

**Miniature Canister (MiniCan)  
Corrosion experiment progress  
report 4 for 2008–2011**

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June 2012

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ISSN 1651-4416

SKB P-12-13

ID 1335197

# **Miniature Canister (MiniCan) Corrosion experiment progress report 4 for 2008–2011**

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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## Executive Summary

To ensure the safe encapsulation of spent nuclear fuel rods for geological disposal, SKB of Sweden are considering using the Copper-Iron Canister, which consists of an outer copper canister and a cast iron insert. Over the years a programme of laboratory work has been carried out to investigate a range of corrosion issues associated with the canister, including the possibility of expansion of the outer copper canister as a result of the anaerobic corrosion of the cast iron insert. Previous experimental work using stacks of test specimens has not shown any evidence of corrosion-induced expansion. However, as a further step in developing an understanding of the likely performance of the canister in a repository environment, Serco has set up a series of experiments in SKB's Äspö Hard Rock Laboratory (HRL) using inactive model canisters, in which leaks were deliberately introduced into the outer copper canister while surrounded by bentonite, with the aim of obtaining information about the internal corrosion evolution of the internal environment. The experiments use five small-scale model canisters (300 mm long × 150 mm diameter) that simulate the main features of the SKB canister design (hence the project name, 'MiniCan'). The main aim of the work is to examine how corrosion of the cast iron insert will evolve if a leak is present in the outer copper canister.

This report describes the progress on the five experiments running at the Äspö Hard Rock Laboratory and the data obtained from the start of the experiments in late 2006 up to Winter 2011. The full details of the design and installation of the experiments are given in a previous report and this report concentrates on summarising and interpreting the data obtained to date. This report follows the earlier progress reports presenting results up to December 2010. The current document (progress report 4) describes work up to December 2011.

The current report presents the results of the water analyses obtained in 2007, 2008 and 2010 including gas composition and microbial activity. These data show an increase in the dissolved iron concentration inside the support cage, together with a decrease in the pH. Both these observations appear to be mainly due to microbial activity, but it is also possible that abiotic processes could have contributed to changes in the local chemistry. Microbial analysis has shown the presence of sulphate-reducing bacteria (SRB) and autotrophic acetogens. The presence of low density bentonite appears to stimulate the growth of SRB, but recent studies reported in the literature indicate that high density fully compacted bentonite inhibits SRB activity. A further set of water samples was taken for analysis at the end of 2010 and these results are also included in this report. These data show a similar trend as before, with increases in the dissolved iron concentration inside the support cage and a decrease in the pH. Further water analysis on Experiment 3 was carried out before it was removed for analysis, but the results from this analysis are presented in a separate report.

The electrochemical measurements provide an in situ  $E_h$  value which is comparable with published data. The  $E_h$  value inside the boreholes decreased with time as oxygen was consumed by microbial activity, reaction with minerals in the surrounding rock and/or corrosion of the MiniCan experiment and its support cage.

Corrosion rates have been obtained using a range of electrochemical methods. The copper corrosion rate was initially measured electrochemically as being  $<3.5 \mu\text{m yr}^{-1}$ , but the measured corrosion rates of iron and copper appear to have accelerated to unexpectedly high values. The electrochemically measured corrosion rate of iron was considerably higher ( $>1 \text{ mm yr}^{-1}$  in some cases) than expected on the basis of laboratory experiments in the absence of microbial activity. The increase in corrosion rates appeared to coincide with a minimum value for the  $E_h$  being reached and this may correspond to the onset of enhanced anaerobic microbial activity (e.g. SRB) and hence increased production of sulphide. Based on reports in the literature there is reason to believe that the corrosion rate of iron measured using the Linear Polarisation Resistance (LPR) and AC Impedance (ACI) techniques may overestimate the corrosion rate. However, recent analysis of the iron weight loss coupon from Experiment 3 indicates that the corrosion rate was actually at least  $500 \mu\text{m yr}^{-1}$ .

The corrosion potentials of the copper and iron electrodes are compared with published Pourbaix diagrams for iron and copper in the presence of chloride and sulphur species and found to be consistent with corrosion by dissolved sulphide to produce metal sulphide films.

The corrosion rates measured using the electrochemical noise technique yielded values that were significantly lower than the values measured using the LPR and ACI techniques. The lowest corrosion rates for copper were measured using the electrical resistance technique using copper wires. This technique gave corrosion rates of less than  $1 \mu\text{m yr}^{-1}$  in Experiment 2 (low density bentonite) and Experiment 5 (no bentonite). Experiment 3 was dismantled during 2011 and a weight loss measurement was carried out on the copper weight loss coupon from this experiment. The corrosion rate derived from the weight loss measurement for Experiment 3 was compared with the corrosion rate measured electrochemically and found to be considerably lower ( $0.15 \mu\text{m yr}^{-1}$ ). Detailed analysis of the dismantling and analysis of the data from Experiment 3 is presented in a separate report.

It should be noted that only one experiment (Experiment 4) is a close representation of the proposed SKB disposal concept as it uses compacted bentonite, whereas the other experiments use low density bentonite or no bentonite at all. The results from these experiments (e.g. high levels of microbial activity and high corrosion rates) are therefore only applicable to a fault situation where the density of the bentonite is compromised.

A small scale electrochemical experiment was operated during 2010 consisting of carbon steel and copper electrodes embedded in anoxic compacted bentonite. Electrochemical potential and corrosion rate measurements were carried out on the copper and carbon steel electrodes. The copper corrosion rate passed through a peak due to an oxygen spike during cell manufacture, but the corrosion rate fell to a value of  $<3 \mu\text{m yr}^{-1}$  after the oxygen had been consumed by corrosion reactions.

