients for Radionuclides in Intermediate Level Radioactive Waste - A Literature Review, Report in Confidence to BNFL (awaiting publication).
- STUART, M.E., BRADLEY, A.D., SMITH, B. and PEACHEY, D. (1989) Isolation, Purification and Characterisation of Humic Acid Substances from Drigg Groundwater, Rep. Fluid Processes Res. Group, Br. Geol. Surv., (in preparation).
- THENG, B. K. G. (1979): Formation and Properties of Clay-Polymer Complexes, *Developments in Soil Science*, Vol. 9, Elsevier, Amsterdam, 362 p.
- TURNER, D.R., WHITFIELD, M. and DICKSON, A.G. (1981) The Equilibrium Speciation of Dissolved Components in Freshwater and Seawater at 25°C and 1 atm pressure, *Geochim. Cosmochim. Acta*, **45**(6), 855-81.
- UWIST (January 1987) The UWIST Thermodynamic Database Library, submitted to the Department of the Environment, London.
- WARWICK, P., SHAW, P., WILLIAMS, G.N. and HOOKER, P.J. (1988) Preliminary Studies of Cobalt Complexation in Groundwater, *Radiochim. Acta*, **44/45**, 59-63.
- WILLIAMS, G.M., ROSS, C.A.M., STUART, A., HITCHMAN, S.P., ALEXANDER, L.S. (1984) Controls on Contaminant Migration at the Villa Farm Lagoons, *Quarterly J. Eng. Geol.*, **17**, 39-55, London.

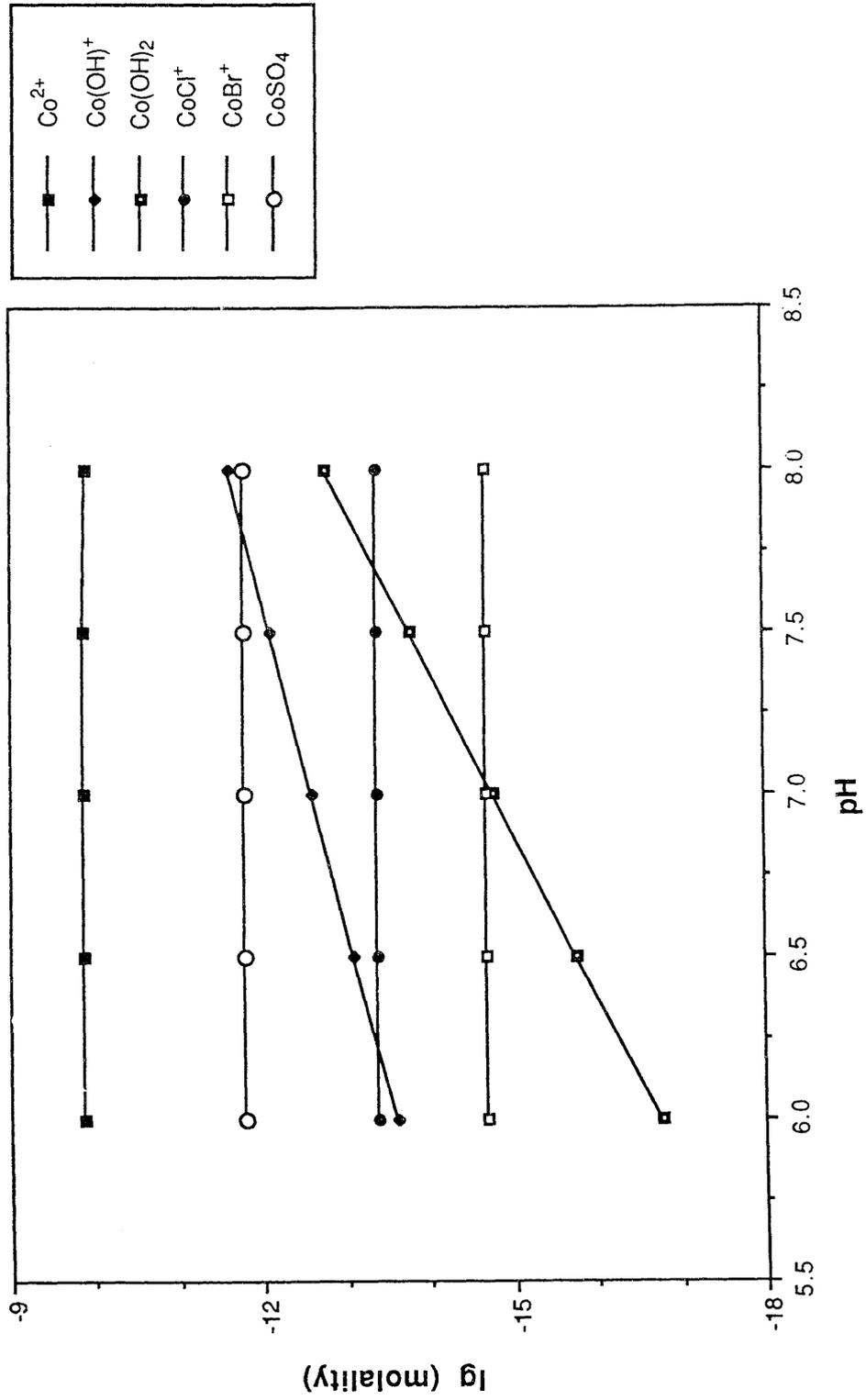
Appendix A: Speciation Profiles

This appendix contains a series of speciation profiles for cobalt and nickel which summarize the results of this modelling study. The speciation was modelled for two different samples from the experimental site (samples 2 and 3). The speciation of these elements in sample 1 was not considered because this sample was taken prior to the start of the pumping test (see Part I), and the radionuclides will be introduced to the aquifer after a finite pumping time. In the pumping test, which has been described more fully elsewhere (BRIGHTMAN et al. in prep., FALCK et al. 1989), sample 2 was taken 60 minutes after the start of pumping and sample 3 after 340 minutes of pumping.

For the reasons described in Part I, the Eh speciation profiles are presented at two different pH values, 7.0 and 7.5.

