Technical Report

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Analysis of Electrochemistry Cells

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Executive Summary

In previous work for SKB, an electrochemical cell was developed to measure pH, corrosion potential of steel and redox potential in artificial groundwater, in the presence of a mass of anaerobically corroding steel wires. Two cells were run for over 7,500 hours. At the end of the test period, the cells were dismantled and the solutions and specimens analysed, to provide a better understanding of the environment within the test cells and the reactions that had taken place on the surfaces of the test electrodes.

A thorough visual examination of the electrodes and the cells was carried out and photographs were taken. The wires in the test cells were black, although the film formed in Cell 1 appeared to be thinner than in Cell 2. Some green slime was present in both cells, but not to the same extent. Microscopic examination indicated that the slime was microbial in origin.

The solutions were analysed for silicon, iron, calcium, sodium, organic carbon and total inorganic carbon. Given the uncertainties in the analytical techniques, the analyses were within the range expected based on the weights added to make up the test solutions.

The composition of the corrosion product on the steel wires was determined by Raman spectroscopy measurements. The corrosion product was shown to be predominantly magnetite (Fe_3O_4), but there was also an indication of goethite (FeOOH) on samples that were analysed while still wet. This supports the hypothesis of a dual layer oxide film being formed during the anaerobic corrosion of iron.

The surfaces of the silver-silver chloride reference electrode and the gold redox electrode were examined by scanning electron microscopy and electron microprobe analysis. There was no evidence for loss of the porous chloride coating from the surface of the reference electrode.

The potential of the silver-silver chloride electrode from Cell 1 was measured against a stored silver-silver chloride electrode to check the hypothesis that the silver chloride electrode used in the test cell had converted to a platinum hydrogen electrode. Initially this electrode showed a highly negative potential value, as was observed previously in the test cell, but approximately 14 hours after immersion the electrode assumed the correct potential. The reason for this behaviour is not clear. The effect of changing the pH on the potential of the reference electrode was examined and it was found that it was independent of pH, showing that the potential was not determined by the central platinum wire.

The Calomel electrode from Cell 2 was found to have drifted by about 30 mV and the possible reasons for this are discussed in the report.

The operation of the pH electrodes from the two cells was checked in solutions of known pH. They were found to be behaving normally and linearly. The calibration of the pH electrodes in various buffer solutions needs to be performed with care as the time to equilibrate to a change in pH can be several days.

Due to an experimental difficulty, the test solutions in the electrochemical cells had been contaminated with di-butyl phthalate. The effect of di-butyl phthalate on the pH and composition of artificial groundwater was determined by carrying out a separate experiment in which a sample of groundwater was placed in contact with DBP for 56 days. The organic contaminants in the groundwater were analysed by GC-MS. The organic compounds

were either di-butyl phthalate or related compounds. The larger molecules may have been residual contaminants from the manufacture of DBP; the smaller molecules may have been contamination in the original DBP or degradation products from DBP in the test cells.

In general, analysis of the cell contents has contributed to a deeper understanding of the processes occurring in anoxic groundwater containing corroding steel and highlighted some of the experimental considerations that should be taken into account in making electrochemical measurements in simulated repository conditions.

Contents

1 Introduction

In previous work for SKB, a corrosion cell was developed to measure electrochemical parameters in the presence of anaerobically corroding steel. The aim of the experiments was to develop techniques for measuring electrochemical parameters under simulated repository conditions. Two electrochemical cells were set up and monitored for several months /1,2/. The cells contained a glass pH electrode, a steel wire for measuring the corrosion potential of steel, a gold electrode for measuring the redox potential and a reference electrode, which was a silver-silver chloride electrode in Cell 1 and a glass calomel electrode in Cell 2. In addition a freshly prepared silver-silver chloride electrode and a commercial silver-silver chloride electrode (Clarke Electromedical) were monitored against a calomel electrode in a simulated groundwater (Cell 3), to test the long-term stability of the reference electrodes. Cell 1 and Cell 2 were sealed to maintain an anoxic environment and were backfilled with hydrogen. Cell 3 was naturally aerated.

On completion of the experiments, Cell 1 and Cell 2 were dismantled and the solutions and specimens analysed, to provide a fuller understanding of the environment within the test cells and the reactions that may have taken place on the surfaces of the test electrodes. Before dismantling, Cell 1 was operated for 11,200 hours and Cell 2 for 7,500 hours. This report contains details of the measurements that were carried out and discusses their implications for understanding the results of the previous electrochemical measurements.

2 Experimental Programme

2.1 Decommissioning and visual inspection

The following steps were carried out with the two electrochemical cells:

1. The cells were removed from the water bath and a visual inspection of the internal components through the cell wall was carried out. Close-up photographs were obtained.
2. The manometer columns were removed and the cells were placed in a nitrogen-purged low-oxygen (<10 ppm oxygen) glove box.
3. The cells were dismantled inside the glovebox and the test liquid decanted into steam-cleaned sample jars, in readiness for chemical analysis.
4. The steel wires were removed from the test cells and stored in fresh artificial bentonite-equilibrated groundwater, prior to corrosion product analysis.
5. The potentials of the reference electrodes were checked against fresh reference electrodes and the responses of the pH electrodes were tested.

Details of the measurements carried out are given in the following sections.

2.2 Analysis of contents of electrochemical cells

2.2.1 Analysis of test solutions

A sample of the test liquid was decanted into a gas-tight vessel and transferred to an analytical laboratory.

Immediately after opening the transfer vessel, total alkalinity was measured by titrating a sample against a standardised nitric acid solution using methyl orange indicator to determine the end points. Alkalinity is expressed as concentration of calcium carbonate.

A sample of the solution was acidified to ensure iron species were soluble, then analysed for iron, silicon, sodium, calcium and potassium by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The chloride content of the solution was analysed by pre-treating the sample using a continuous-flow auto-analyser to develop colour using standard chemistries. The concentration was determined colorimetrically using an on-line UV/visible spectrometer.

Samples were analysed for total organic carbon (TOC), by the following procedure. The samples were acidified using concentrated phosphoric acid and bubbled with carbon-free air to remove carbonate. They were then catalytically oxidised using persulphate and ultraviolet light to convert organic carbon to carbon dioxide. The TOC concentrations in the samples were calculated by quantification of the CO_2 produced using a non-dispersive infra-red detector in comparison with standards. If there were any organic particulates in the solution, such as microbial material, they may not have been fully oxidised by the ultra violet radiation, so the TOC may have underestimated the total organic content.

2.2.2 Analysis of corrosion products

Samples of the steel wires from each test cell were analysed using Raman spectroscopy to determine the composition of the corrosion product films. The samples were transferred by sealing them in glass capillaries inside a glovebox to ensure that they were not oxidised by air. Samples were analysed dry (after placing the wires on tissues), wet (after direct removal from the test solution) and wiped (using tissue to remove loose surface product and reveal the adherent sub-layer). Ten to twelve wires were placed in each vial. Each wire was approximately 1 cm long.

Raman spectroscopy is an optical technique whereby chemical and phase specific information can be obtained non-destructively with a spatial resolution of 2–4 µm. A Renishaw Raman Microscope was used. Spectra were recorded in the back-scattered geometry, using a x5 high numerical aperture objective lens, giving a spatial resolution of some 10 µm. The exciting laser wavelength was 632.8 nm (from an air-cooled HeNe ion laser). The power was approximately 20 mW. The intensity and position of the bands in a laser Raman spectrum depend both on the chemical composition and the crystal phase composition of the sample. For example, ZrO_2 will have a different spectrum from Cr_2O_3 but tetragonal and monoclinic ZrO_2 will also be different. However, ZrO_2 and TiO_2 if present as the same phase (e.g. tetragonal) will exhibit similar spectra, although the exact band positions will be different due to the difference in atomic mass of Zr and Ti.

2.2.3 Examination of the electrodes

2.2.3.1 Examination of the silver-silver chloride electrode from Cell 1

After 11,200 hours the potential of the silver-silver chloride electrode from cell 1 was checked in a number of ways (section 2.3.1). It was then rinsed carefully in distilled water and green slimy deposits near the surface of the silver-silver chloride electrode were examined using optical microscopy and electron microprobe analysis. Scanning electron micrographs of the surface morphology of any residual coatings were obtained.

2.2.3.2 Examination of gold electrode

After rinsing carefully in distilled water, the surfaces of the gold E_h electrodes in Cell 1 and Cell 2 were examined by electron microprobe analysis, to determine whether any materials had plated out on to their surfaces during the experiments. Scanning electron micrographs of the electrode surfaces were obtained.

2.3 Tests on electrodes used in electrochemical cells

2.3.1 Recalibration of silver-silver chloride electrode from Cell 1

Four silver-silver chloride electrodes were fabricated according to the procedure described in reference /2/. They were labelled No. 1 to No. 4. Silver-silver chloride electrode No. 1 was monitored against a calomel reference electrode in Cell 3. Silver-silver chloride reference electrode No. 2 was used in Cell 1. Silver-silver chloride electrodes No. 3 and No. 4 were stored in naturally aerated 0.01M NaCl with their contacts shorted together and used as required as reference potential standards. They were returned to the 0.01M NaCl solution with shorted contacts after use.

In addition, three calomel electrodes were constructed with the simulated groundwater as the reference electrolyte. The reference electrode used in Cell 2 was one of these electrodes and was designated as Calomel (Cell 2). Another electrode was installed permanently into Cell 3 and was designated as Calomel (Cell 3). The third calomel electrode was remade on numerous occasions and was used as a standard potential to check the stability of Calomel (Cell 3) and also to crosscheck the potential of the silver-silver chloride electrodes. The third calomel electrode was designated Calomel (New).

Four hundred and seventy hours after commissioning Cell 1, the gold wire, the iron wire and the pH electrode all shifted in potential by –0.823 V. This was attributed to a sudden change in the potential of the reference electrode but it was not possible to investigate this further at the time without aborting the experiment. The data were corrected for this potential shift /2/ and the post-decommissioning analysis described in this report was carried out to justify the reference potential correction and to investigate the possible origin of the potential shift. On the basis of this unexpected result a calomel reference electrode was used in Cell 2, instead of a silver-silver chloride electrode.

After 11,200 hours the potential of silver-silver chloride electrode No. 2 from Cell 1 was measured against a silver-silver chloride electrode that had been prepared at the same time as electrode No. 2 but stored in a 0.01M chloride solution for several months (silver-silver chloride electrode No. 4). The stored electrode was inserted into the test cell after its lid was removed inside the anoxic glovebox. The measurements were made via a voltage follower connected to a datalogger.

The silver-silver chloride reference electrode used in Cell 1 was fabricated by silver-plating a platinum wire, followed by chloridisation of the silver to produce silver chloride /2/. If spalling of the silver chloride coating had occurred, then the platinum wire could have been exposed to the solution. Hence, a possible explanation for the potential shifts of –0.823 V observed in Cell 1 is that if the platinum wire at the centre of the reference electrode had been exposed to the solution it could have determined the potential of the reference electrode. To test this hypothesis, the reference electrode from Cell 1 was tested for its response to pH; if platinum wire had been exposed a potential-pH dependence would be expected. The effect of pH on the potential of AgCl (No. 2) was tested by placing the electrode in a range of buffer solutions, to determine whether it was behaving as a hydrogen electrode as a result of spallation of the silver chloride coating.

The experiments were performed in air using a small bench-top cell. The potential for the following cell was measured in three buffer solutions at 21ºC.

–ve | Calomel (New) | groundwater || 1M NaCl + Buffer | AgCl (No 2) | Ag | +ve

The buffer solutions were as follows: Russell BC45 (potassium hydrogen phthalate, pH 4); Russell BC7S (potassium dihydrogen orthophosphate and disodium hydrogen orthophosphate, pH 7); and Russell (Na_2CO_3, $NaHCO_3$, pH9).

2.3.2 Recalibration of calomel electrode from Cell 2

The calomel reference electrode removed from Cell 2 was tested by measuring the potential against one of the stored silver-silver chloride electrodes (AgCl No. 4).