The main conclusions from the project to date are as follows:

1. Water analysis has shown that there are compositional differences between the water inside the support cages compared to the external borehole water. These can be explained on the basis of enhanced corrosion of the iron and microbial activity inside the support cages. There has been a large increase in the concentration of dissolved iron, which is mainly present in the form of  $\text{Fe}^{2+}$ , and a parallel decrease in the pH from the groundwater pH value of  $\sim 7.6$  to a value inside the support cage of  $\sim 6.6$ .
2. Microbial analysis has demonstrated that SRB are active in the experimental boreholes.
3.  $E_h$  measurements have shown that the test conditions within the support cages around the MiniCan experiments became reducing over a period of a few thousand hours at the start of the experiments.
4. The corrosion potentials of the copper and iron electrodes in the experiments with low density bentonite (Experiments 1 to 3) are consistent with the formation of copper sulphide and iron sulphide corrosion products.
5. The electrochemically measured corrosion rates have increased for both copper and iron. Analysis of the weight loss sample in Experiment 3 has confirmed that the corrosion rate for iron is at least  $500 \mu\text{m yr}^{-1}$ . The corrosion rates measured for iron by LPR and ACI are overestimated due to the electrochemical properties of the sulphide films formed on the surface by SRB activity by a factor of approximately  $\times 5$ .
6. The corrosion rate of copper in compacted bentonite (Experiment 4) was initially of the order of  $1 \mu\text{m yr}^{-1}$  but it appears that later measurements are not valid, possibly because the swelling pressure exerted by the bentonite has disrupted the electrical connections.
7. High corrosion rates have been measured electrochemically for copper in low density bentonite and unconditioned groundwater, but these values are believed to be an overestimate caused by the surface precipitation of iron sulphide produced by corrosion of cast iron in the vicinity (as observed when Experiment 3 was dismantled). The measured values are considerably higher than that measured by weight loss in Experiment 3, where a value of  $0.15 \mu\text{m yr}^{-1}$  was obtained.
8. Strain gauge measurements showed that no expansion of the copper canister had occurred as a result of corrosion of the cast iron insert.
9. It should be recognised that these test conditions are not directly comparable with the proposed repository conditions. It appears that the low density bentonite is conducive to microbial activity, particularly that of SRB, and this has led to an increase in the corrosion rate of the cast iron. However, the copper corrosion rates measured by the electrical resistance method in low density bentonite and raw groundwater are considerably lower ( $< 1 \mu\text{m yr}^{-1}$ ). In fully compacted bentonite microbial activity will be limited by the low activity of water and the corrosion rate is likely to be determined by the rate of diffusion of sulphide through the bentonite buffer.

# Contents

<b>1</b>	<b>Introduction</b>	7
<b>2</b>	<b>Experimental</b>	9
2.1	Test layout and test conditions	9
<b>3</b>	<b>Monitoring performance of model canisters</b>	13
3.1	Water analysis	13
3.2	Pressure	14
3.3	Strain	14
3.4	Corrosion coupons	14
3.5	Mounting system for sensors and corrosion test pieces	15
3.6	Electrical connections	15
3.7	Monitoring equipment	15
3.8	Electrochemical cell	16
<b>4</b>	<b>Results</b>	17
4.1	Water analysis	17
4.1.1	Sulphide	24
4.1.2	Iron concentrations	24
4.1.3	pH	25
4.1.4	Other elements	25
4.1.5	Gas analysis	29
4.1.6	Microbial analysis	29
4.1.7	Pressure	29
4.2	Electrochemical potential measurements	32
4.2.1	Experiment 1: Low density bentonite	32
4.2.2	Experiment 2: Low density bentonite	34
4.2.3	Experiment 3: Low density bentonite	35
4.2.4	Experiment 4: Compacted bentonite	35
4.2.5	Experiment 5: No bentonite	38
4.3	Electrochemical corrosion rate measurements	40
4.4	Copper wire resistance measurements	46
4.5	Strain gauge data	46
4.6	Evolution of electrochemical noise data	50
4.7	Electrochemical cell	53
<b>5</b>	<b>Discussion</b>	55
5.1	Water analysis and microbial activity	55
5.2	Electrochemical measurements	56
5.2.1	$E_h$ measurements	56
5.2.2	Corrosion potential of copper and iron	56
5.3	Corrosion rate measurements	60
5.3.1	Iron corrosion rates	60
5.3.2	Copper corrosion rates	60
5.3.3	Application of corrosion rate results to SKB repository	61
5.4	Strain gauge measurements	62
<b>6</b>	<b>Future work</b>	63
<b>7</b>	<b>Conclusions</b>	65
<b>8</b>	<b>Acknowledgments</b>	67
<b>9</b>	<b>References</b>	69
<b>Appendix 1</b>	Electrochemical corrosion rate measurements January to December 2011	71

# 1 Introduction

To ensure the safe encapsulation of spent nuclear fuel rods for geological disposal, SKB of Sweden are considering using the Copper-Iron Canister, which consists of an outer copper canister and a cast iron insert. A programme of work has been carried out over a number of years to investigate a range of corrosion issues associated with the canister, including the possibility of expansion of the outer copper canister as a result of the anaerobic corrosion of the cast iron insert. Experimental work using stacks of copper and iron test specimens has not shown any evidence of corrosion-induced expansion [1]. However, as a further step in developing an understanding of the likely performance of the canister in a repository environment, Serco has set up a series of experiments in SKB's Äspö Hard Rock Laboratory (HRL) using inactive model canisters, in which leaks were deliberately introduced into the outer copper canister while surrounded by bentonite, with the aim of obtaining information about the internal corrosion evolution of the internal environment [2].

The experiments use small-scale (300 mm long  $\times$  150 mm diameter) model canisters that simulate the main features of the SKB canister design (hence the project name, 'MiniCan'). The main aim of the work is to examine how corrosion of the cast iron insert will develop if a leak is introduced into the outer copper canister, but a number of other issues are also being addressed, such as:

- Does water penetrate into the annulus through a small defect?
- How does corrosion product spread around the annulus from the leak point?
- Does the formation of corrosion product in a constricted annulus cause any expansive damage to the copper canister?
- What is the effect of water penetration on the insert lid seal?
- Is there any detectable corrosion at the copper welds?
- Are there any deleterious galvanic interactions between copper and cast iron?
- Does corrosion lead to failure of the lid on the iron insert?