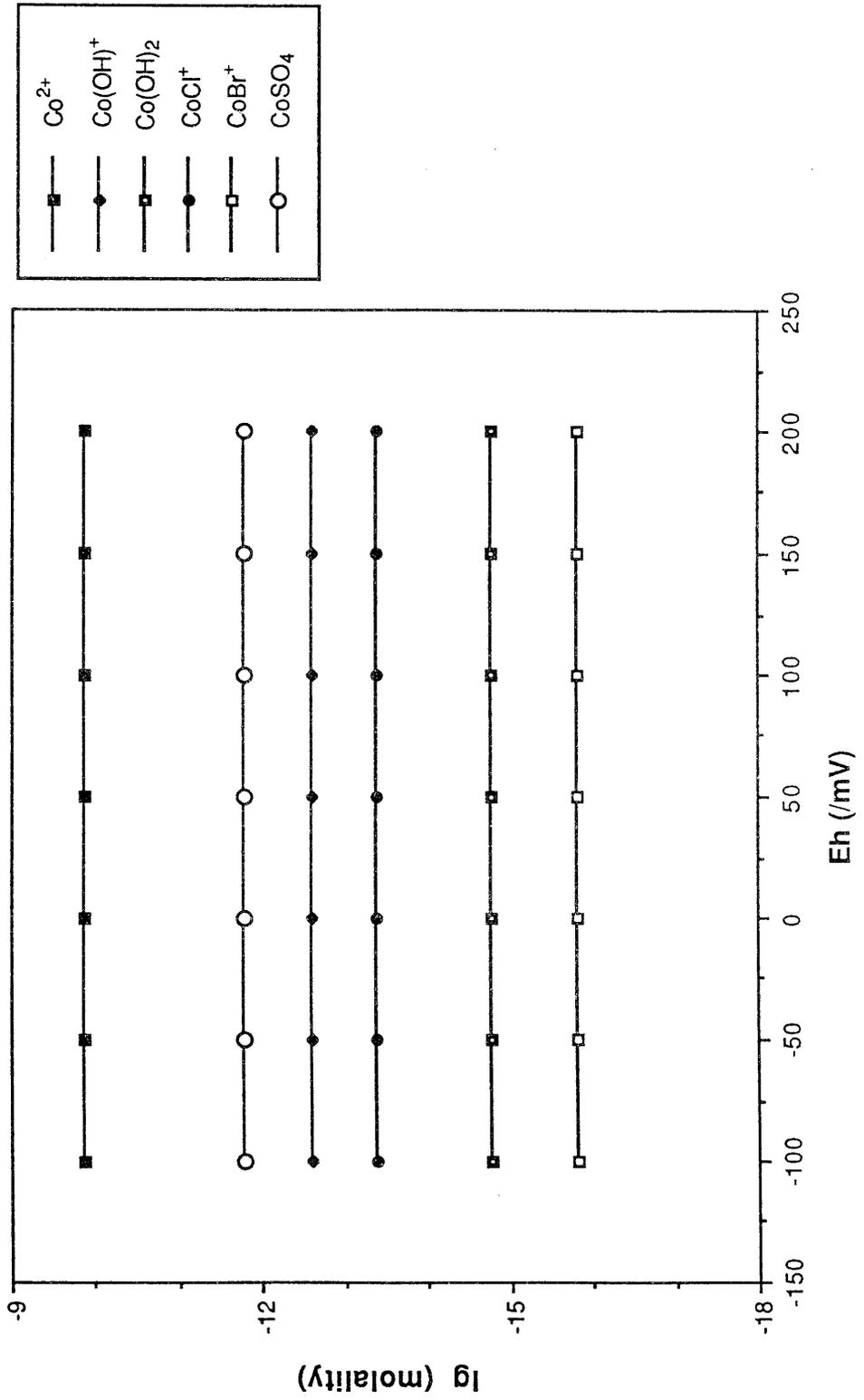
Cobalt speciation vs pH, Drigg sample 2

Temperature = 25°C, Eh = 117mV



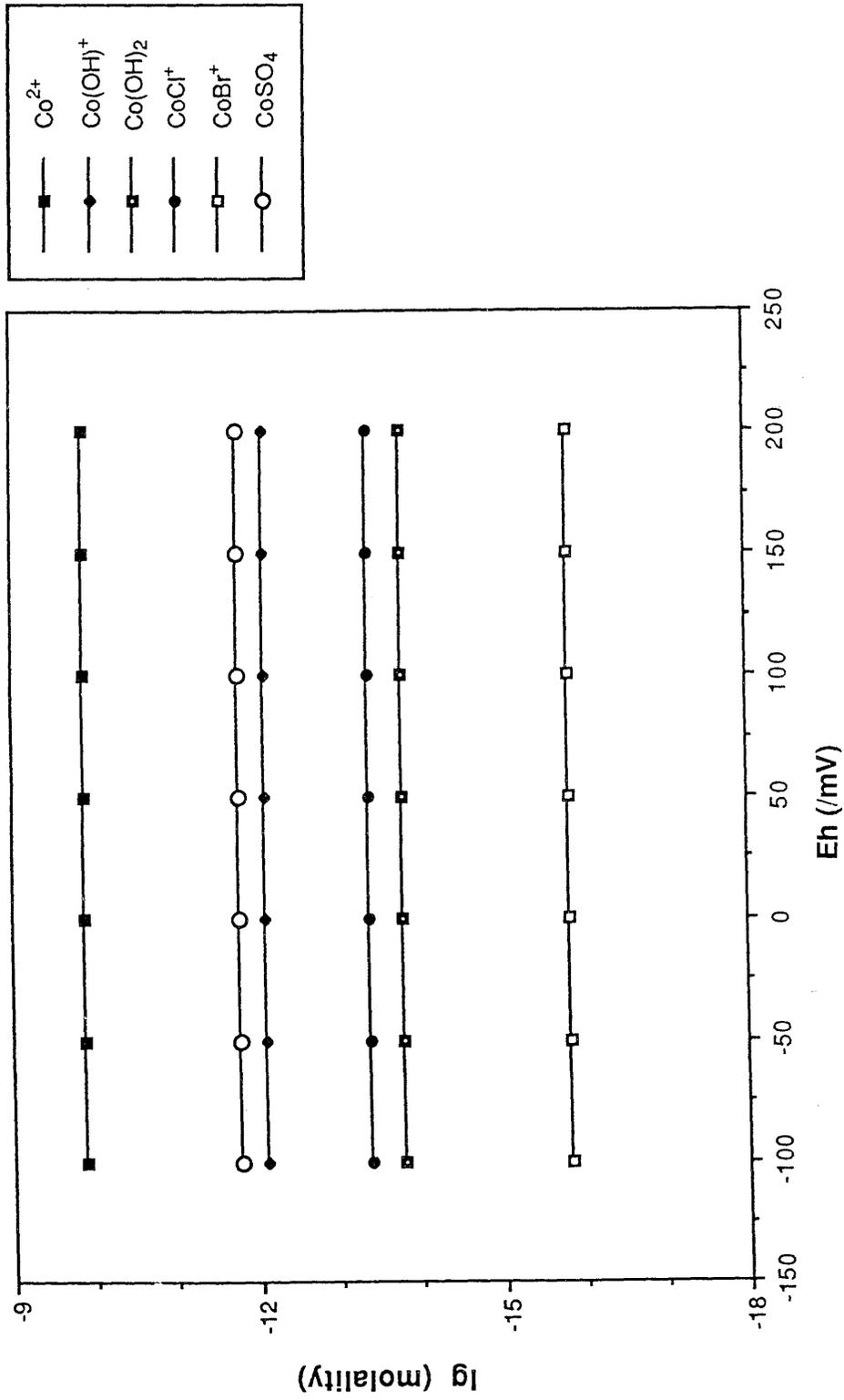
Cobalt speciation vs Eh, Drigg sample 2

Temperature = 25°C, pH = 7.0



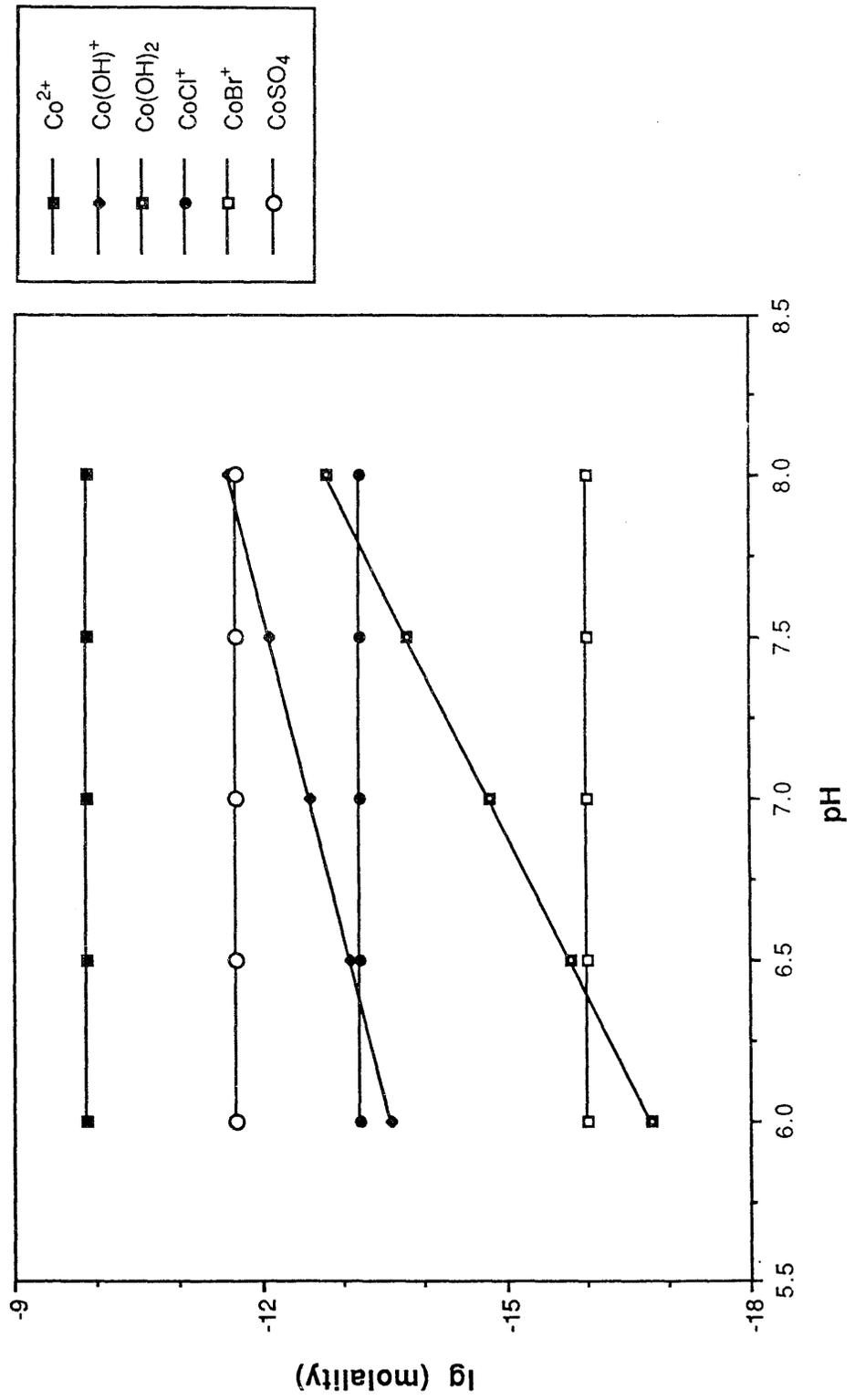
Cobalt speciation vs Eh, Drigg sample 2

Temperature = 25°C, pH = 7.5



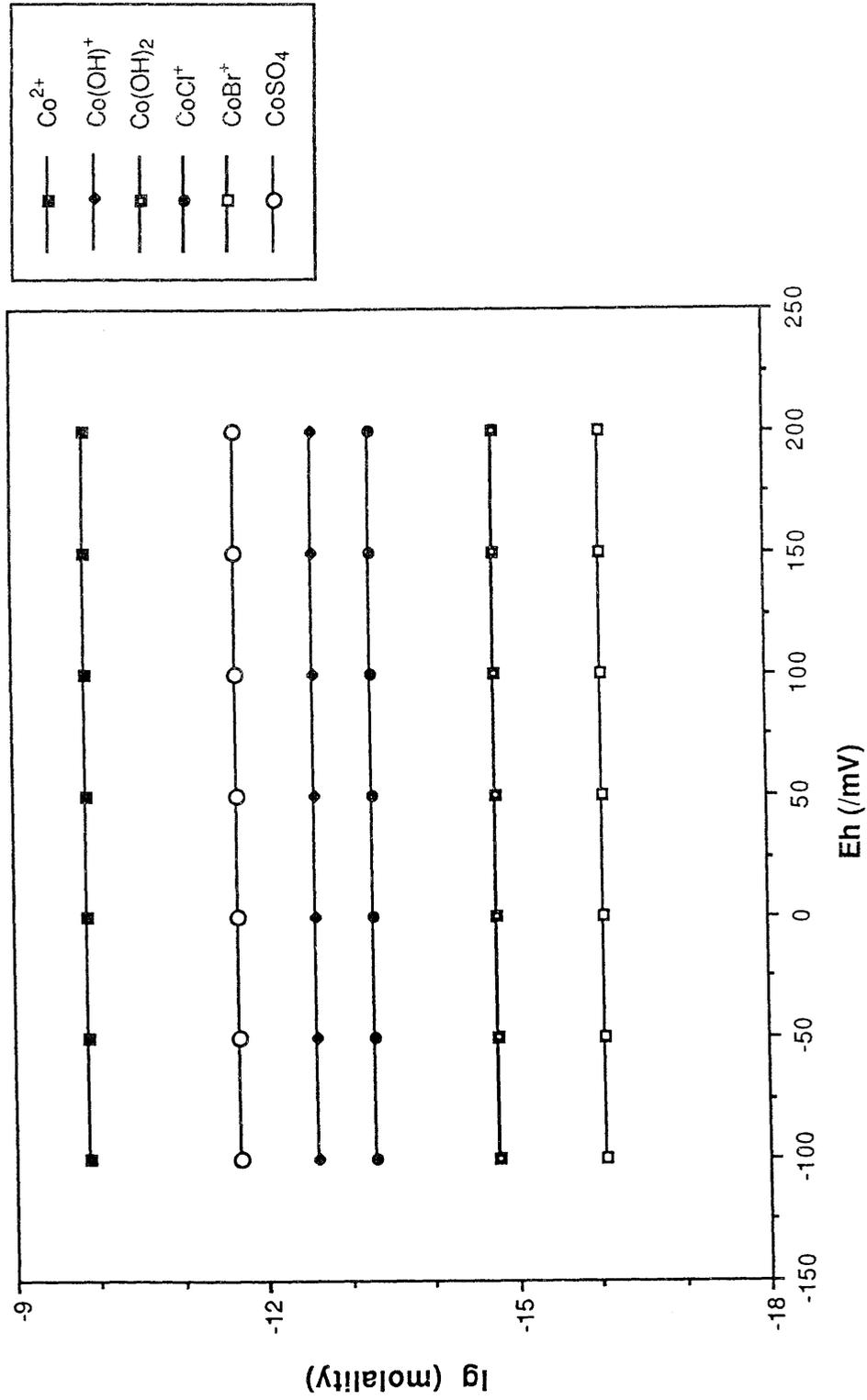
Cobalt speciation vs pH, Drigg sample 3

Temperature = 25°C, Eh = 140mV



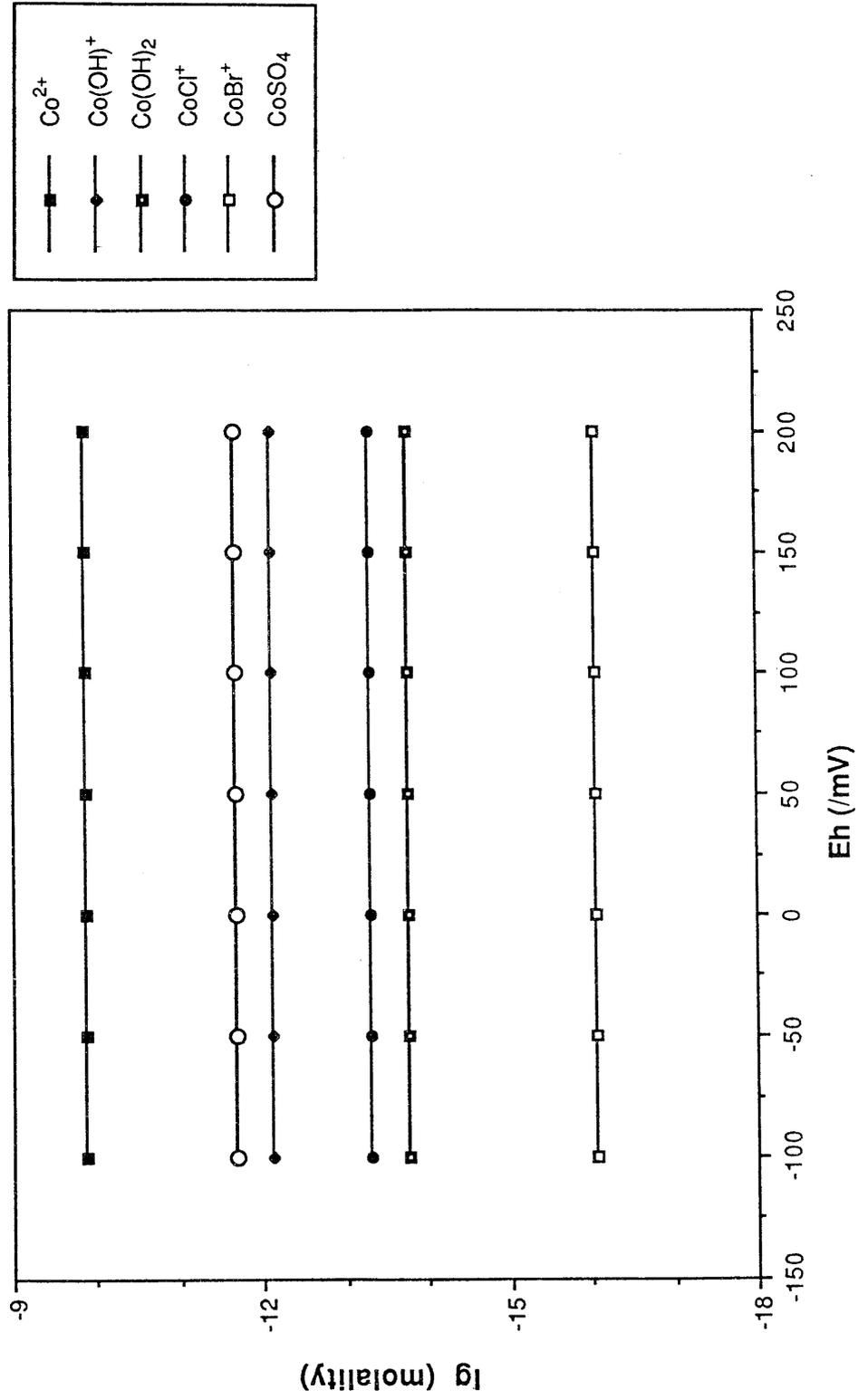
Cobalt speciation vs Eh, Drigg sample 3

Temperature = 25°C, pH = 7.0



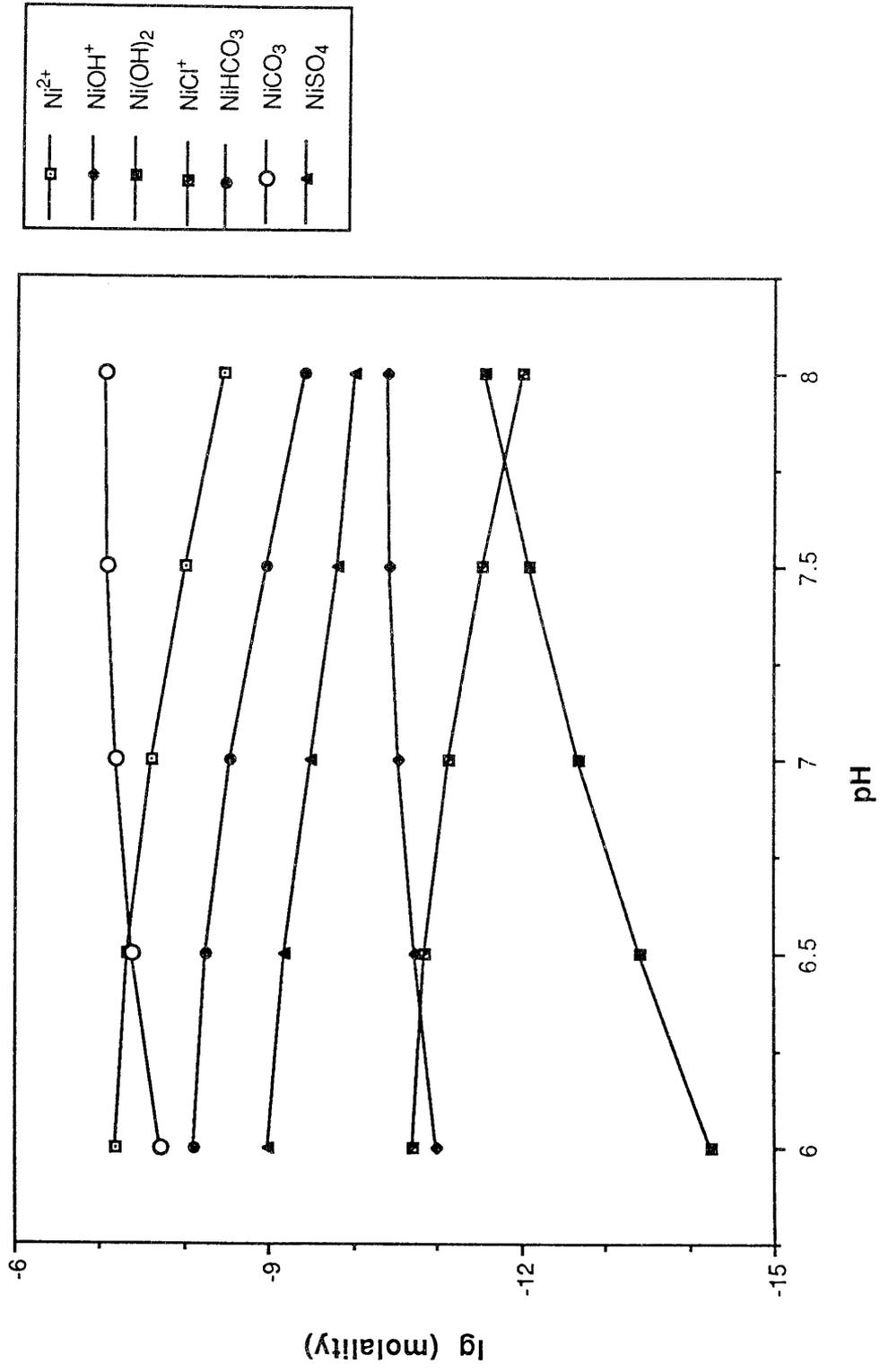
Cobalt speciation vs Eh, Drigg sample 3

Temperature = 25°C, pH = 7.5



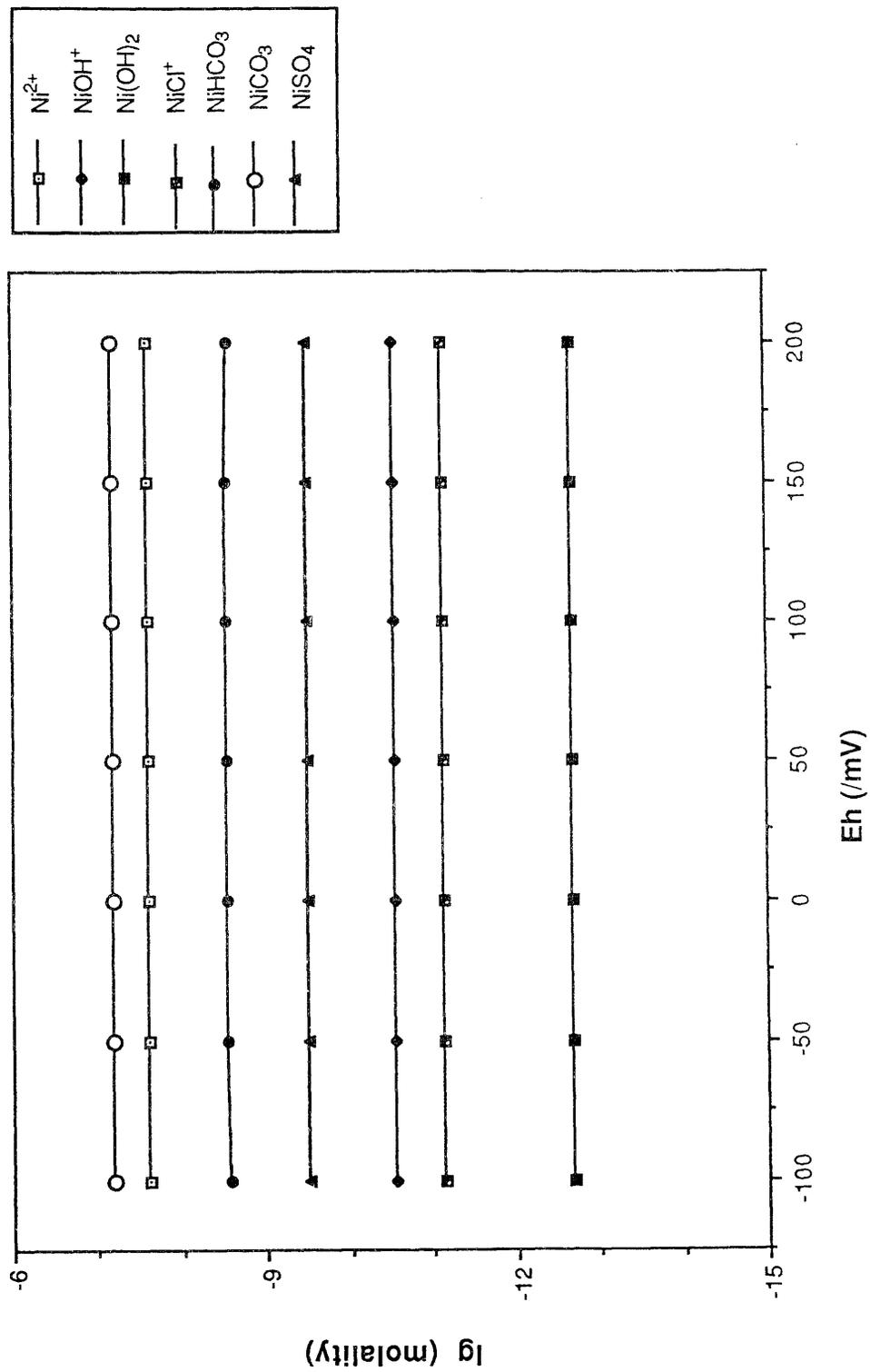
Nickel speciation vs pH, Drigg sample 2