2.3.3 Recalibration of pH electrodes from Cell 1 and Cell 2

The outputs from the glass pH electrodes in both cells were checked in buffer solutions at pH 4, pH 7 and pH 9. The electrodes were placed into an H cell with a calomel reference electrode, in groundwater at 31ºC. The cell configuration was:

(–ve) | Calomel (New) | groundwater || 1M NaCl + Buffer | glass electrode | (+ve)

2.4 Effect of di butyl phthalate on test solution

It was previously found that a decrease in pH occurred in the electrochemical test cells /2/. Possible reasons for the fall in pH were (i) degradation of di-butyl phthalate contamination, which had entered the cell during filling of the test cell, and (ii) dissolution of silicates (e.g. cristobalite) from the glass. Therefore, in parallel with the measurements outlined above, some separate experiments were carried out to investigate the possible effects of DBP on the pH of groundwater. A photograph of the cell used for this experiment is shown in Figure 2-1. The cells were equipped with proprietary silver-silver chloride electrodes (Metrohm 6.0726.100) and pH electrodes (Metrohm 6.0130.100). Two cells were set up containing 150 ml artificial bentonite-equilibrated groundwater and they were deoxygenated by purging with nitrogen inside a nitrogen-purged glovebox. After 21 days, 30 ml of DBP was added to the artificial groundwater in one of cells and 30 ml groundwater was added to the other cell to ensure the total volumes remained the same in both cells. The potential of the glass electrodes in the two cells was measured against the silver/silver chloride reference electrode for a total period of 56 days.

In order to determine the composition of any contamination in the aqueous phase a separate experiment was set up in which 200 ml of DBP was added to 800 ml of artificial bentonite-equilibrated groundwater inside the glove box. The vessel was left for 56 days and then a sample of the aqueous phase was analysed using gas chromatography – mass spectroscopy (GC-MS) to determine if any organic species were present in the aqueous phase. The analysis was carried out as follows: 250 ml of sample were placed into a separating funnel and spiked with an isotopically labelled standard. The sample was then extracted with dichloromethane. The extract was dried over anhydrous sodium sulphate and then blown down to 1ml under a stream of nitrogen. The samples were analysed on a Hewlett-Packard 6890/5973 gas chromatograph-mass spectrometer operating in scan mode.

Figure 2-1. *Photograph of cell used for testing effect of di-butyl-phthalate on test solution.*

3 Results

3.1 Visual Inspection of test cells

Photographs of the electrochemical cells before dismantling are shown in Figure 3-1 and Figure 3-2. The main points from the visual examination were as follows:

- The corrosion product observed in Cell 1 was not as blue/black as the corrosion product in Cell 2. This implies that a thicker oxide layer had formed in Cell 2, despite the shorter life of this cell.
- Cell 1 was still producing gas.
- In Cell 1 a pale green slime had formed on the AgCl electrode at the meniscus between the solution-air glass interface and also at the solution-air interface. This appeared to be algal growth.
- In Cell 1 there had been some transfer of water (~2 ml) from the reaction vessel into the manometer. This was not apparent in Cell 2 and was related to the specific design of Cell 1: the connecting arm between the two vessels of the cell was sloping towards the DBP reservoir. The design was changed for Cell 2.
- In Cell 1 the steel wire electrode was touching the mass of steel wires.

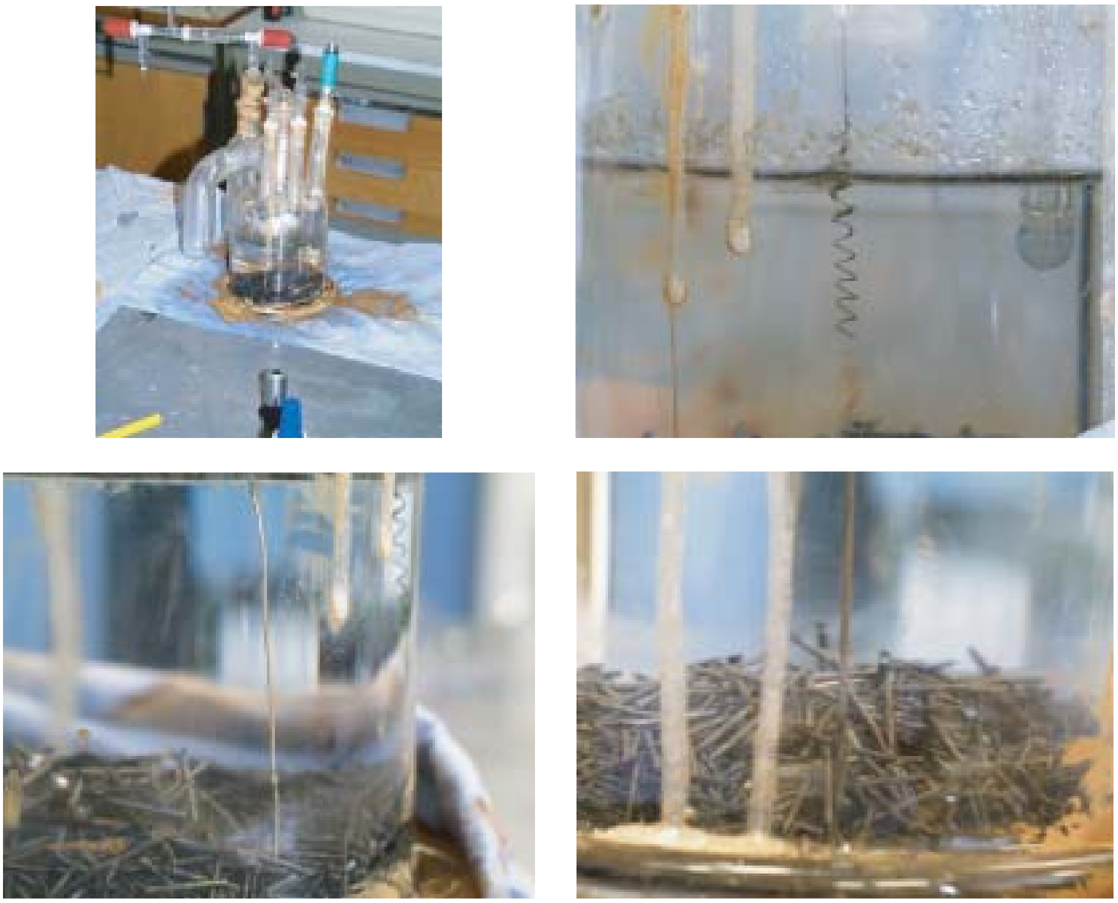


__Figure 3-1.__ Photographs of electrochemical test Cell 1 on completion of tests.

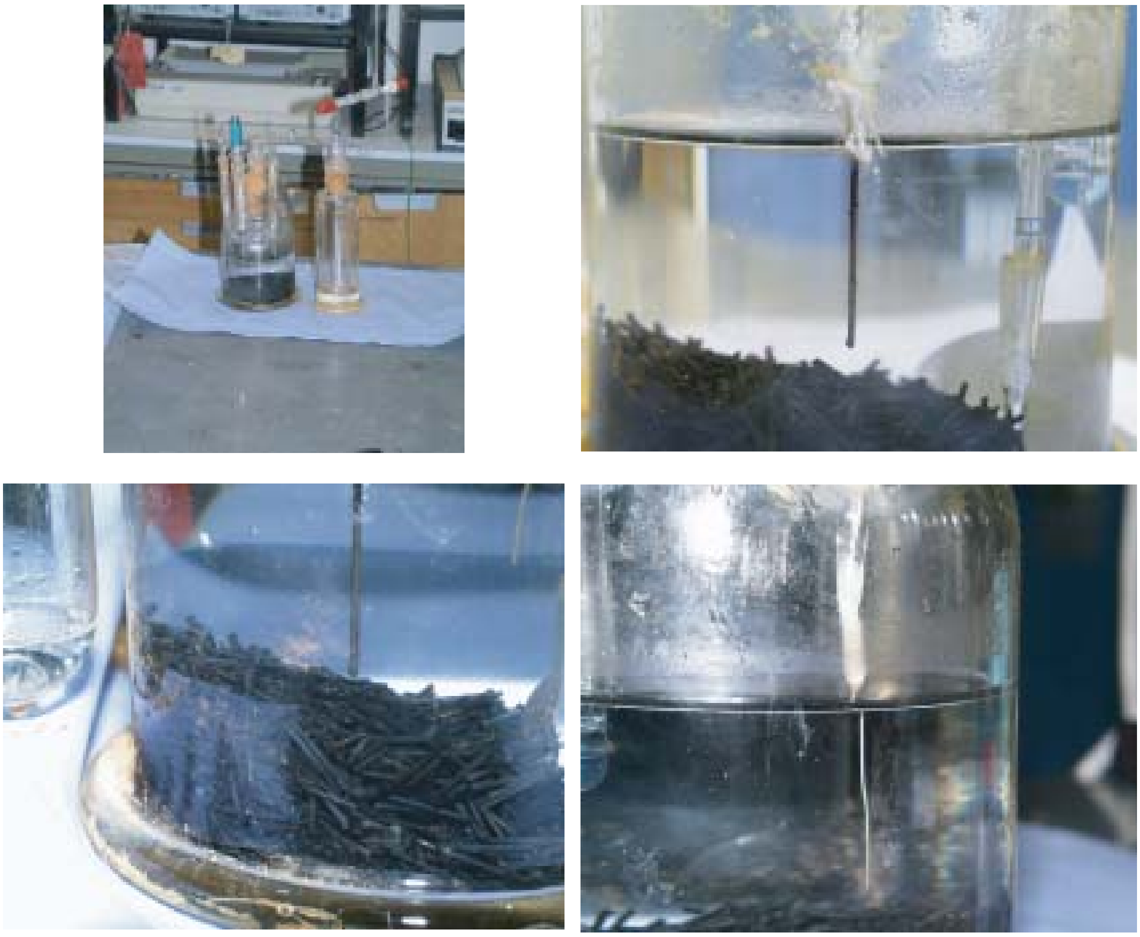


Figure 3-2. Photographs of electrochemical test Cell 2 on completion of tests.

- In Cell 2 there was a yellow stain around the joint of the calomel electrode.
- In Cell 2 there was some hint of green deposit or algal growth at the solution meniscus but there was much less than in Cell 1.
- Cell 2 contained a slug of DBP, which was visible as a separate liquid phase.

3.1.1 Examination of green slime

A sample of green slime from Cell 1 was examined using Raman spectroscopy, but no spectra could be obtained. The sample simply fluoresced, suggesting that it was mainly polymeric in nature, rather than a mineral. It was also examined using optical microscopy; there was no evidence of crystallinity. The material appeared to be cellular in nature, with long thin structures with walls surrounding a central vascular space, suggesting that it was biological in origin (possibly algae). Under white transmitted light some areas appeared brownish, suggesting that there was some inorganic material also caught up in the organic material.

Scanning electron micrographs of the green slime are shown in Figure 3-3 and an EDX analysis of slime on the surface of the silver chloride wire is shown in Figure 3-4. The presence of iron in the material agrees with the visual observation of some corrosion product incorporated into the slime (see above). The source of the high concentration of silicon is not clear, but may have been due to dissolution of the glass test vessel.