The experiments were set up between September 2006 and February 2007 and the detailed design, experimental setup and initial results up to May 2008 are reported in reference [3]. The five experiments are automatically monitored and the scheduled experimental data were obtained and analysed. This progress report includes the data obtained up to Winter 2011 and follows three previous progress reports that presented data up to December 2010 [4,5,6]. Further progress reports will be produced in due course. One of the MiniCan experiments, Experiment 3, was removed for analysis during 2011 and details of this analysis are presented in a separate report [7].

## 2 Experimental

The five experiments setup in the boreholes at Äspö HRL are being logged automatically by computer-controlled data logging equipment. The detailed experimental layout and test conditions are given in reference [3] and summarised below.

### 2.1 Test layout and test conditions

Figure 2-1 shows the layout of the experiments in the boreholes in the Äspö HRL, Figure 2-2 shows the layout of the canisters and the other test pieces inside the support cages and Figure 2-3 shows the insertion of the copper model canisters into the support cages. A summary of the test environments inside the five experiments is given in Table 2-1. In three out of the five experiments a layer of bentonite was mounted inside an annulus between two concentric cylinders around the model canister. The purpose of the bentonite is to condition the chemistry of the incoming groundwater so that it is representative of the repository situation. However, it should be noted that these experiments use a lower bentonite density than is proposed for the SKB repository. The cage prevents direct contact between the bentonite and the surface of the canister in order to avoid blockage of the defect introduced into the copper container. The bentonite holder was filled with compacted bentonite pellets mixed with bentonite powder at a density designed to give a high permeability and low swelling pressure, with the aim of allowing bentonite-conditioned groundwater to reach the model canister rapidly.

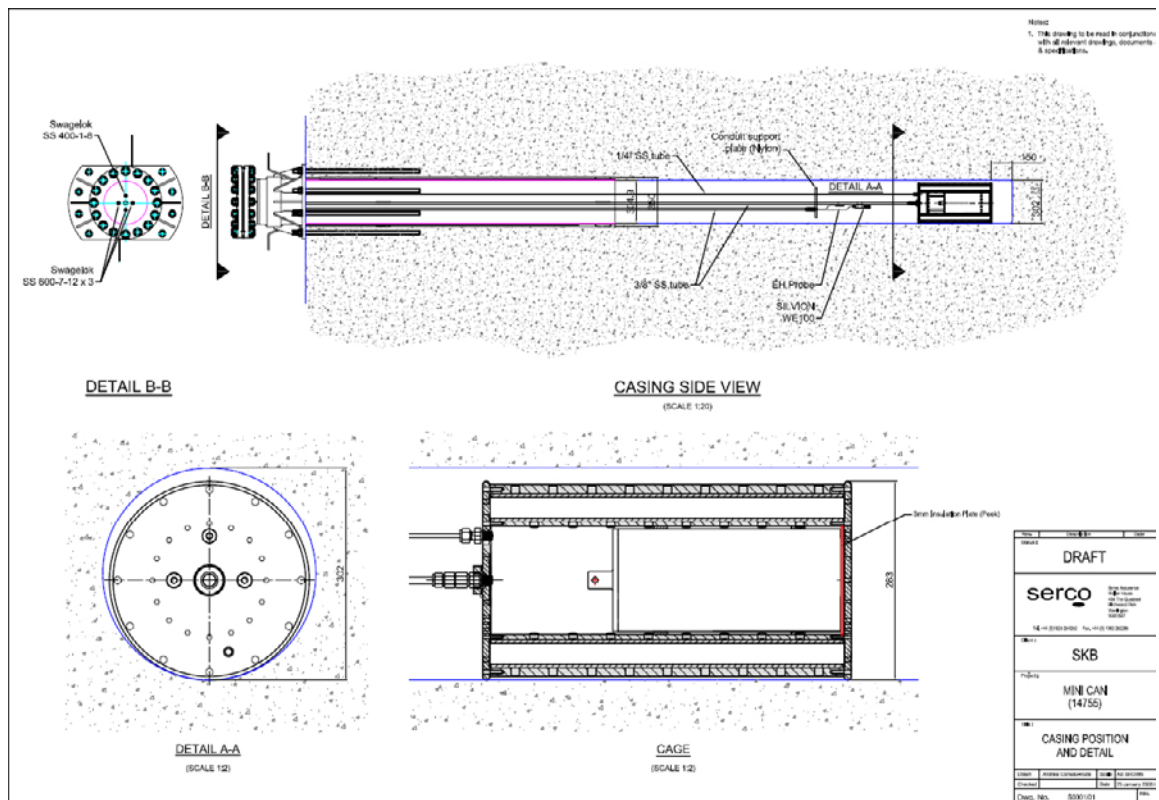


Figure 2-1. Layout of model canister experiments in borehole.