Temperature = 25°C, Eh = 117mV



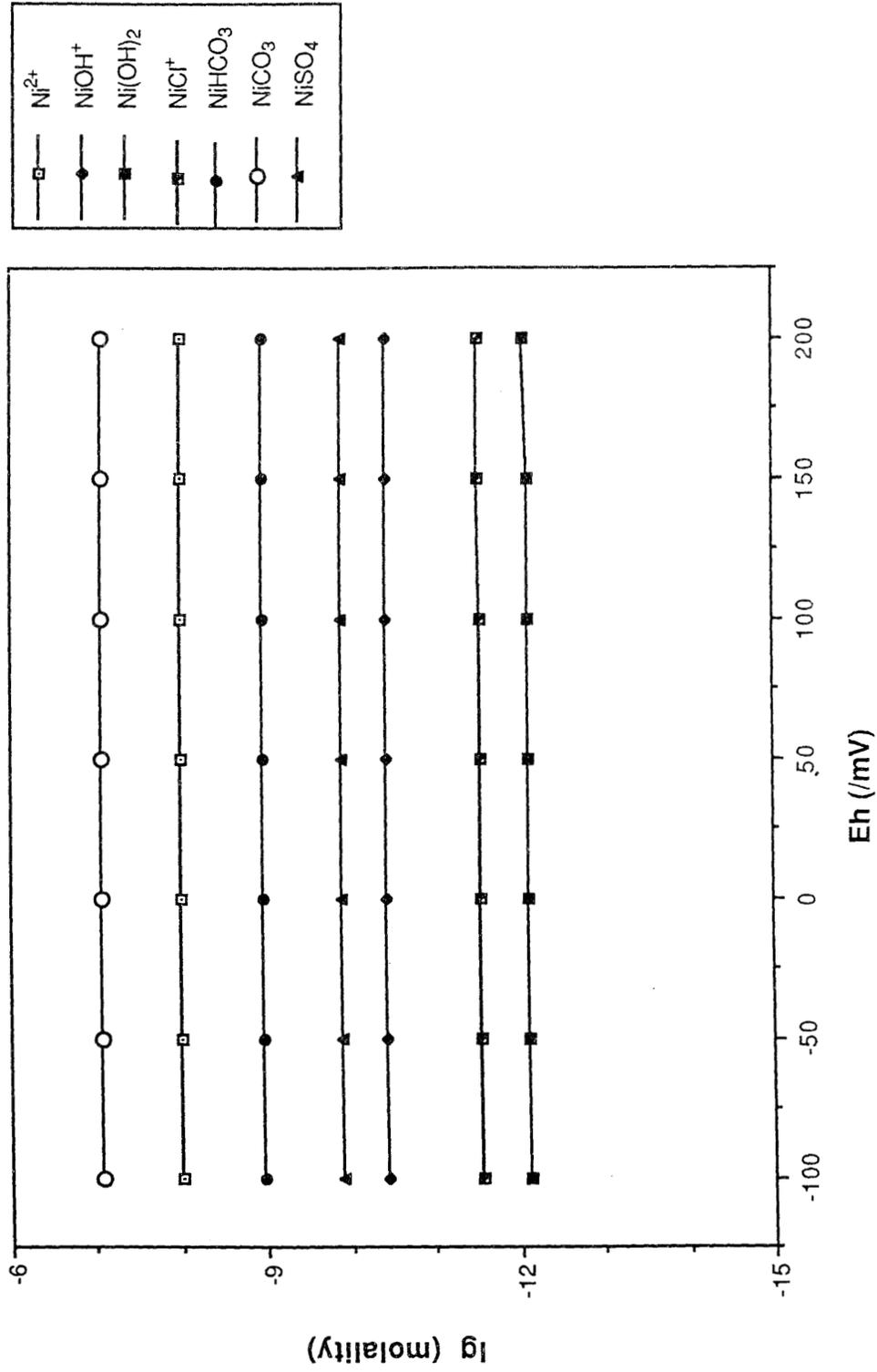
Nickel speciation vs Eh, Drigg sample 2

Temperature = 25°C, pH = 7.0



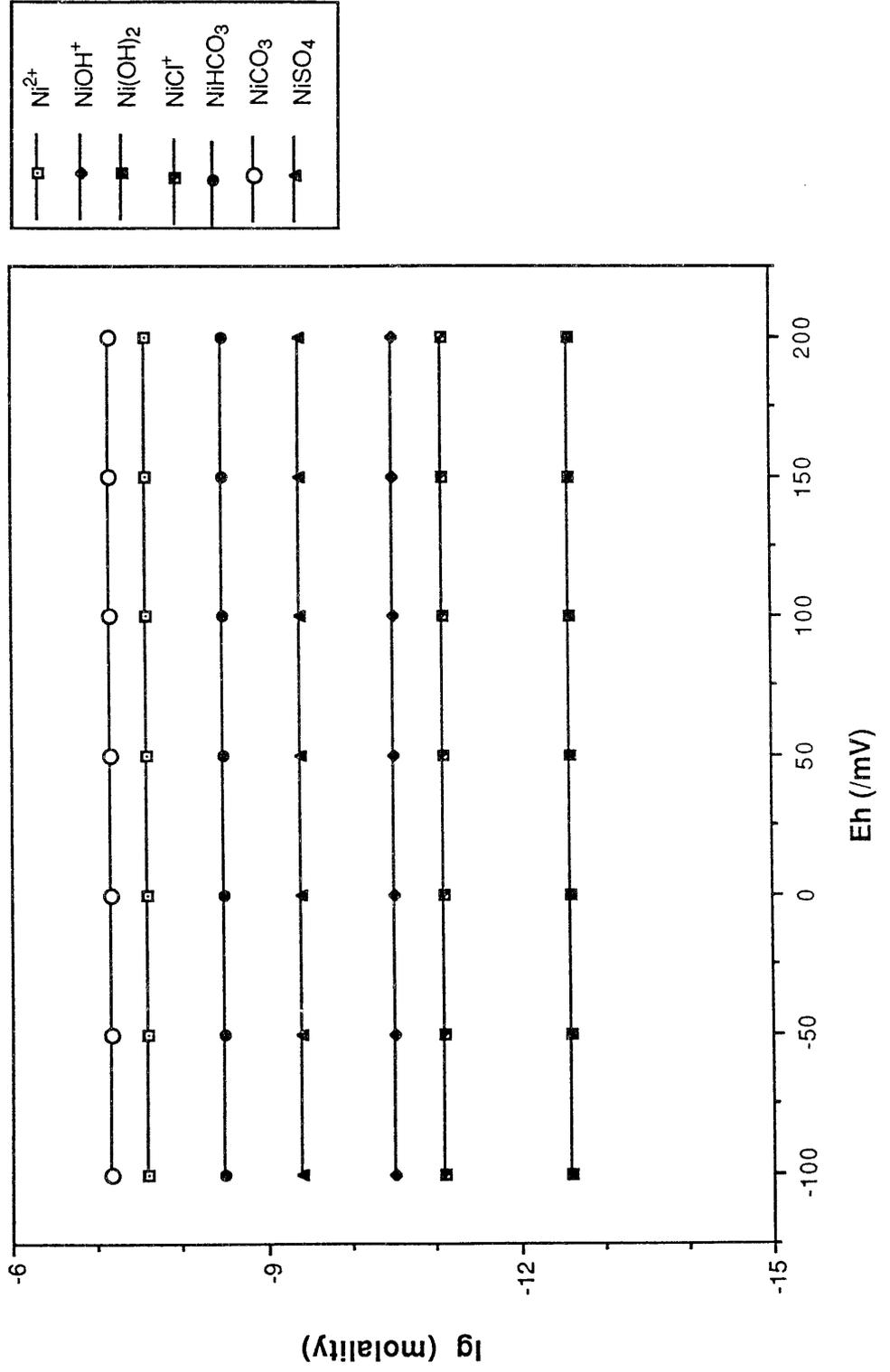
Nickel speciation vs Eh, Drigg sample 2

Temperature = 25°C, pH = 7.5



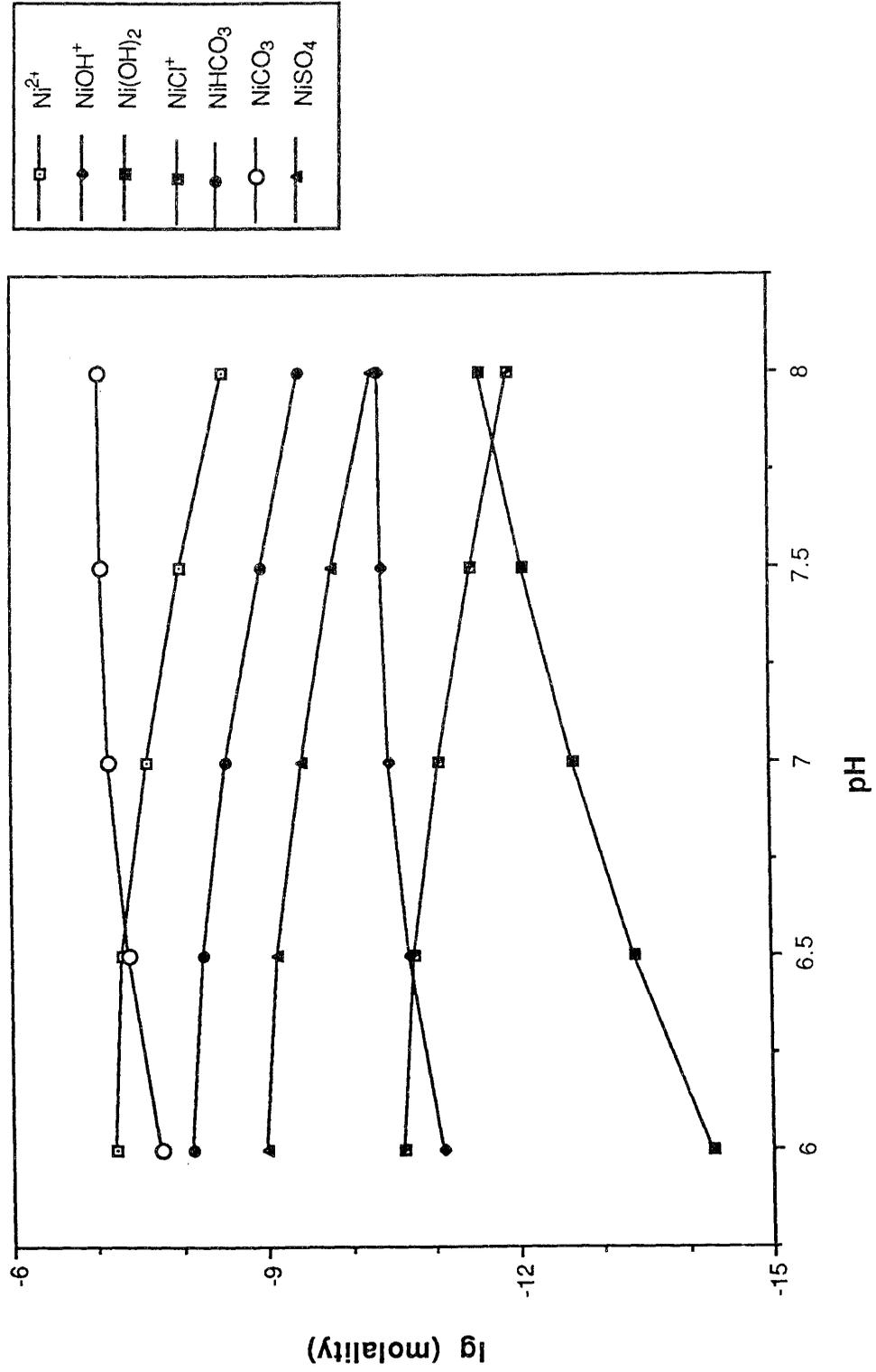
Nickel speciation vs Eh, Drigg sample 3

Temperature = 25°C, pH = 7.0



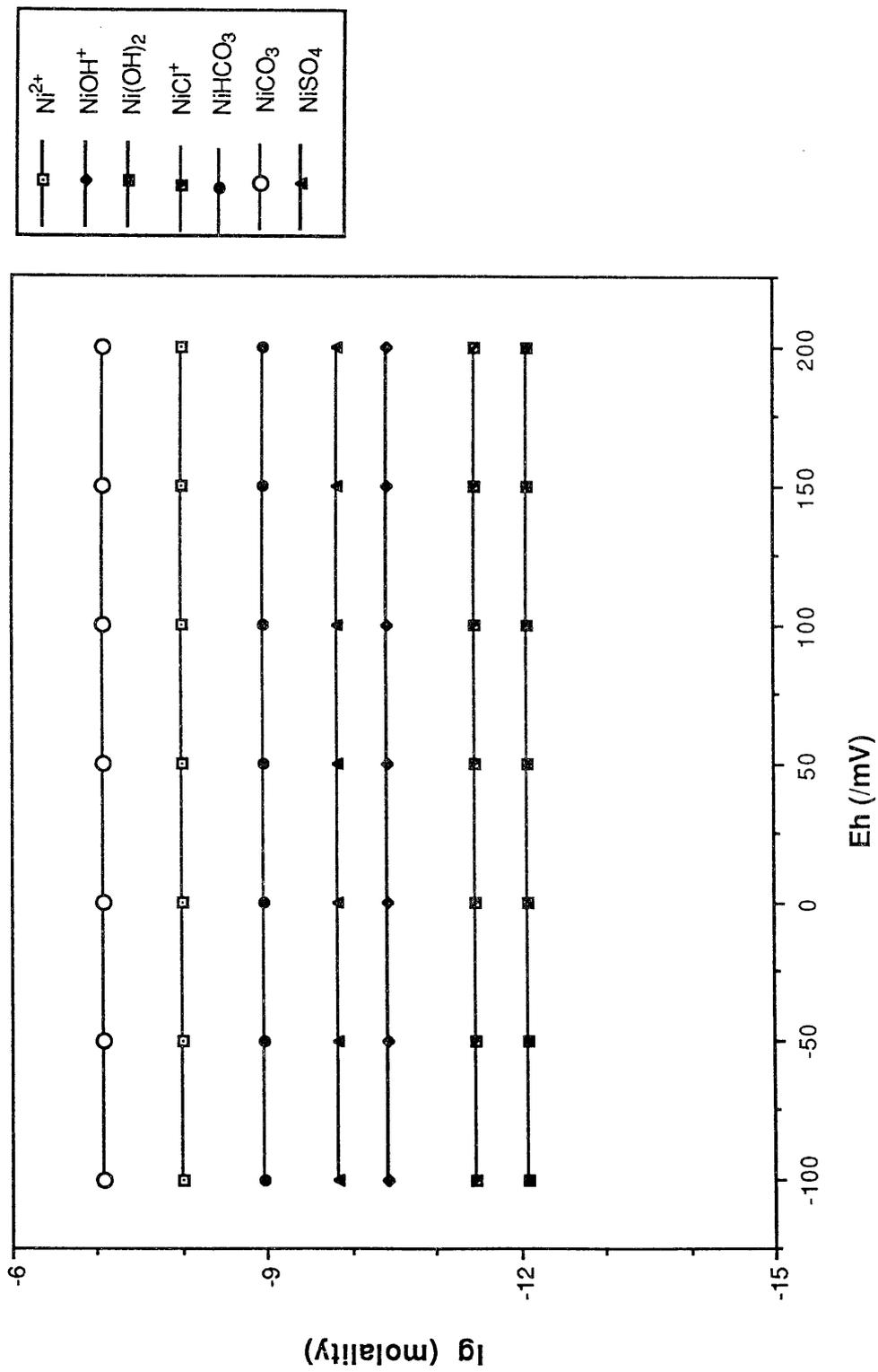
Nickel speciation vs pH, Drigg sample 3

Temperature = 25°C, Eh = 140mV



Nickel speciation vs Eh, Drigg sample 3

Temperature = 25°C, pH = 7.5



Species	lg β	Species	log β	Species	log β
FeSO ₄ ⁺	-8.970	MnSO ₄	2.26	HEDTA ³⁻	11.05
FeSO ₄ ²⁻	-7.630	Mn(NO ₃) ₂	0.6	H ₂ EDTA ²⁻	17.78
FeCl ₄ ⁻	-13.8	Mn ³⁺	-25.51	H ₃ EDTA ⁻	20.80