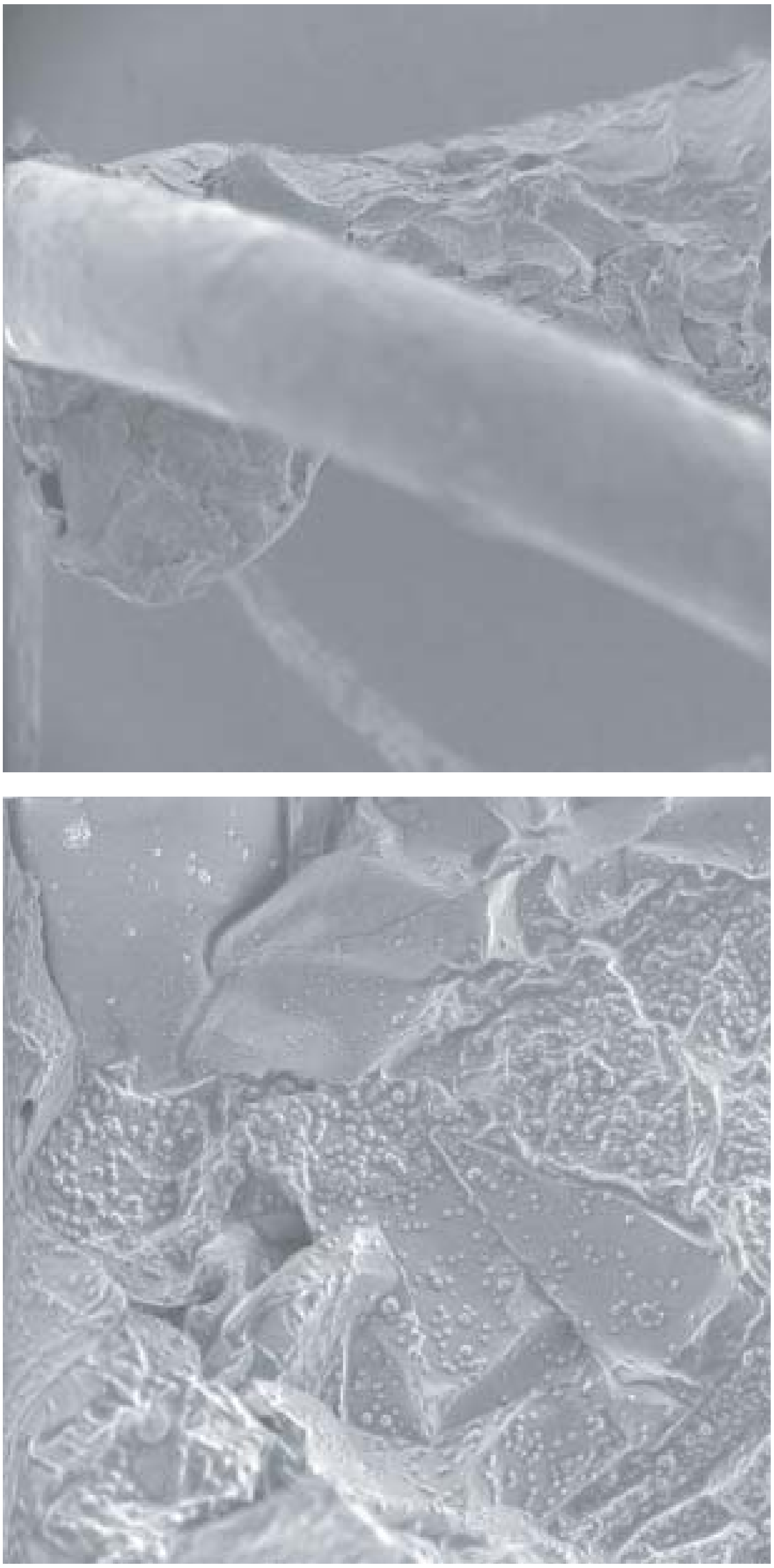


Figure 3-3. *Scanning electron micrographs of green slime on surface of silver chloride reference electrode (top x70; bottom x700).*

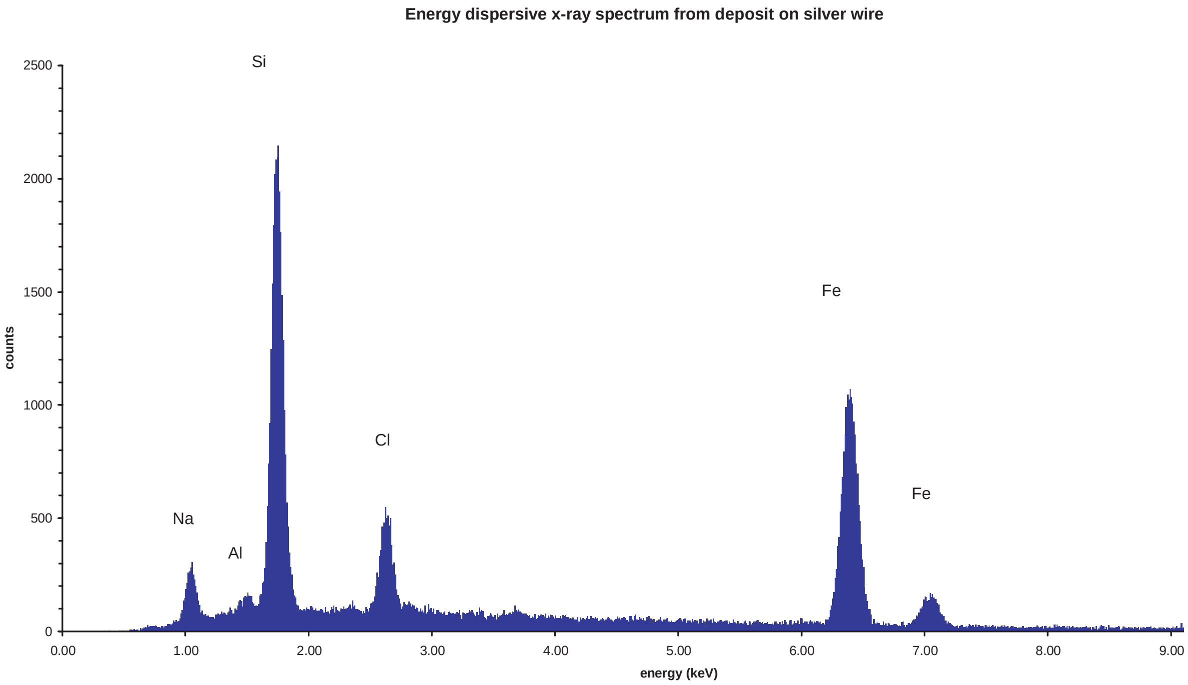


Figure 3-4. *EDX analysis of material on surface of silver chloride reference electrode.*

3.2 Analysis of the contents of the electrochemical cells

3.2.1 Analysis of test solutions

3.2.1.1 Analysis of the aqueous phase

The results of the water analyses are reported in Table 3-1. Measurement uncertainty is estimated at ±20% for results greater than an order of magnitude of the limit of detection (LoD). Given the uncertainty in the results the analyses are within the range expected based on the weights of sodium chloride and sodium carbonate used to make up the artificial groundwater (31.56 g/litre sodium chloride and 1.06 g/litre sodium carbonate).

It is possible that the potassium measured for Cell 1 is an impurity in the sodium chloride used to make up the test solution, although the measured level is approximately three times the upper limit according to the reagent supplier's catalogue. (Analytical grade sodium chloride contains potassium impurity at a concentration of <0.01%; this concentration would correspond to an impurity concentration of ~3 mg/litre, compared to the measured value of ~9 mg/litre.) The calcium impurity level in the reagent is given as <0.002% and this may readily account for the concentrations of calcium measured in the test solutions.

The total organic carbon measured includes contamination by di-butyl phthalate (DBP) and the possible presence of microbial contamination (e.g. algae). The TOC value underestimates the microbial contamination because it would not have been fully oxidised.

Table 3-1. Analysis of water in electrochemical cells 1 and 2 (in mg/litre).

Determinand	LoD	Cell 1	LoD	Cell 2	Expected
Iron	0.007	0.25	0.01	0.08	
Potassium	0.1	9.1	nm	nm	
Calcium	0.02	0.70	0.01	0.8	
Sodium	0.2	1.4×10^4	0.3	1.1×10^4	1.29×10^4
Silicon	0.04	33	0.06	3.1	
TOC	10	350	10	420	
Chloride	100	2.0×10^4	100	1.9×10^4	1.91×10^4
Total Alkalinity as $CaCO_3$	10	830	10	780	1001

Notes:
nm = not measured.
A separate assessment of LoD (limit of detection) was made before each analysis.

3.2.1.2 Speciation of organics

The results of the analysis of the DBP contamination in the aqueous phase from the separate cell set up to investigate DBP contamination are given in Table 3-2. Results are quoted as µg/L. Results for two separate extractions are shown. The results are semi-quantitative and peak assignments are tentative. The formulae of the tentatively assigned compounds are as follows:

di-butyl phthalate: $C_6H_4(COO.C_4H_9)_2$

1-butanol: $CH_3(CH_2)_3OH$

butyl benzoate: $C_6H_5CO_2(CH_2)_3CH_3$

2-(2-butoxyethoxy) ethanol: $CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OH$

butyl-2-ethylhexyl phthalate: $C_6H_4(COO.C_4H_8.C.(C_4H_9)(C_2H_5).CH_3)_2$

The extraction efficiency is expressed as a percentage of the isotopically labelled standard recovered. The total mass of organic material measured after the extraction process, excluding the unidentified peaks, was ~13 mg/l, which after taking the extraction efficiencies into account gives an original concentration of ~23 to 37 mg/l. This is considerably lower than the measured TOC in the electrochemical cells of 350–420 mg/l. It is possible that the difference between the two measurements is due to the presence of suspended organic microbial material in the electrochemical cell. The species detected were either di-butyl phthalate or related compounds. The larger molecules may have been residual contaminants from the manufacture of DBP; the smaller molecules may be contamination in the original DBP or degradation products from the DBP. The solubility of the contamination species appears to be higher than that of the DBP itself. The purity of the DBP is given as 99% by the suppliers.

Some peaks were unidentified and were tentatively allocated by the analyst to silicone wax. This seems unlikely, as silicone greases were not used in the construction, filling or dismantling of the glassware.

Table 3-2. Results of GC-MS Analysis of Water Samples.

Observed Peaks	**Ext Blank**	**GR4408**	**GR4408 (D)**
Customer Ref.		**A**	**A**
% Recovery	**68**	**57**	**35**
Major Peak 1	Toluene	Dibutyl phthalate	2-(2-butoxyethoxy) ethanol
Concentration µg/L	**49.9**	**5467.8**	**6084.0**
Major Peak 2	Chloroform	2-(2-butoxyethoxy) ethanol	Dibutyl phthalate
Concentration µg/L	**35.7**	**5342.5**	**5916.2**
Major Peak 3	Benzene	1-butanol	1-butanol
Concentration µg/L	**6.3**	**1533.7**	**637.4**
Major Peak 4	2,6-di-tert-butylbenzoquinone	Butyl benzoate	Butyl benzoate
Concentration µg/L	**3.2**	**392.8**	**425.0**
Major Peak 5	Dibutyl phthalate	Unknown*	Unknown*
Concentration µg/L	**2.1**	**285.7**	**323.9**
Major Peak 6	1,1-bis(p-tolyl)ethane	Unknown*	Unknown*
Concentration µg/L	**1.3**	**275.8**	**317.7**
Major peak 7	1,2,3-trimethyl-4-propenylnapthalene	Unknown*	Unknown*
Concentration µg/L	**1.2**	**270.1**	**301.4**
Major Peak 8	Di(2-ethylhexyl)phthalate	Unknown*	Unknown*
Concentration µg/L	**0.6**	**243.8**	**284.7**
Major Peak 9		Unknown*	Unknown*
Concentration µg/L		**224.4**	**264.0**
Major Peak 10		Butyl-2-ethylhexyl phthalate	Unknown*
Concentration µg/L		**195.0**	**226.3**

* Tentatively attributed by analyst to silicone wax

3.2.2 Analysis of corrosion products

Several spectra were recorded from each set of wires. An example of the spectra measured for wires removed from Cell 1 is shown in Figure 3-5. The Raman spectra obtained from the black areas of the corroded wires in Cell 1 were all characteristic of magnetite, Fe_3O_4. There was no evidence for the presence of iron carbonate. Reference spectra for various iron corrosion products are shown in Figure 3-6.

The spectra of samples taken from Cell 2 and analysed in the wet, wiped and dry states are shown in Figure 3-7 to Figure 3-9. The “wiped” and the “dried” samples from Cell 2 showed a strong match to magnetite, Fe_3O_4. The spectrum from the wet samples shows two bands, at 380 cm^{-1} (small and broad), which is probably associated with FeOOH (goethite), and at 660 cm^{-1} (sharp and relatively intense). The latter band is probably attributable to Fe_3O_4, although the peak was very sharp for a spinel. This might indicate that the magnetite was very crystalline or at least a more ordered phase in this sample. Normally this band would be expected to be considerably broader since the spinel structure is generally highly defected. Alternatively it could have been due to some “metastable” iron oxide/hydroxide phase, which happened to be in a spinel like structure of Fe_3O_4. It was not obviously any other possible materials, such as Fe_2O_3, FeO, $Fe(OH)_x$, nitrate, sulphate, Ca-X, Na-X or glass.

It is possible that the Raman analysis detected a bi-layer structure consisting of a friable outer layer with an inner magnetite layer. The penetration depth of the HeNe laser light on these materials is estimated to be a few tenths of microns, up to maybe a micron.

The position of the bands in the wet sample were also shifted slightly from the reference spectra: the 660 cm^{-1} (magnetite) band was shifted to lower wavenumbers and the 380 cm^{-1} band (goethite) band was shifted to higher wavenumbers. This may indicate some biaxial stress distribution in the deposit, although, caution must be exercised in this interpretation since these bands are weak and/or broad so exact positions may be uncertain.