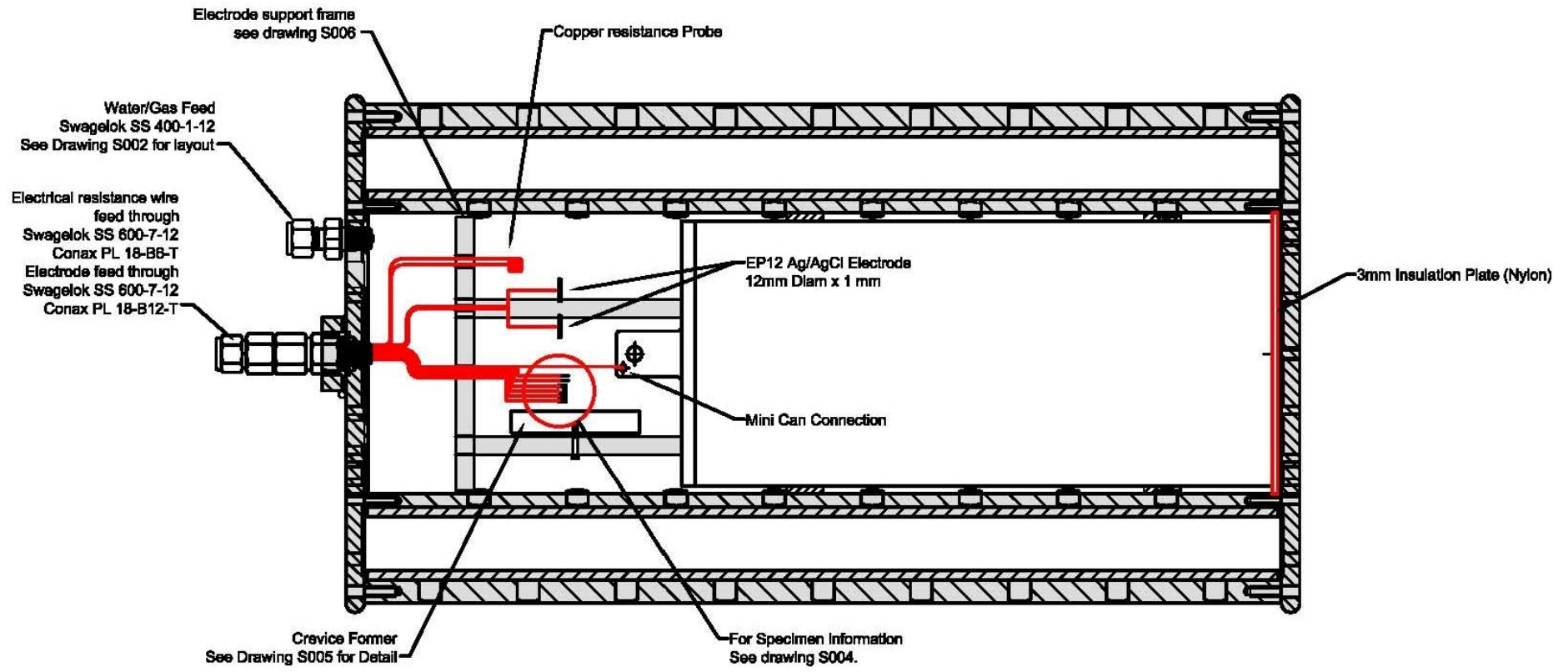


Figure 2-2. Layout of model canister and sensors inside support cage.





**Figure 2-3.** Left: Strain gauges mounted on model canister; Centre: Positioning of bentonite pellets inside annulus of support cage; Right: insertion of model canister assembly into support cage.

**Table 2-1. Summary of test conditions for model canister experiments.**

Experiment number (Borehole number)	Environment and defect details
1 (KA3386A02)	Low density, high permeability bentonite in annulus around model canister. Single defect near top weld, pointing vertically upwards. Strain gauges fitted.
2 (KA3386A03)	Low density, high permeability bentonite in annulus around model canister. Single defect near top weld, pointing vertically downwards. Electrical resistance corrosion rate probes fitted.
3 (KA3386A04)	Low density, high permeability bentonite in annulus around model canister. Two defects, one near top weld, pointing vertically upwards, near bottom weld, pointing vertically downwards.
4 (KA3386A05)	Compacted bentonite. Single defect near top weld, pointing vertically downwards. Strain gauges fitted.
5 (KA3386A06)	No bentonite, direct contact of groundwater on model canister. Two defects, both near top weld, one pointing vertically upwards, the other vertically downwards. Electrical resistance corrosion rate probes fitted.

In the fourth experiment the model canister was surrounded by compacted bentonite, to simulate as exactly as possible the real exposure conditions in the repository, although in this situation it is expected that the extent of corrosion will be limited by the supply of water and diffusion of sulphide through the compacted, low permeability bentonite [8]. In this experiment, where the model canister was in direct contact with the compacted bentonite, there was no inner cylinder and hence no annulus of bentonite, but rings of saturated compacted bentonite were machined to slide over the model canister, inside the outer cylinder. Clay Technology (Lund, Sweden) machined the rings to size. The use of fully saturated bentonite should minimise the time required to achieve full saturation and hence to achieve the full swelling pressure of the bentonite. The thicknesses of the outer cylinder of the support cage and the outer filter cylinder were selected to withstand the swelling pressure exerted by the compacted bentonite (7 MPa). Small holes or slots were machined in the compact bentonite rings to accommodate electrodes and corrosion coupons in the compacted bentonite, and strain gauges on the surface of the model canister.

The fifth experiment was set up without any bentonite around the model canister so that the model canister is exposed directly to raw groundwater without any conditioning by bentonite. This experiment was included to provide a comparison with the experiments with bentonite present and to examine whether any biofilm develops on the surface of the canister and to examine its effect on corrosion behaviour. For this experiment, where the canister is directly exposed to groundwater, the perforated steel cage was used to hold the model canister, but no bentonite was placed inside it. Consequently the groundwater enters directly into the vicinity of the model canister.

### 3 Monitoring performance of model canisters

A number of parameters have been measured and monitored over the period since the experiments were set up in late 2006 to December 2011, as follows:

- Electrochemical potential of gold and platinum, and the redox potential,  $E_h$ .
- Corrosion potential of cast iron, copper and the miniature canister itself.
- Response of strain gauges on two experiments.
- In situ corrosion rate measurements for copper and cast iron.
- Water composition (including gas analysis and microbial measurements).

The reference electrodes used were:

- Two small silver-silver chloride reference disc electrodes inside each support cage (World precision instruments EP series).
- Long-life reference electrodes for cathodic protection (CP) purposes (Silvion silver-silver chloride reference electrodes), which were mounted outside the support cage but immersed in the borehole water.

The redox potential of the environment was measured by means of a gold wire and a platinum flag located near to the model canister inside the support cage and an  $E_h$  sensor located outside the supporting cage (Cumberland Electrochemical Ltd Pt/Ir mixed metal oxide, MOx, probe, which has been successfully used embedded in cementitious grout to monitor fluctuations in redox conditions).

The sensors were supported from a nylon support rack inside the void above the model canister (see Figure 2-2). All reference electrodes were calibrated before installation.