FeBr ²⁺	-12.41	MnO ₄ ²⁻	-118.440	H ₄ EDTA	23.01
FeBr ₂ ⁺	-12.34	MnO ₄ ⁻	-127.79	H ₅ EDTA ⁺	24.52
FeH ₃ SiO ₄	-13.97	Mn ₂ (OH) ³⁺	-10.56	H ₆ EDTA ²⁺	24.28
FeNO ₃ ²⁺	-12.01	Mn ₂ (OH) ₃ ⁺	-23.90	Ca(EDTA) ²⁻	12.460
Fe(OH) ₄ ²⁻	-46.0	Mn(OH) ₄ ²⁻	-48.30	Ca(HEDTA) ⁻	15.86
FeHCO ₃ ⁺	11.43	MnCO ₃	6.50	Mg(EDTA) ²⁻	10.37
FeCl ⁺	0.32	MnBr ⁺	0.13	Mg(HEDTA) ⁻	14.66
FeCl ²	0.81	MnNO ₃ ⁺	0.20	Na(EDTA) ³⁻	2.63
ZnOH ⁺	-8.96	MnCl ²⁺	-24.65	Na(HEDTA) ²⁻	12.42
Zn(OH) ₂	-16.90	NiOH ⁺	-9.86	Na ₂ (EDTA) ²⁻	3.94
Zn(OH) ₃ ⁻	-28.4	Ni(OH) ₂	-19.0	Fe(EDTA) ²⁻	16.002
HZnO ₂ ⁻	-28.81	Ni(OH) ₃ ⁻	-30.0	Fe(HEDTA) ⁻	19.172
Zn(OH) ₄ ²⁻	-41.20	Ni(OH) ₄ ²⁻	-44.0	Fe(H ₂ EDTA)	22.299
Zn ₂ (OH) ³⁺	-9.00	Ni ₂ (OH) ³⁺	-10.7	Fe(EDTA)(OH) ³⁻	6.301
Zn ₂ (OH) ₆ ²⁻	-57.80	Ni ₄ (OH) ₄ ⁴⁺	-27.74	Fe(EDTA)(OH) ₂ ⁴⁻	-4.38