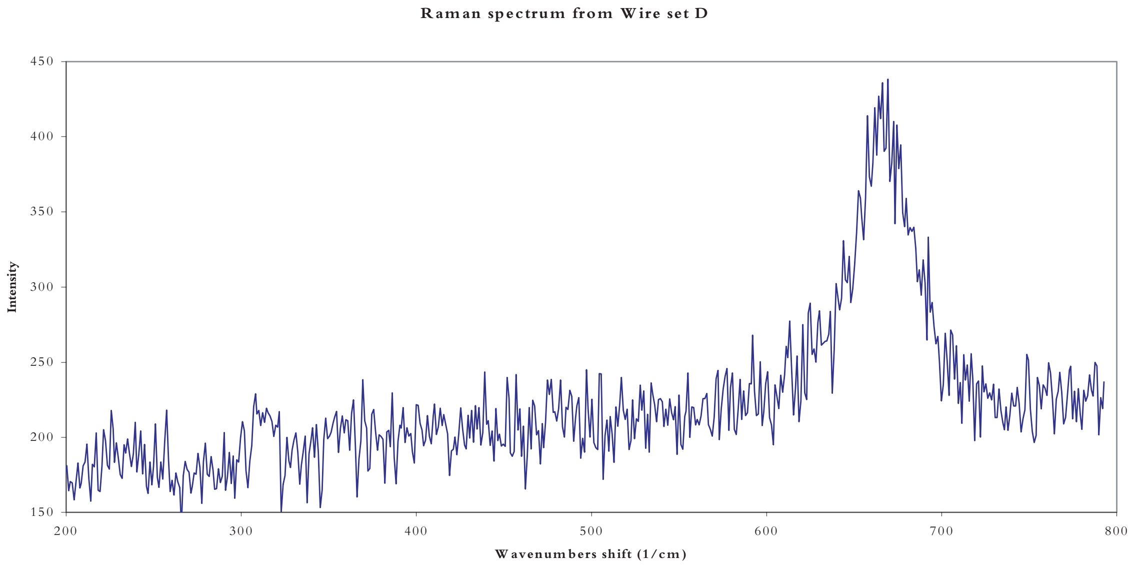


Figure 3-5. *Raman spectra from wires analysed in the dry state.*

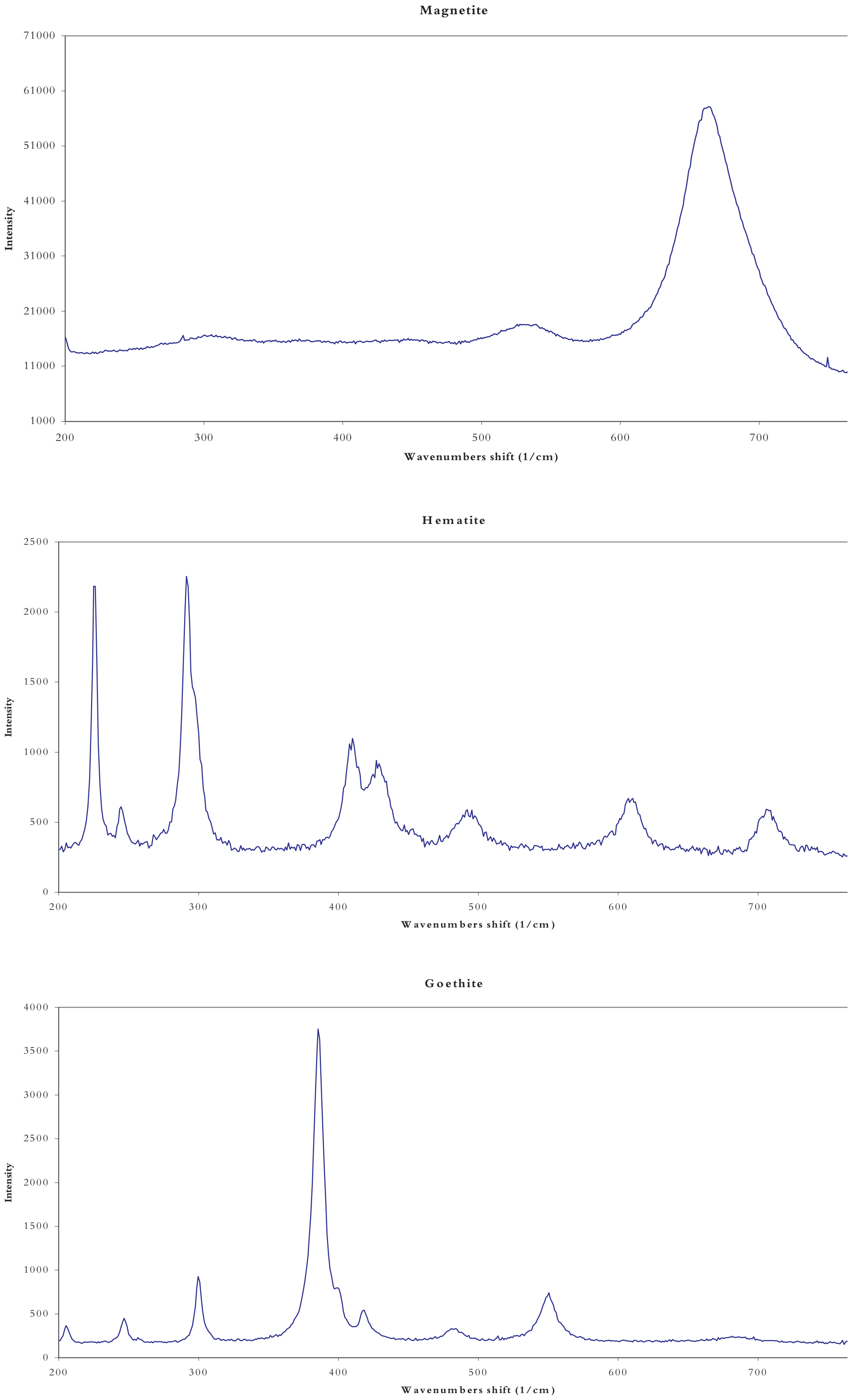


Figure 3-6. *Raman spectra from standard iron oxides /4/.*

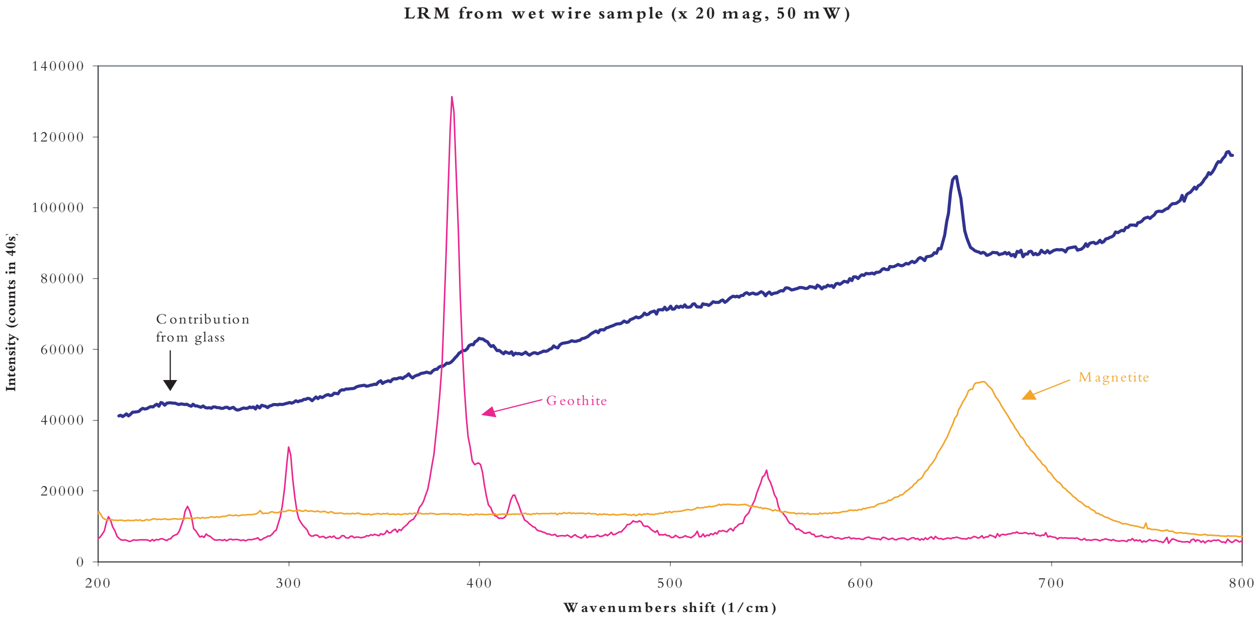


Figure 3-7. Raman spectra from samples removed from electrochemical Cell 2 and analysed in the wet condition.

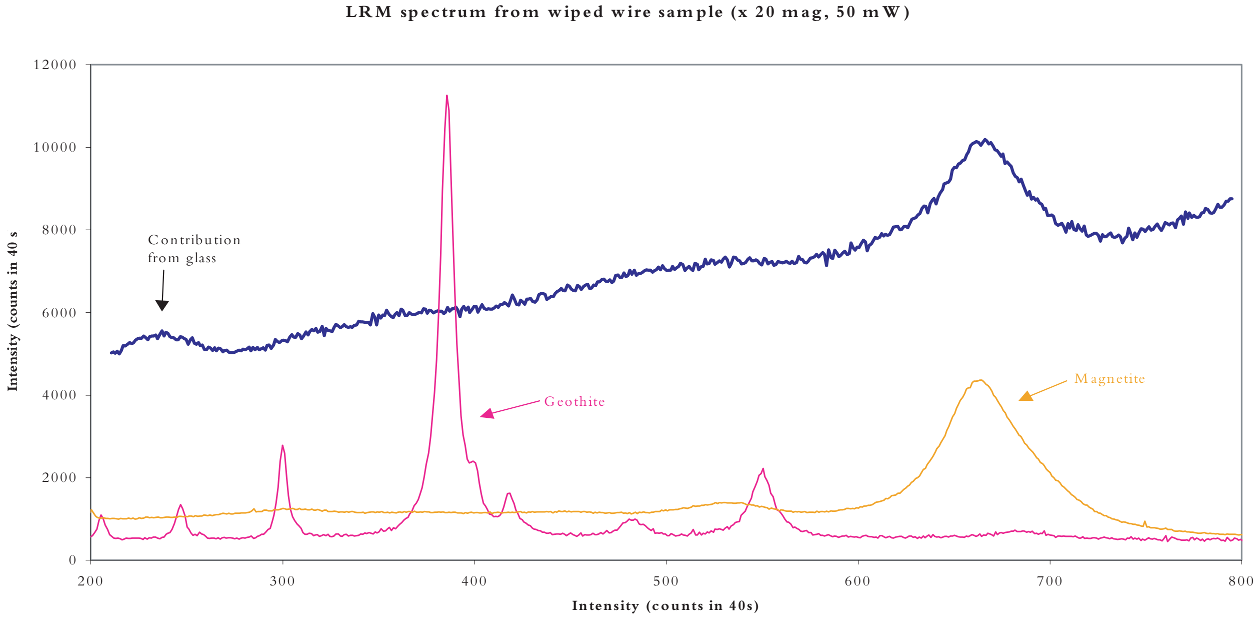


Figure 3-8. Raman spectra from samples removed from electrochemical Cell 2 and analysed after wiping the surface.