#### 3.1 Water analysis

After installation, water samples were taken for analysis at periodic intervals. Äspö staff carried out the required water analysis. Water samples were extracted through stainless steel tubes that passed out through the borehole flange. For each borehole it was possible to extract samples from both within the support cage itself and from the borehole surrounding the model canister experiment. There was a continuous bleed of gas from each borehole flange to prevent the development of a gas-filled space within the borehole. This gas is assumed to be nitrogen (see Section 4.1.5). The concentration of dissolved gases was determined by Microbial Analytics Sweden AB. The concentrations of the following gases were measured:  $H_2$ , He,  $O_2$ ,  $N_2$ , Ar,  $CH_4$ ,  $CO_2$ , CO,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_3H_8$ ,  $C_3H_6$ . The microbial analysis was also carried out by Microbial Analytics and was used to measure a number of parameters including the following:

1. The total number of microorganisms.
2. The number of aerobic cultivable bacteria.
3. Biomass measured as adenosine triphosphate.
4. The most probable number of the following types of bacteria were determined: sulphate-reducing bacteria and autotrophic acetogens.

A programme of water analysis was carried out regularly in the period February to August 2007 and then no more water samples were taken until October 2008, in order to allow the water chemistry to stabilise without any perturbations. Additional water samples were taken at the end of 2010. The results from the 2007, 2008 and 2010 analyses are included in the current report.

## 3.2 Pressure

The water pressure in the boreholes was initially measured by means of an analogue pressure gauge that was attached to the flanges on each borehole. Later an electrical pressure gauge was attached to the outlet pipe on the flange and the output was recorded on the datalogging equipment.

## 3.3 Strain

Strain gauges were applied to measure changes in the strain on the outer surface of two of the copper canisters (Tests 1 and 4). The aim of these measurements was to provide an indication of whether expansion caused by internal corrosion has caused any dimensional changes. Standard strain gauge monitoring technology using bi-axial strain gauges was applied (e.g. Techni-Measure Ltd) using cyanoacrylate adhesives and protected with waterproof coatings.

Experiments 1 and 4 both had two strain gauges mounted on the outer surface of the canister, one near the top (1a,b and 4a,b) and one near the middle (1c,d and 4c,d), with each strain gauge comprised of two perpendicular elements (see Figure 2-3). The elements were oriented at 45° to the vertical axis of the canister. The (a) and (c) elements, and the (b) and (d) elements for each of the sensors were oriented in the same direction with respect to the vertical axis of the canister.

## 3.4 Corrosion coupons

A number of types of corrosion coupons were mounted within the cage used for the model canister experiments, as follows:

- *Plain corrosion coupons of copper and cast iron.* The corrosion rate of the materials will be determined from weight loss measurements at the end of experiments. One weight loss sample for each material was installed in each experiment. These coupons were suspended from the nylon mounting rack using polypropylene thread.
- *Coupons of copper and cast iron that are electrically connected to the exterior of the borehole.* These were designed to allow the corrosion potential of the electrodes to be measured. It was also possible to carry out electrochemical measurements of the corrosion rate of these coupons using; linear polarisation resistance, LPR, AC impedance, ACI, and electrochemical noise, ECN. Platinised titanium gauze was used as the counter electrode in a conventional 3-electrode electrochemical cell. Electrical connections were made to the coupons using copper wire for the copper coupons and carbon steel wire for the cast iron coupons.
- *Copper electrical resistance wire probes.* These were set up to measure the corrosion rate of copper using the technique proposed previously by VTT (e.g. [9]). Each coil consisted of a total length of 112.5 cm of 1 mm diameter copper wire (99.9% purity, Advent Cu513918). The length of wire was divided into three regions each of 37.5 cm length by applying heat shrinkable, adhesive-lined polymer tubing to the end sections, leaving the middle section exposed to the test environment. The complete wire was formed into a spiral with a diameter of ~1 cm. The two screened lengths were used as reference resistances and the change in the resistance of the exposed length was used to calculate the corrosion rate. This information was processed by the ACM Field Machine electrochemical unit.
- *Stress corrosion test specimens.* Four Wedge Opening-loaded (WOL) specimens were mounted in the boreholes. They were machined from a scrap copper lid provided by SKB and they were pre-cracked to give a range of stress intensity factors. In addition four U-bend specimens were manufactured from the same lid material, with dimensions of 2.5×80×20 mm. Two U-bend specimens and two WOL specimens were mounted in each of experiment boreholes 3 and 4, by loosely suspending them from the stainless steel push rod using plastic connectors. They were thus exposed directly to the groundwater. They will be examined for any indications of stress corrosion cracking (SCC) at the end of the experiments.

- *Copper-cast iron-copper sandwich specimens to investigate jacking effects.* These specimens were based on the multi-crevice assembly specimen used in previous galvanic corrosion experiments [10], in which cast iron castellated nuts were tightened against sheets of copper. The aim of these specimens was to investigate a number of possible corrosion mechanisms, including crevice corrosion, galvanic corrosion and expansive corrosion. They consisted of a sheet of copper which was clamped against a block of cast iron using a ring of nylon bolts. To investigate the effect of separation distance between mating surfaces a series of steps was machined into the surface of the cast iron to give separation distances between the mating surfaces ranging from direct contact around the edges of the specimens, increasing in steps of 10  $\mu\text{m}$  to 30  $\mu\text{m}$ . The materials used for the sandwich specimens were prepared from copper sheet and the same type of cast iron used for the insert in the model canisters. The specimens will be removed and examined at the end of the exposure period.

The corrosion coupons present in Experiment 3 have been examined and the results of this examination are given in a separate report [7].

### **3.5 Mounting system for sensors and corrosion test pieces**

The corrosion coupons and environmental sensors were supported in a nylon rack which was placed inside the stainless steel support cage above the model canisters before the support cage was sealed. It rested on the top of the model canisters by means of support legs. Electrical connections were taken out through Conax compression fittings in the support cage lid. For Test 4, where the model canister was embedded in compacted bentonite, the corrosion coupons and sensors were placed in slots that were machined into the compacted bentonite before it was loaded into the supporting cage.