ZnCO ₃	5.30	NiCl ⁺	0.025	Fe(EDTA) ⁻	14.513
Zn(CO ₃) ₂ ²⁻	9.63	NiHCO ₃ ⁺	12.47	Fe(HEDTA)	16.123
ZnHCO ₃ ⁺	11.83	NiCO ₃	6.87	Fe(EDTA)(OH) ²⁻	6.702
ZnSO ₄	2.34	Ni(CO ₃) ₂ ²⁻	10.11	Fe(EDTA)(OH) ₂ ³⁻	-4.81
Zn(SO ₄) ₂ ²⁻	3.10	NiSO ₄	2.29	Fe(EDTA)(OH) ₂ ⁴⁻	12.216
Zn(SO ₄) ₃ ⁴⁻	1.70	Ni(SO ₄) ₂ ²⁻	1.405	Mn(EDTA) ²⁻	15.492
Zn(SO ₄) ₄ ⁶⁻	1.7	HOAc	4.76	Mn(HEDTA) ⁻	19.012
ZnCl ⁺	0.46	Ca(OAc) ⁺	1.12	Mn(EDTA) ⁻	2.313
ZnCl ₃ ⁻	0.50	Mg(OAc) ⁺	1.28	Ba(EDTA) ²⁻	9.482
ZnCl ₄ ²⁻	0.20	Na(OAc)	-0.18	Ba(HEDTA) ⁻	16.912
ZnCl(OH)	-7.51	Fe(OAc) ⁺	1.4	Sr(EDTA) ²⁻	10.31
ZnBr ⁺	-0.62	Fe(OAc) ²⁺	-9.0	Sr(HEDTA) ⁻	14.66
ZnBr ₂	-0.98	Fe(OAc) ₂ ⁺	-5.459	Co(EDTA) ²⁻	17.942
ZnBr ₃ ⁻	1.80	Fe(OAc) ₃	-3.449	Co(HEDTA) ⁻	21.362
ZnS	39.535	Mn(OAc) ⁺	1.22	Co(EDTA) ⁻	12.823
Zn(HS) ₂	108.074	Ba(OAc) ⁺	1.07	Co(HEDTA)	16.013