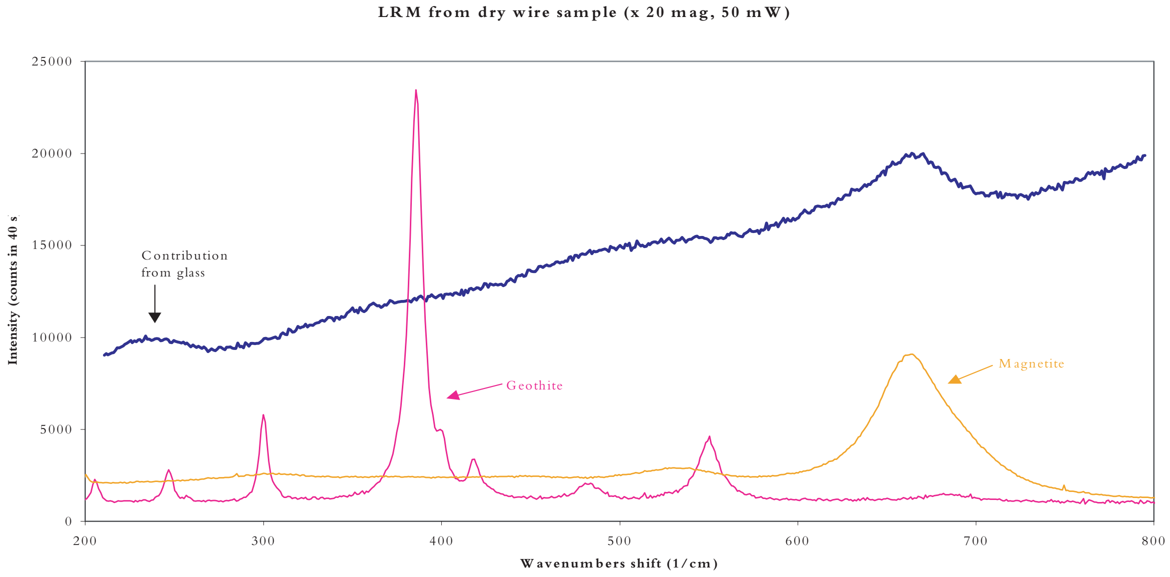


Figure 3-9. *Raman spectra from samples removed from electrochemical Cell 2 and analysed in the dry condition.*

3.2.3 Examination of the electrodes

3.2.3.1 Examination of silver chloride reference electrode

An SEM examination of the surface of the silver chloride electrode was carried out, as shown in Figure 3-10. There was no evidence for loss of the porous chloride coating from the surface of the electrode.

3.2.3.2 Examination of gold redox electrode

The surface of the gold electrode was examined by scanning electron microscopy (SEM). Energy dispersive X-ray analyses (EDX) was carried out on particles observed on the surface of the gold electrode. Photographs of the particles are shown in Figure 3-11 and EDX analyses of selected areas are shown in Figure 3-12. The EDX spectra show that the dark elongated particles visible in the SEM images contained a trace of iron and silver, which presumably originate from the iron and silver/silver chloride electrodes immersed in the test solution. In view of the poor signal to noise ratio it is possible that the material was predominantly organic – it may have been microbial material. The presence of calcium, aluminium and silicon in a particle on the gold electrode suggests that it may have been composed of calcium aluminosilicate (e.g. from the glassware or dust contamination).

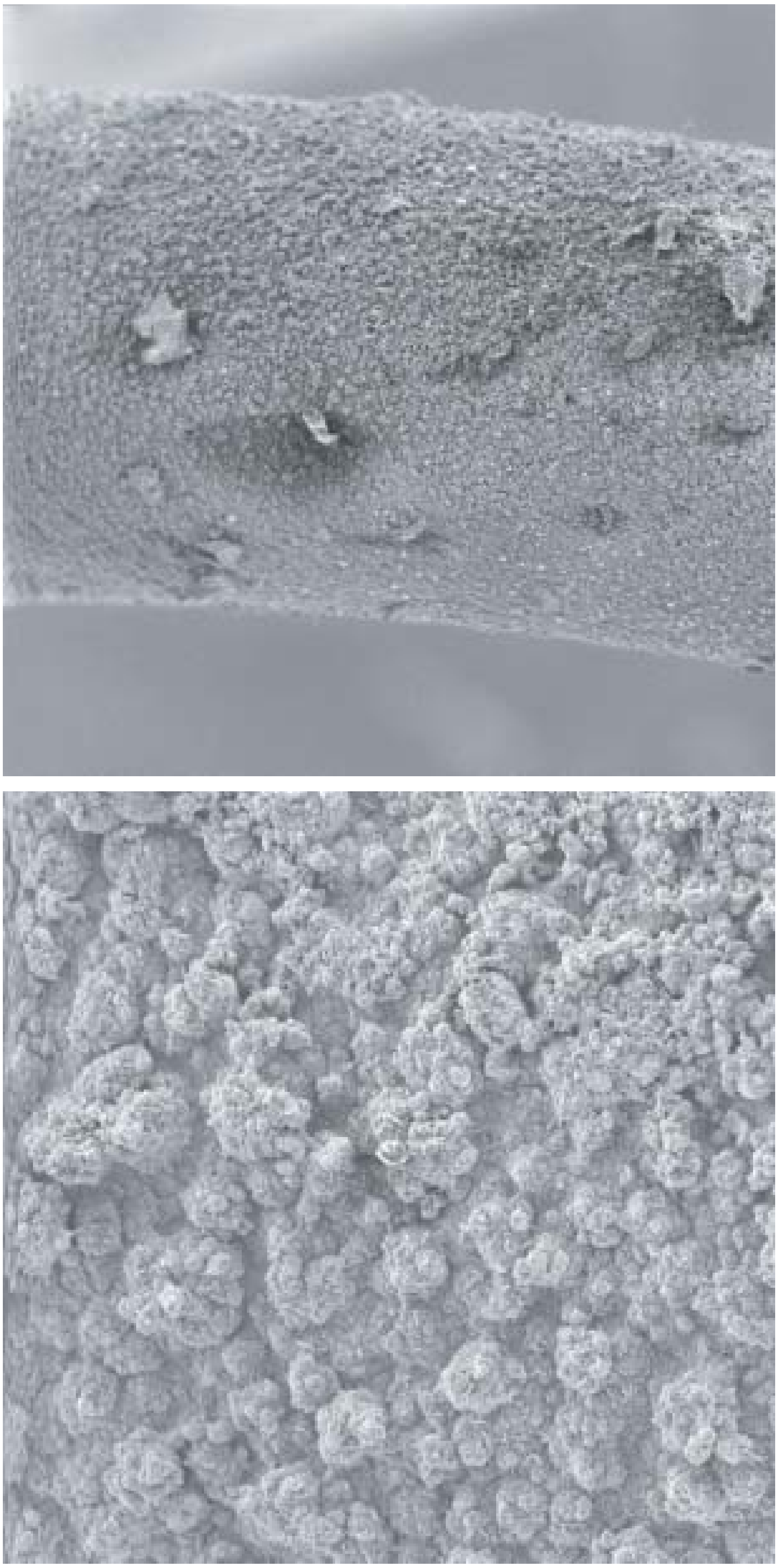
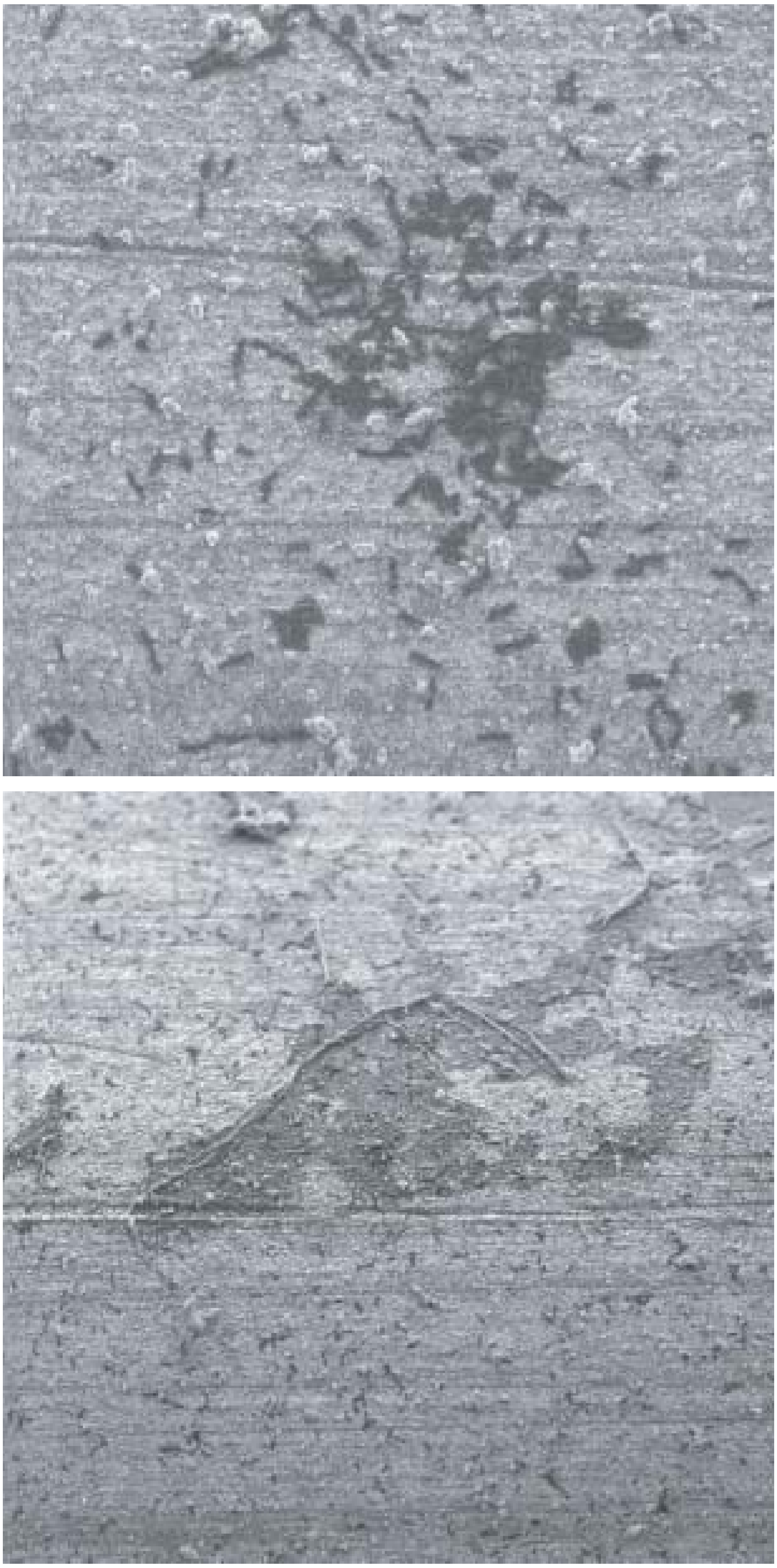
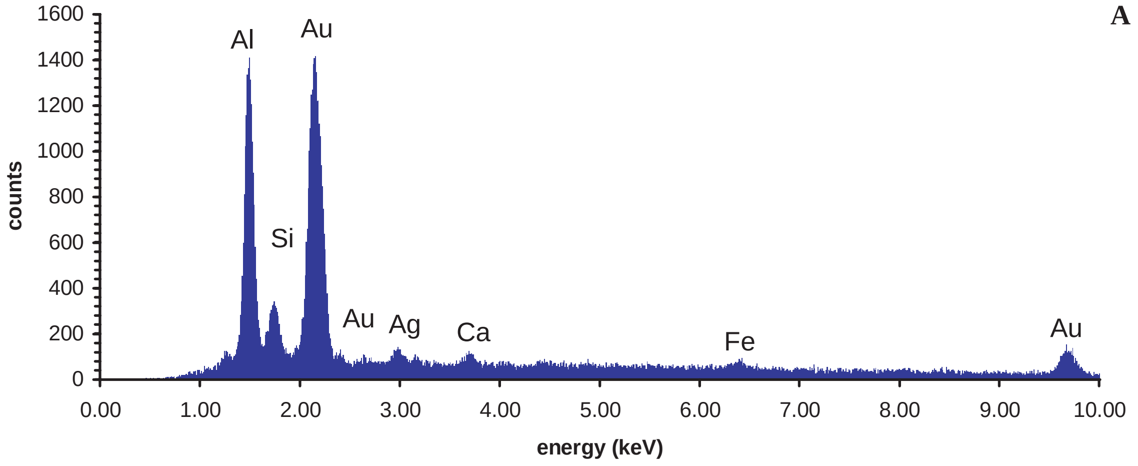


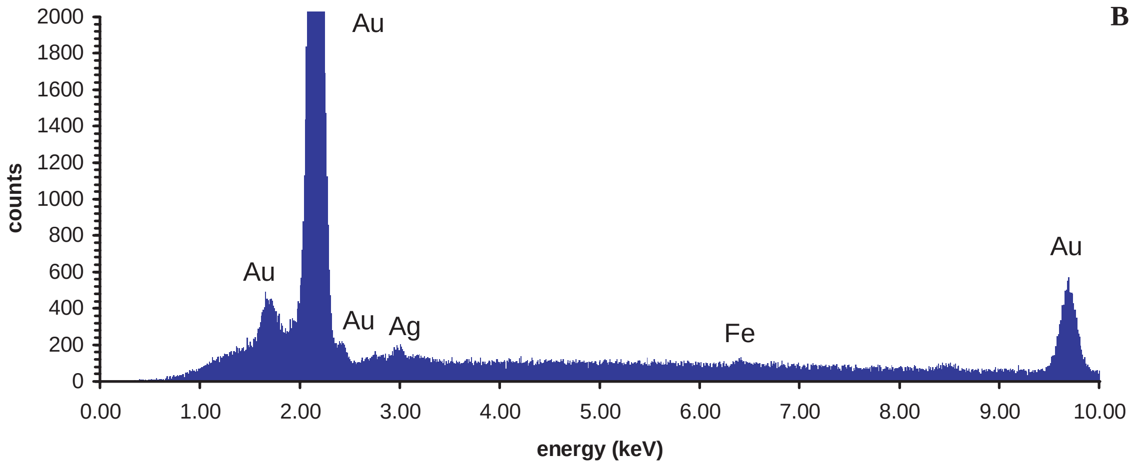
Figure 3-10. *Scanning electron micrographs of surface of silver chloride reference electrode (top x220; bottom x2,000).*