### **3.6 Electrical connections**

A summary of the sensors in each of the experiments and the conduits required for the connecting cables and details of output from each experiment is reported in reference [3]. Connecting wires from metal samples inside the canister cage (i.e. corrosion coupons and the model canister itself) were passed through compression glands (316L stainless steel Conax fittings) and connected to cables that were taken out to the external environment through stainless steel tubes which were attached to the supporting cages using Swagelok-type pressure fittings. All connections were made using soldered joints which were then sheathed in heat shrink. It should be noted that the electrochemical measurements rely on the integrity of the sheathing system throughout the experiments and the success of the sheathing will only be confirmed when the experiments are dismantled and the sheathing can be examined. The tubes were passed through the stainless steel flange at the entrance to the boreholes using bulkhead compression fittings.

### **3.7 Monitoring equipment**

The electrochemical monitoring is being performed using an ACM Ltd Field Machine and an Agilent datalogger. The ACM equipment is being used to carry out the electrochemical measurements of corrosion rate (10 channels) and measurements of electrical resistance of the copper wire electrodes (2 channels), and the Agilent datalogger is used to monitor the potentials of the various electrodes, together with monitoring the strain gauges. The datalogging equipment is located in a control room near the boreholes and data is then transmitted via the Internet to the UK for analysis.

### 3.8 Electrochemical cell

In order to obtain experimental measurements of the electrochemical behaviour of carbon steel embedded in compacted bentonite an electrochemical cell had previously been set up to measure the redox potential,  $E_h$ , and the corrosion potential of a steel electrode in compacted bentonite. This work was carried out as part of the NF-PRO project on near-field processes in a repository [11]. In the current MiniCan programme a second cell was set up using a similar technique, but a copper working electrode and an additional silver-silver chloride electrode were added to the set of electrodes tested previously. The design of the cell was as follows. A compacted bentonite holder of the design used for gas generation experiments [11] was modified by inserting a Conax pressure fitting in the top lid. This allowed electrical connections to be made to a gold wire, a steel wire and a copper wire which were embedded in compacted bentonite. The compacted bentonite was inserted into the sample holder in three sections consisting only of compacted bentonite. Holes were then drilled into the compacted bentonite and the test electrodes, a 1 mm diameter gold wire, a 1 mm carbon steel wire, which had been pickled, and a 1 mm copper wire, were then inserted into the holes in the compacted bentonite. The Conax fitting was then tightened around the wires to give a pressure-tight seal. Electrical connection was also made to the stainless steel holder, which acted as a counter electrode. The sample holder was placed in a polythene beaker and the assembly was mounted inside a glass cell, which had a glass-to-metal seal in the lid to allow electrical connections to be made to the test assembly. The whole assembly was placed in a nitrogen-purged glovebox to ensure that when the experiment was started the oxygen concentration was under 5 ppm. It was found that it was possible to measure a potential between the electrodes even before the test solution was placed around the sample holder, due to the residual water in the bentonite. The test solution was placed around the sample holder and a silver-silver chloride reference electrode was placed in the test solution. The potential of the gold, steel, copper and stainless steel were monitored with respect to the silver-silver chloride electrode as the artificial groundwater penetrated into the bentonite. The test solution used for the experiment was 1M NaCl solution at pH 8.4. After a few days the lid of the glass cell was fixed to the body using epoxy adhesive, allowed to cure then withdrawn from the nitrogen-purged glovebox and placed in an oil bath at a temperature of 30°C. On removing the cell from the glovebox after preparation of the cell was complete, the electrode potentials increased to more positive values, indicating possible oxygen ingress. Because of this concern, the cell was returned to the glovebox where continued monitoring of the electrode potentials was conducted. After a week the potentials had reduced to values comparable to the original potentials (i.e. prior to possible oxygen ingress). The cell has since been resealed and monitoring is continuing outside the glovebox, with no indications of further oxygen ingress.

Corrosion rate measurements were carried out periodically (i.e. every 2–3 months) using two standard electrochemical techniques, Linear Polarisation Resistance, (LPR) and Electrochemical Impedance Spectroscopy (EIS, also known as AC Impedance, ACI). Both of these techniques were conducted in accordance with the relevant ASTM standards for electrochemical corrosion rate measurements.

## 4 Results

It should be noted that the raw data for the electrochemical measurements are presented in Appendices 1 to 3 and the data from the microbial and gas analyses are presented in a report from Microbial Analytics [12].