Zn(HS) ₃	155.796	Sr(OAc) ⁺	1.08	Zn(EDTA)	18.122
ZnNO ₃ ⁺	0.40	Co(OAc) ⁺	1.24	Zn(HEDTA) ⁻	21.542
Zn(NO ₃) ₂	-0.30	Co(OAc) ₂	0.38	Zn(EDTA)(OH) ³⁻	5.65
Zn(NO ₃) ₃ ⁻	-1.50	Co(OAc) ₃ ⁻	0.87	Ni(HEDTA) ⁻	25.694
MnOH ⁺	-10.59	Zn(OAc) ⁺	1.56	Ni(EDTA) ²⁻	20.372
Mn(OH) ₃ ⁻	-34.800	Zn(OAc) ₂	2.53	Ni(EDTA)(OH) ³⁻	7.42
MnCl ⁺	0.61	Zn(OAc) ₃ ⁻	1.60		
MnCl ₂	0.04	Zn(OAc) ₄ ²⁻	1.36		
MnCl ₃ ⁻	-0.35	Ni(OAc) ⁺	1.29		
MnHCO ₃ ⁺	11.60	Ni(OAc) ₂	1.15		

Appendix C: Calculation of Carbonate Activities Necessary for Precipitation of Cobalt- and Nickel-Carbonate

a) Calculation of $a(\text{CO}_3^{2-})$ for Precipitation of Cobalt-Carbonate

Given the reaction:



it is possible to calculate the concentration of carbonate necessary to exceed the solubility product of CoCO_3 and hence precipitate cobalt carbonate.