Figure 3-11. *Scanning electron micrograph of surface of gold redox electrode (top x2,500; bottom x700).*

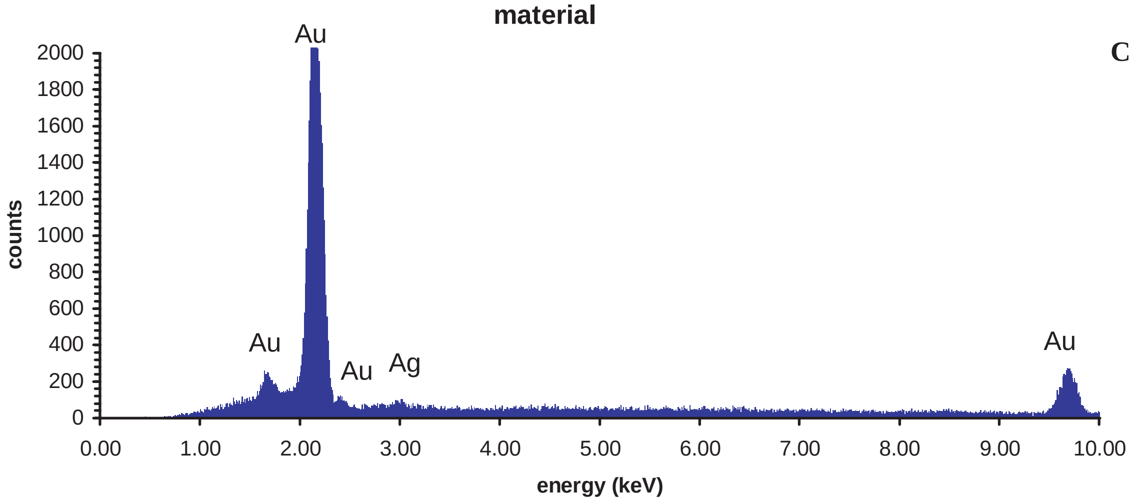




Energy dispersive x-ray spectrum from triangular 50 micron particle on gold wire



Energy dispersive x-ray spectrum from 10 micron concentration of dark contrast material



Energy dispersive x-ray spectrum from point analysis on dark contrast material

Figure 3-12. A-B: *EDAX analyses of gold electrode.* ***C:*** *EDAX spectrum of surface of gold electrode.*

3.3 Tests on electrodes used in electrochemical cells

3.3.1 Recalibration of silver-silver chloride electrode from Cell 1

The potential of the silver-silver chloride electrode used as the reference electrode in Cell 1 (electrode No. 2) was measured against the standard silver-silver chloride electrode No. 4. The latter was inserted into the test solution in Cell 1 immediately after the cell had been broken open inside an anaerobic box. The results of the potential measurements are shown in Figure 3-13. Initially the reference electrode showed a potential difference of –0.776 V relative to the stored Ag/AgCl electrode. This value is consistent with the anomalous potential achieved in Cell 1 /2/ after 470 hours of operation. However the potential difference rapidly became more positive in value and, after approximately 14 hours immersion, the reference electrode from Cell 1 assumed the correct potential of 0 Volts for the following cell:

–ve | Ag | AgCl (No. 4) | groundwater | AgCl (cell 1) | Ag +ve $E_{theoretical}$ = 0 Volts

Providing the standard silver chloride electrode (No. 4) is assumed to have the correct theoretical potential then this result confirms that the constant shift in the potentials measured for all electrodes while monitoring Cell 1 /2/ was due to a sudden change in the reference electrode potential. The nature of the electrochemical process driving this sudden change in reference potential in the Cell 1 environment and its subsequent recovery when the cell was broken open is not clear.

The repeatability of the standard potential for silver-silver chloride electrode No. 4 was checked at intervals throughout the life of Cells 1 and 2 by measuring its potential with respect to a freshly prepared calomel with an electrolyte of simulated groundwater.

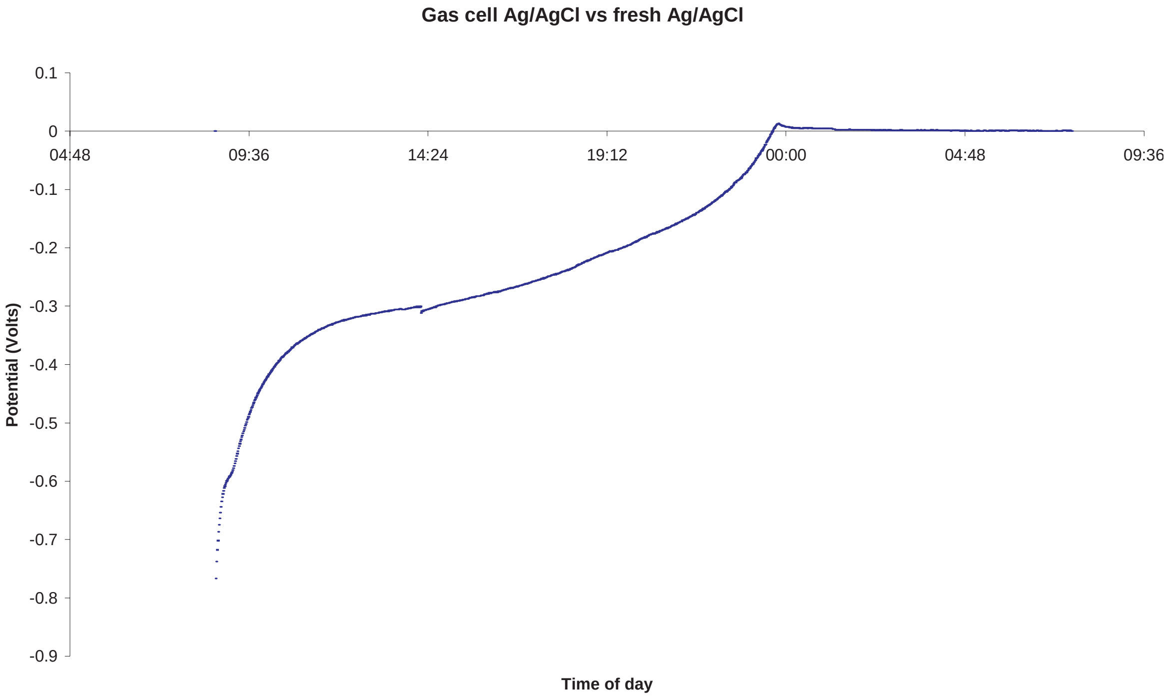


Figure 3-13. Potential of silver chloride reference electrode removed from cell 1 measured against a stored silver chloride electrode.

The potential of a silver-silver chloride electrode depends upon the activity of chloride ions in the test solution and is given by

$$E = E^o_{AgCl^-} (2.30RT/nF) \log [a_{Cl^-}]$$

where a_{Cl^-} is the activity of chloride ion and E^o_{AgCl} is the standard potential. The activity is calculated by taking the product of the concentration (molality) and the activity coefficient. A similar equation can be written for the calomel half cell. For calomel, the dependency of the measured potential on chloride is the same as for silver-silver chloride but the standard potential is different, viz.

$$E = E^o_{Hg_2Cl_2} - (2.30RT/nF) \log [a_{Cl^-}]$$

The pre-exponential factor approximates to a value of 0.059 V if n is unity. Using values for $E^o_{Hg_2Cl_2}$ and $E^o_{AgCl^-}$ of +0.268 and +0.222 V vs NHE respectively, the effect of concentration can be calculated. The calculated potentials for some half cells relevant to this report and the corresponding measured values are presented below. The correction of molarity (M) to molality (m) has been ignored, as the error introduced by doing so is small.

Half cell	**Mean Activity coefficient**[1]	**Calculated E / V vs standard hydrogen**	**E measured**
Hg¦Hg_2Cl_2|KCl (sat)	0.583 (4.5m KCl)	0.241	0.2420
Hg¦Hg_2Cl_2|KCl (1M)	0.604	0.281	0.2810
Hg¦Hg_2Cl_2|KCl (0.1M)	0.770	0.334	0.3335
Hg¦Hg_2Cl_2|NaCl (0.54M)	0.683 (0.5m NaCl)	0.293	–
Ag|AgCl|NaCl (1M)	0.657	0.233	
Ag|AgCl|NaCl (0.1M)	0.778	0.288	
Ag|AgCl|NaCl (0.54M)	0.683 (0.5m)	0.248	0.2477, 0.2485 /2/
Ag|AgCl|KCl (3.5M)	0.572	0.204	
Ag|AgCl|NaCl (0.01M)	0.902[2]	0.343	

Using these calculated values the potential of the complete cell:

(–ve) Hg | Hg_2Cl_2 | groundwater (0.54M) | AgCl | Ag (+ve)

should have the value –0.047 Volts. The measured potential of silver-silver chloride No. 4 versus Calomel (new) in groundwater was –0.047 ± 0.002 V throughout this work programme.

In a control experiment run for 8,000 hours at 30ºC (Cell 3), silver-silver chloride electrode (No. 1) maintained a stable, predictable potential with respect to a calomel electrode in a simulated groundwater electrolyte, Calomel (Cell 3) /2/. The potential of this electrode was –0.045 V vs calomel in the early part of this trial. The potential became more positive with time due to evaporation of water from this cell and it became necessary to add water to the cell at intervals to prolong the trial. A large negative shift in the silver chloride reference potential was not observed in this experiment. However, the control experiment was not performed under anoxic conditions so it is not possible at this stage to exclude the effect of reduced oxygen partial pressure or increased hydrogen pressure on the observed reference potential in Cell 1. There is no theoretical reason to expect such a dependence.

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[1] The mean activity coefficients of 1:1 electrolytes at 25°C are from Robinson and Stokes, Trans. Faraday Soc., **45**, 612, 1949.

[2] from D. Dobos, Electrochemical Data, Elsevier, 1975.

It was postulated that the silver-silver chloride reference electrode could have behaved as a platinum electrode with a pH sensitivity if spallation of the silver chloride coating had occurred, thus exposing the underlying platinum substrate /2/. Therefore, the silver-silver chloride electrode (No. 2) from cell 1 was tested for its response to pH in the following cell at 21ºC:

–ve | Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffer | AgCl | Ag | +ve

The results of the measurements in the range of buffers are given below:

Buffer pH	**4**	**7**	**9**
Potential at 21ºC/V	–0.0482	–0.0502	–0.0503

These results show that the potential of the reference electrode removed from Cell 1 was not affected by changing the pH of the solution and that if spallation of the chloride coating had occurred then the platinum was not determining the potential. Furthermore, no spallation of the silver chloride coating was observed during the SEM examination of this electrode.

To investigate the possible role of junction potential and temperature on the measured potentials reported above, some additional measurements were carried out. Consider the following cell:

(–ve) Hg | Hg_2Cl_2 | groundwater || 1M NaCl | AgCl | Ag (+ve)

Neglecting in the first instance the liquid junction potential that forms between 0.5M and 1M NaCl and using the half-cell potentials given on the previous page, then the potential for the cell above is –0.060 V. The liquid junction potential for the interface shown as || in the cell above is given by an expression of the form:

$E_{LJP} = (t_+ - t_-)\ (RT/nF)\ \log\ (C_2/C_1)$

where $C_2 > C_1$. If the positive ion is the more mobile one then the C_1 interface becomes positively charged compared with C_2. The transport numbers are proportional to the molar conductivities of the ions which are 50 and 74 ($ohm^{-1}\ cm^2\ mol^{-1}$) for Na^+ and Cl^- respectively at 25ºC[3]. The transport numbers are given by $t_{Na+} = 50/(50+74)$ and $t_{Cl-} = 74/(50+74)$, so that t_{Na+} is 0.40 and t_{Cl-} is 0.60. Therefore E_{LJP} is –0.20 × 0.059 × log (1m/0.5m) = –0.0035 V. Allowing for the liquid junction effects above gives a cell potential of the order of –0.063 V for the cell at 25ºC. The measured value for this cell was –0.050 V. The discrepancy between the two values indicates some instability in the Cell 1 reference electrode but considering that corrections have not been made for temperature effects on the potential value then the deviation is not unreasonable.