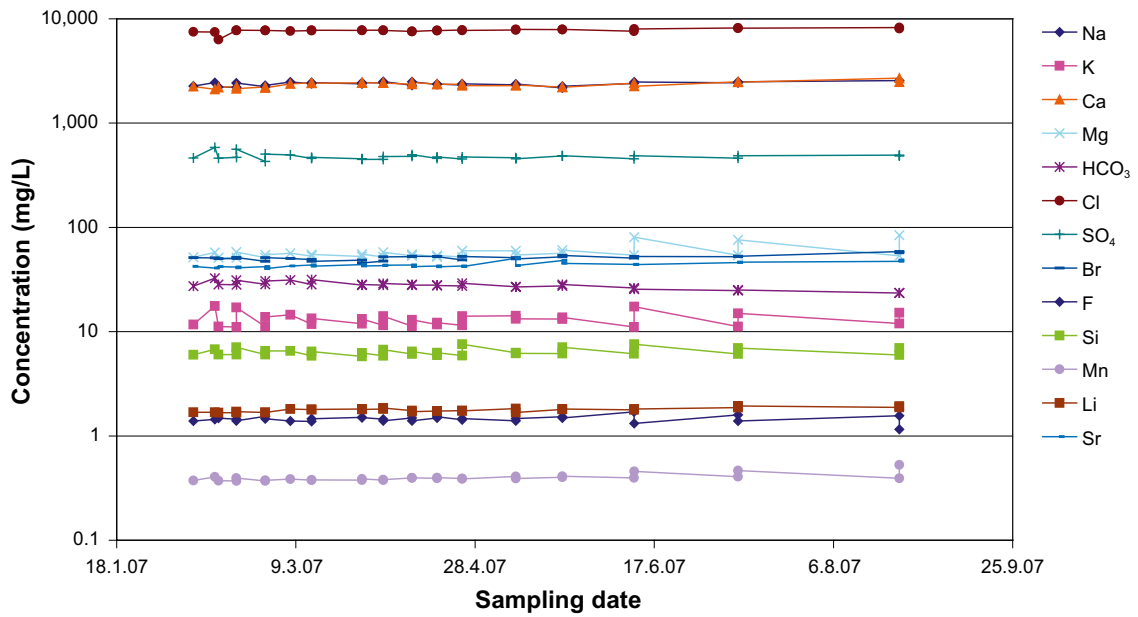
### 4.1 Water analysis

The results from the water analyses ( $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , sulphide,  $\text{Fe}^{2+}$  and pH) taken from both within the support cage and external to the support cage in the borehole for the five experiments for samples taken in May 2007, October 2008 and December 2010 are given in Table 4-1. In December 2010 data were obtained from both outside and inside the support cages in Experiments 1 to 5 (except for Experiment 4, where it was not possible to extract a water sample from within the support cage containing compacted bentonite), whereas in 2007 and 2008 data from outside the support cages were only obtained for Experiment 2. The previous data obtained up to October 2007 [3] (Figure 4-1 to Figure 4-8) showed small differences between the internal and external compositions. The data given in Table 4-1 are shown graphically in Figure 4-9 to 4-11 for sulphide, iron and pH respectively, to show the effect of time on the variation in the values. The results for each of these parameters are reviewed below.

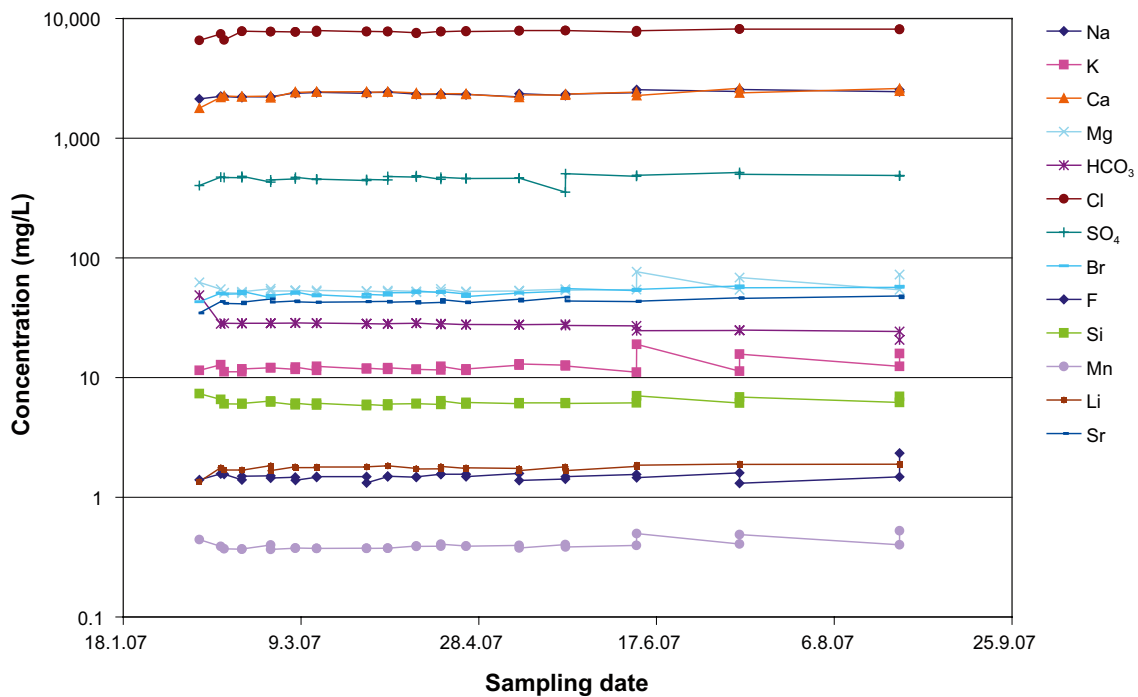
**Table 4-1. Chemical composition of the water from inside and the outside (the letter G after the experiment number indicates that the samples were taken from within the borehole but outside the model canister support cage) of the Model Canister experiments sampled in 05-2007, 10-2008 and 12-2010.**

Experiment	SO <sub>4</sub> <sup>2-</sup> (mgL <sup>-1</sup> ) (± 12%)			HCO <sub>3</sub> <sup>-</sup> (mgL <sup>-1</sup> ) (± 4%)			sulphide (mgL <sup>-1</sup> ) (± 32%)			Fe <sup>2+</sup> (mgL <sup>-1</sup> ) (0.05–1 mg/l ± 13% 1–3 mg/l ± 8%)			pH		
	05–2007	10–2008	12–2010	05–2007	10–2008	12–2010	05–2007	10–2008	12–2010	05–2007	10–2008	12–2010	05–2007	10–2008	12–2010
1	486	417	376	28	19	14	0.036	0.021	0.037	11.1	19.2	55.69	7.4	7.3	6.47
1G			462			17			0.080			0.11			7.47
2	506	413	430	27	20	14	0.057	0.020	0.044	2.33	4.15	22.56	7.6	7.4	6.72
2G	354	481	444	28	23	17	0.062	0.023	0.055	0.16	0.15	0.11	7.6	7.6	7.61
3	439	410	400	51	38	32	0.037	0.022	0.059	0.82	15.7	9.91	7.6	7.2	7.32
3G			411			34			0.049			0.23			7.47
4G			385			43			0.049			0.29			7.42
5	605	567	525	14	8	6	0.051	0.030	0.084	6.30	11.1	29.20	7.6	6.8	6.68
5G			432			21			0.059			0.19			7.58

Note: It is not possible to extract any water for analysis from inside the support cage of Experiment 4, because of the presence of compacted bentonite.