$$[\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Co}^{2+}]}$$

Assuming the worst possible case, where the concentration of Co is equal to the total concentration, and substituting in the above equation gives:

$$[\text{Co}]_{\text{tot}} = 1.34 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\begin{aligned} [\text{CO}_3^{2-}] &= \frac{1.05 \times 10^{-10}}{1.34 \times 10^{-10}} \text{ mol dm}^{-3} \\ &= 0.78 \text{ mol dm}^{-3} \end{aligned}$$

This concentration is far larger than the measured concentration of inorganic carbon in the experimental samples, and so the precipitation of CoCO_3 is predicted not to occur.

b) Calculation of $a(\text{CO}_3^{2-})$ for Precipitation of Nickel-Carbonate

Given the reaction:



it is possible to calculate the concentration of carbonate necessary to exceed the solubility

product of NiCO_3 and hence precipitate Nickel carbonate.

$$[\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ni}^{2+}]}$$

Assuming the worst possible case, where the concentration of Ni is equal to the total concentration, and substituting in the above equation gives:

$$[\text{Ni}]_{\text{tot}} = 9.41 \times 10^{-8} \text{ mol dm}^{-3}$$

$$[\text{CO}_3^{2-}] = \frac{1.34 \times 10^{-7}}{9.41 \times 10^{-8}} \text{ mol dm}^{-3}$$

$$= 1.42 \text{ mol dm}^{-3}$$

This concentration is far larger than the measured concentration of inorganic carbon in the experimental samples, and so the precipitation of CoCO_3 is predicted not to occur.