Two further cell potential measurements confirm this result and provide further confidence in the electrodes, viz.

–ve | Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffers (pH 4) | AgCl (No. X) | Ag | +ve

(X)	**AgCl (No. 4)**	**AgCl (Cell 1)**
Potential at 31ºC/V	–0.057	–0.053

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[3] Ionic conductivities at infinite dilution and 25 °C, are taken from Robinson and Stokes, Electrolyte Solutions, 2nd Edn, 1959, p463 (Butterworths, London).

3.3.2 Recalibration of calomel electrode from Cell 2

The calomel electrode was removed from Cell 2 and after storage for three weeks in fresh artificial groundwater, its potential was measured against silver-silver chloride electrode No. 4, in the following cell:

–ve, Calomel (Cell 2) | groundwater || 1M NaCl | Ag | AgCl (No. 4) | +ve,

E = –0.0244 V; T 30.2ºC

The potential of the cell was below the expected value of –0.057 mV. Therefore the potentials reported for the electrodes measured in Cell 2 /2/ could be in error by as much as 33 mV. It was reported prior to decommissioning Cell 2 that a faint yellow stain could be seen on the calomel electrode. After storage this stain had developed into a distinct algal growth which may have been accelerated by the relatively large increase in oxygen partial pressure which would have occurred after breaking the Cell 2 seals. The location of the algal growth around the diffusion barrier for this reference electrode could be responsible for the error in the reference electrode potential. There was no indication from the Cell 3 control experiment of such a large error in the calomel potential. The calomel electrode (cell 3) was checked periodically against a freshly prepared calomel electrode (new) and in all cases the potential was 0 ± 0.002 V. However, cell 3 was not operated under anoxic conditions.

3.3.3 Recalibration of pH electrodes from Cell 1 and Cell 2

The results from the calibration checks on the glass electrodes from Cell 1 and Cell 2 in buffers of pH 4, 7 and 9 at 30ºC are shown below and in Figure 3-14 and Figure 3-15. A fresh calomel electrode was used.

(–ve) | Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffer | glass electrode (cell 1) | (+ve)

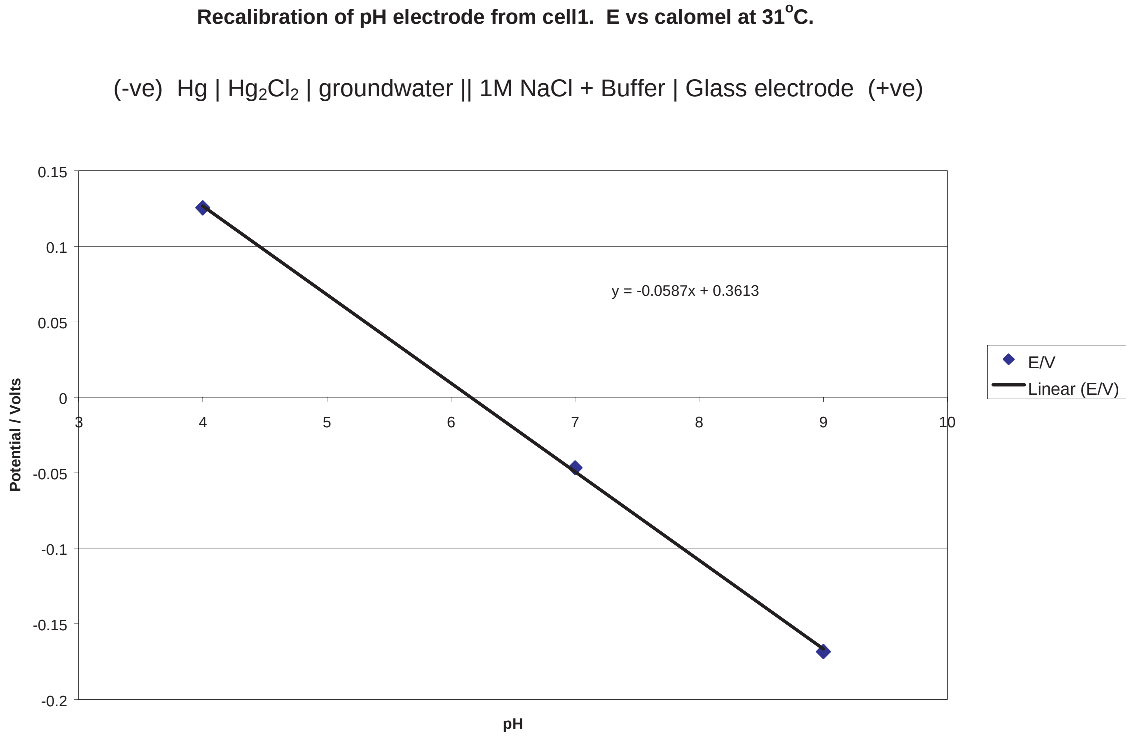
Buffer	**4**	**7**	**9**
Potential at 31ºC	+0.125	–0.046	–0.168

The slope of the calibration plot is –59 mV/pH unit with an intercept at +0.3613 V vs AgCl reference. A similar experiment was performed with the glass electrode from Cell 2:

(–ve) | Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffer | glass electrode (Cell 2) | (+ve)

Buffer	**4**	**7**	**9**
Potential at 31ºC	+0.088	–0.079	–0.198

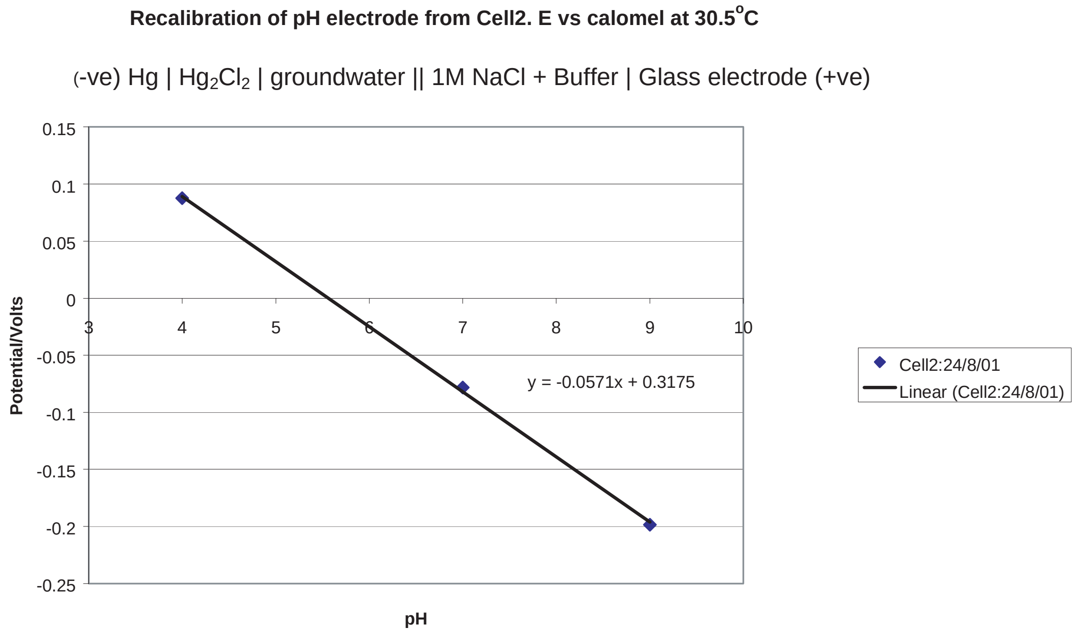
The Nernst slope is –57 mV/pH unit with an intercept of +0.3175 vs calomel reference (in groundwater). There is a discrepancy between the intercept for the potential response of these electrodes that was considered outside the performance bounds normally expected. The experiment was repeated between 29/8/01 and 5/9/01, but the potential of both electrodes was monitored simultaneously against a single reference electrode in the same electrolyte, viz.



Recalibration of pH electrode from cell1. E vs calomel at 31^{o}C.

(-ve) Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffer | Glass electrode (+ve)

Figure 3-14. *Recalibration of pH electrode removed from electrochemical Cell 1 (11/6/01).*



Recalibration of pH electrode from Cell2. E vs calomel at 30.5^{o}C

(-ve) Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffer | Glass electrode (+ve)

Figure 3-15. *Recalibration of pH electrode removed from e0lectrochemical Cell 2 (24/8/01).*

(–ve) | Hg | Hg_2Cl_2 | groundwater || 1M NaCl + Buffer | glass electrode (Cell 1 or Cell 2) | (+ve)

Experiments at 30ºC	**pH** **4**	**7**	**9**
Cell1: 11/6/01	0.1255	–0.047	–0.1684
Cell2: 24/8/01	0.0877	–0.0785	–0.1985
Cell 1: 29/8/01	0.094	–0.077	–0.199
Cell2: 29/8/01	0.0937	–0.077	–0.197
Cell 1: 5/9/01	0.101	–0.075	–0.193
Cell2: 5/9/01	0.099	–0.075	–0.191

There was no further change in potential after 5/9/01. These results show that there was an ageing effect on the calibration of the glass pH electrode – with each batch of fresh buffer the potentials shifted to a more positive value. The potential shift did not affect the slope of the calibration but it did affect the intercept. It took several days to reach a stable equilibrium in these groundwaters, as shown in Figure 3-16. In the anoxic cell monitoring experiments /2/ the glass electrodes would have certainly reached equilibrium and the results would not have been affected by the ageing process described above.

If the expression for the cell potential is corrected to the Normal Hydrogen Electrode (NHE) scale by using the arguments presented in section 3.3.1 then:

$$E[NHE] = -0.058\ pH + 0.624$$

A calibration of these glass electrodes before they were introduced into the two anaerobic cells stipulates an equation of the form /2/:

$$E = -0.0586\ pH + 0.373$$

where E was measured against the reference Ag | AgCl | artificial groundwater. Correcting to the NHE scale then:

$$E[NHE] = -0.0586\ pH + 0.621$$

The agreement between these two calibrations is acceptable.

3.4 Effect of di-butyl phthalate on test solution

The results of monitoring the potential of a glass electrode with respect to a silver chloride electrode, with and without the presence of DBP, are shown in Figure 3-17. A change in potential of 59 mV corresponds to a change of one pH unit. In the absence of DBP the potential of the glass electrode decreased by ~66 mV over a period of c. 2 months, corresponding to a pH decrease of ~1.1 units. When DBP was added, there was a rapid increase in the potential of the glass electrode by approximately 17 mV. This corresponds to a pH decrease of ~0.3 pH units.

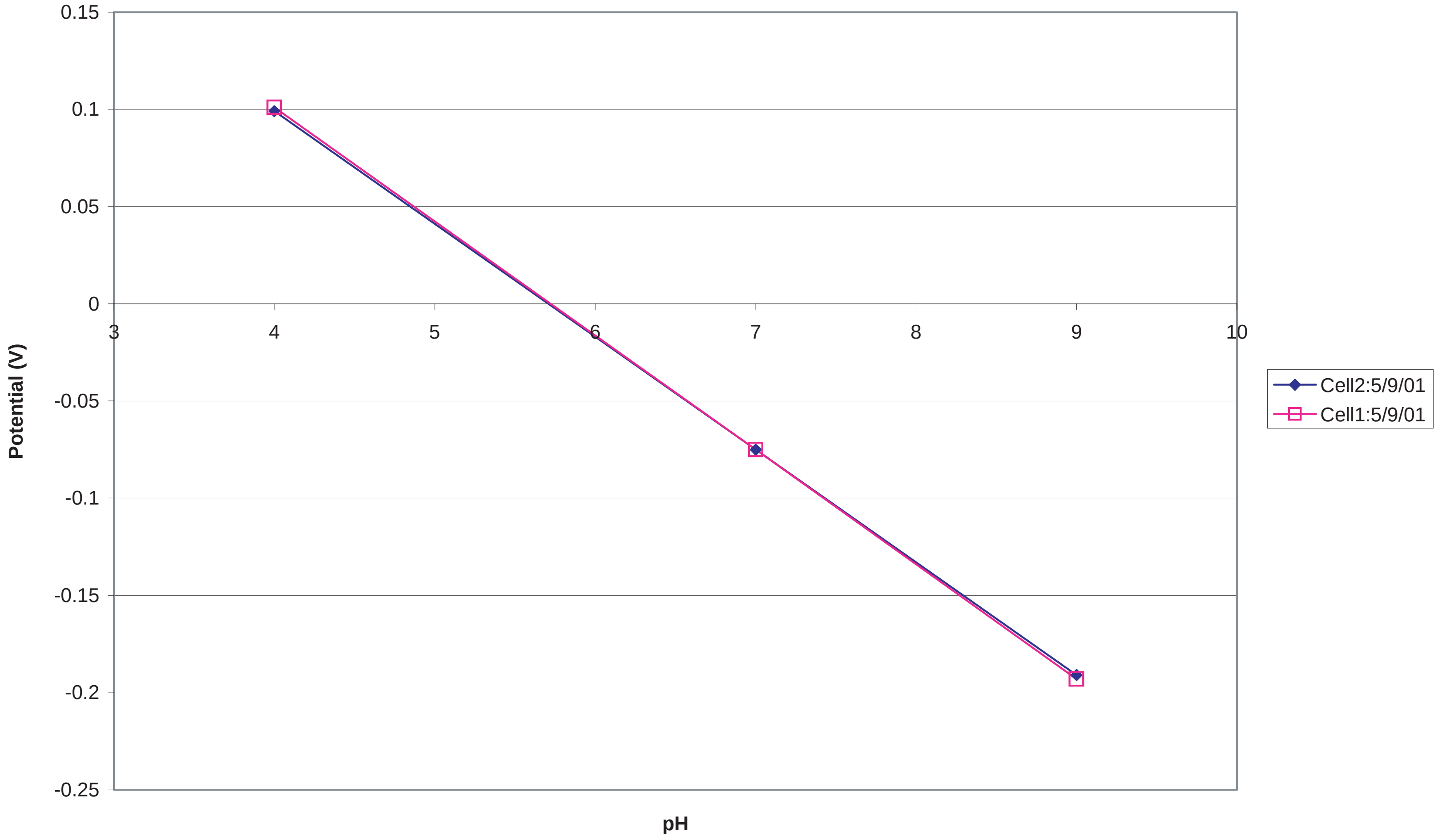


Figure 3-16. *Comparison of glass electrodes after decommissioning cell 1 and cell 2 (5/9/01).*

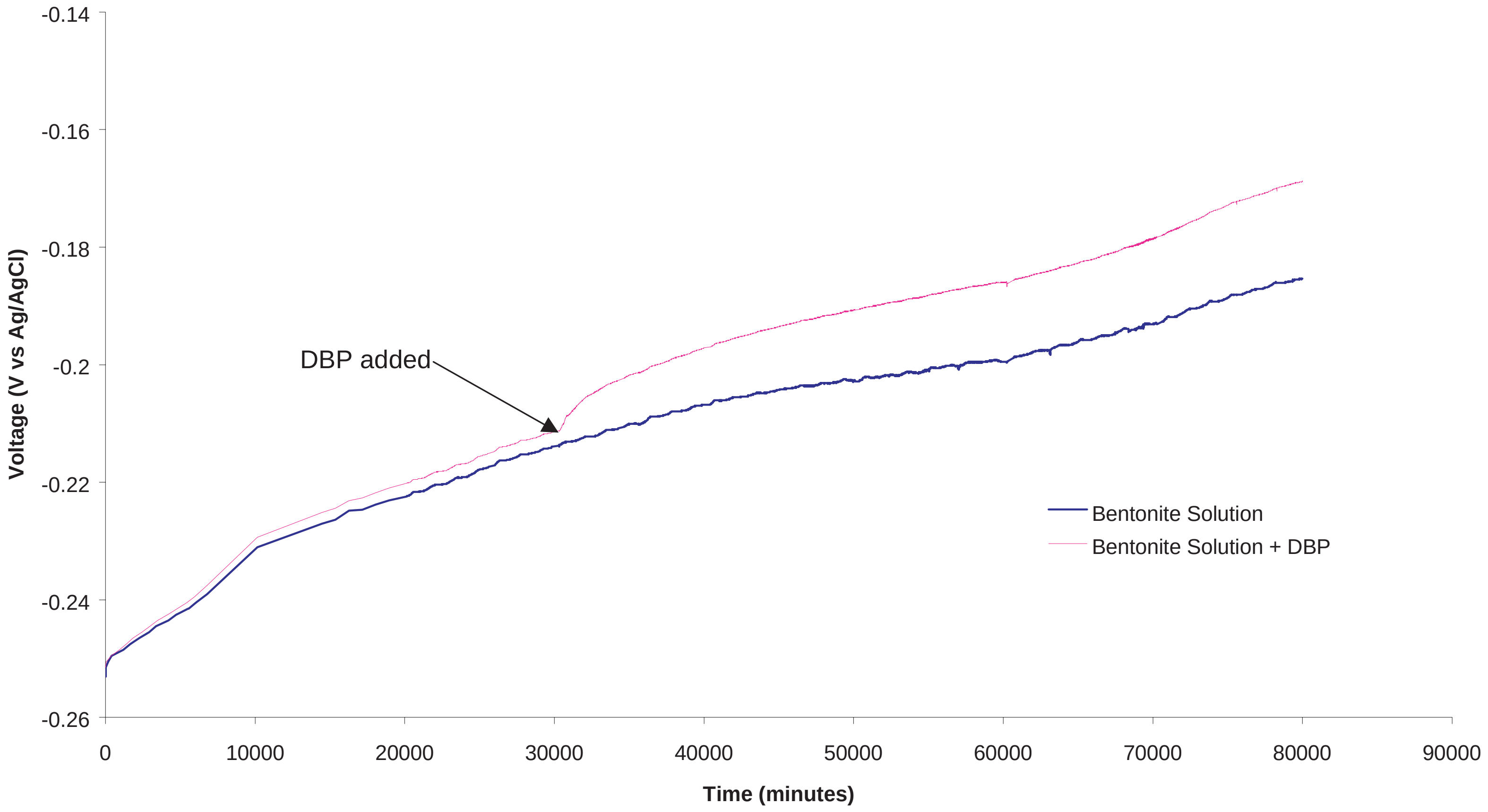


Figure 3-17. *Results of monitoring the potential of the glass pH electrode in artificial bentonite equilibrated groundwater, with and without the presence of DBP.*

4 Discussion and conclusions

4.1 Analysis of solutions

The analyses of the solutions from the electrochemical cells used in the experiments reported previously /2/ have shown that, within the accuracy of the measurements, the analyses of sodium, chloride and carbonate agree with the values used in the preparation of the test solutions. The organic content is made up of two components, namely the di-butyl phthalate contamination that arose from the reservoir on the gas cell and microbial material. The latter probably arose because the solutions used were not sterilised before use. The concentration of organics leached from an aqueous/DBP mixture was considerably less than that measured in the test cells, suggesting that microbial material formed the majority of the organic component.

The solubility of iron (II) is very low at pH 9–10; according to Pourbaix, in water it is approximately 10^{-7} mol / litre /3/, which is equivalent to 0.006 ppm. This value is below that measured for iron dissolved in the test solutions, indicating that they were supersaturated, or that the solubility is different in high ionic strength solutions. There may also have been an effect of algal activity on the concentration of iron measured in the solution.

4.2 Analysis of electrodes

Analysis of the corrosion product has shown that it is predominantly magnetite, Fe_3O_4, in agreement with the overall anaerobic corrosion reaction:

$$3Fe + 4H_2O \Rightarrow Fe_3O_4 + 4H_2$$

There is evidence of a different crystallographic phase at the outer surface of the oxide film, which may be goethite, FeOOH. The reactions leading to the formation of goethite are not clear; one possibility would be oxidation of magnetite to goethite by traces of oxygen in the glove box (which was operating at 10 ppm oxygen or less during dismantling of the test cells).

4.3 Performance of reference electrodes

The Ag/AgCl reference electrode used in Cell 1, for some unidentified reason, had polarised at –0.823 V vs AgCl. The recalibration of the silver-silver chloride electrode (Figure 3-13) showed that the potential of the reference electrode was sensitive to the conditions in the test cell, but the reason for this behaviour has not been established. It appears that the potential shift of –0.823 V was not due to exposure of the central platinum wire, because upon breaking open Cell 1 in the anoxic glove box the reference electrode reverted to its expected equilibrium potential value over a few hours. Furthermore, it was found that after the electrode had returned to its equilibrium potential, the reference electrode behaved normally and it was not sensitive to variations in the pH, which it would have been if the platinum wire was exposed. Examination of the Cell 1 reference electrode by Scanning

Electron Microscopy showed no evidence for AgCl spallation. The unusual polarisation was not due to the chemical nature of the groundwater, and it seems unlikely that it was due to the anoxic conditions because oxygen is not involved in the electrochemical reactions on the reference electrode. There must be some other unidentified cause.

The Calomel electrode in Cell 2 was in error by 30 mV. This could be due to algal growth following decommissioning of Cell 2, as several weeks passed before the calomel was checked.

A general conclusion is that there is still some concern over the reliability of the reference electrodes used in the anoxic cells. The calomel is more reliable than the silver chloride wire but the result for the latter may not be representative of this electrode type. The behaviour of both electrode types was satisfactory over 8,000 hours in a naturally aerated groundwater. It is recommended that further work should be carried out to confirm a suitable reference electrode. This could take the form of measuring the potential of both reference types in the same cell under anoxic conditions.

The calomel electrodes were found to perform satisfactorily in Cell 3, as shown by the fact that the potential difference between a calomel which had been in storage for 8,000 hours and a freshly prepared electrode was only 1.5 mV.

The slopes of the calibration plots for the glass pH electrode (Figure 3-14) were very close to the 59 mV per decade that would be expected on theoretical grounds, demonstrating that the electrode was performing properly. There appears to be an ageing effect when carrying out calibrations of glass electrodes and sufficient time should be allowed for the electrodes to reach equilibrium.

4.4 Change in pH of test solution

As the cells used to study the effect of DBP on pH were sealed the observed decrease in pH must have been due to reaction between the test solution and the glass walls of the test vessel, rather than a change in gas composition. The presence of silicon in the test solutions from the electrochemical cells demonstrates that some attack of the glass had taken place. Loss of carbon dioxide from the dissolved carbonate would have led to an increase in the pH, rather than a decrease. The decrease in pH is also in agreement with that observed in the electrochemical test cells /2/, where a pH drop of about ~0.7 units was observed. In the presence of corroding surfaces the reduction of water to form hydrogen would be expected to result in the release of hydroxide ions and cause an increase in pH. This may explain the smaller decrease in the pH compared to the experiments reported here. It appears therefore that the decrease in pH was due to release of acidic species from the walls of the glass test vessel, such as hydrosilicic acid.

The presence of DBP contamination in the test solution caused a pH reduction of ~0.3 pH units. It is assumed that this was due to a minor water-soluble ionic species present in the DBP, which was not detected in the GC-MS analysis of the organic extract from the aqueous phase (Section 3.2.1.2, Table 3-2).

5 Conclusions

The main conclusions from the work to analyse the contents of the cells used for the electrochemical measurements reported previously /2/ are as follows:

1. The steel electrodes went black as a result of anaerobic corrosion forming a corrosion product consisting predominantly of magnetite (Fe_3O_4).
2. Microbial activity led to the formation of a green slime on some of the electrodes and contributed to the total organic content of the test solution.
3. The composition of the test solutions was as expected based on the weights of chemicals used to prepare them.
4. Although the silver-silver chloride reference electrode had failed during the original experiments, post-test microscopy did not reveal any loss of the silver chloride coating and its potential recovered approximately 14 hours after it was placed in a fresh solution. The reason for this behaviour is not clear. Microbial activity may have affected the stability of the reference electrodes.
5. Post-test calibration showed that the glass pH electrodes behaved satisfactorily. Dissolution of the glass in contact with the test solution led to a long-term pH decrease of ~1 unit and DBP contamination led to a further pH decrease of ~0.3 units.
6. In general, analysis of the cell contents has contributed to a deeper understanding of the processes occurring in anoxic groundwater containing corroding steel and highlighted some of the experimental considerations that should be taken into account in making electrochemical measurements in simulated repository conditions.

6 References

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4 **Reference spectra obtained from the Cal Tech Minerals Database.**

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