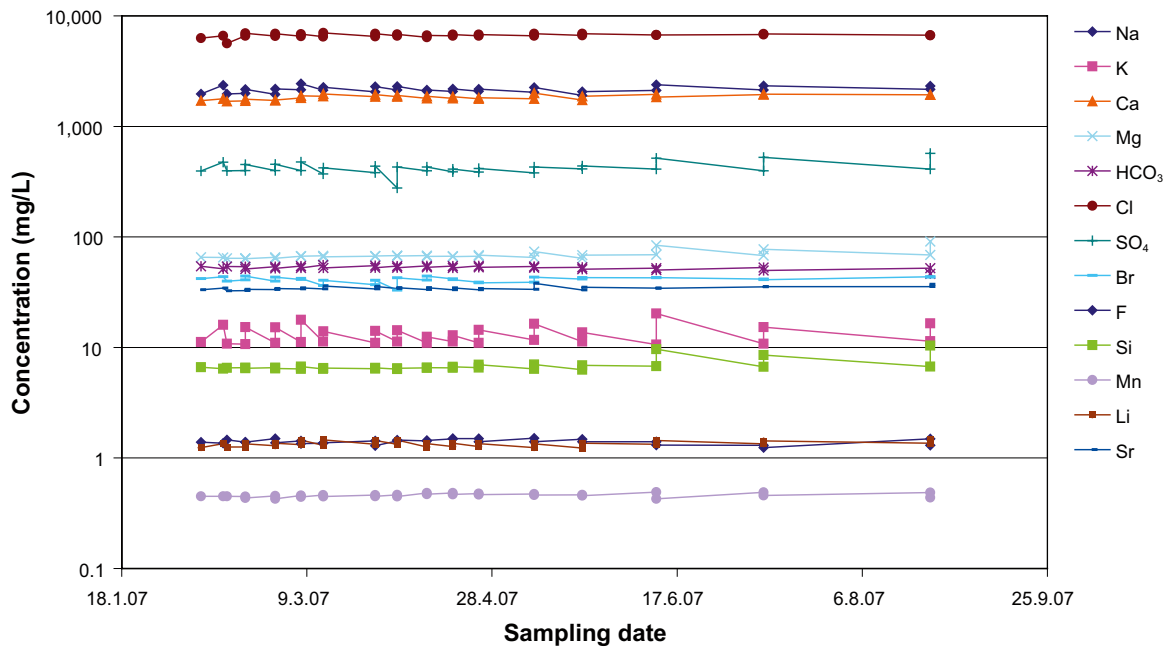


**Figure 4-1.** Summary of water analyses: Experiment 1. For any given sampling date the first concentration shown when approaching along the line from the left hand side of the diagram refers to the analysis in the borehole, but outside the support cage, and the point on the right hand side, but on the same date, refers to the concentration on the inside of the support cage. The results of the iron analyses are shown in Figure 4-7.

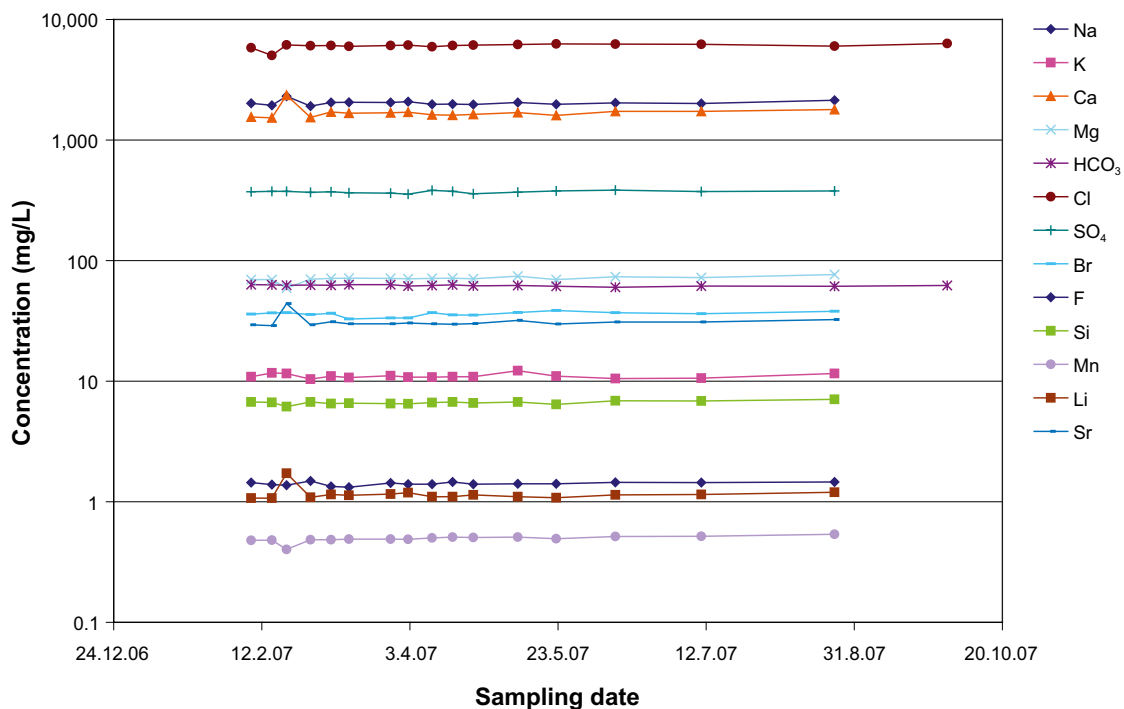


**Figure 4-2.** Summary of water analyses: Experiment 2. For any given sampling date the first concentration shown when approaching along the line from the left hand side of the diagram refers to the analysis in the borehole, but outside the support cage, and the point on the right hand side, but on the same date, refers to the concentration on the inside of the support cage. The results of the iron analyses are shown in Figure 4-7.

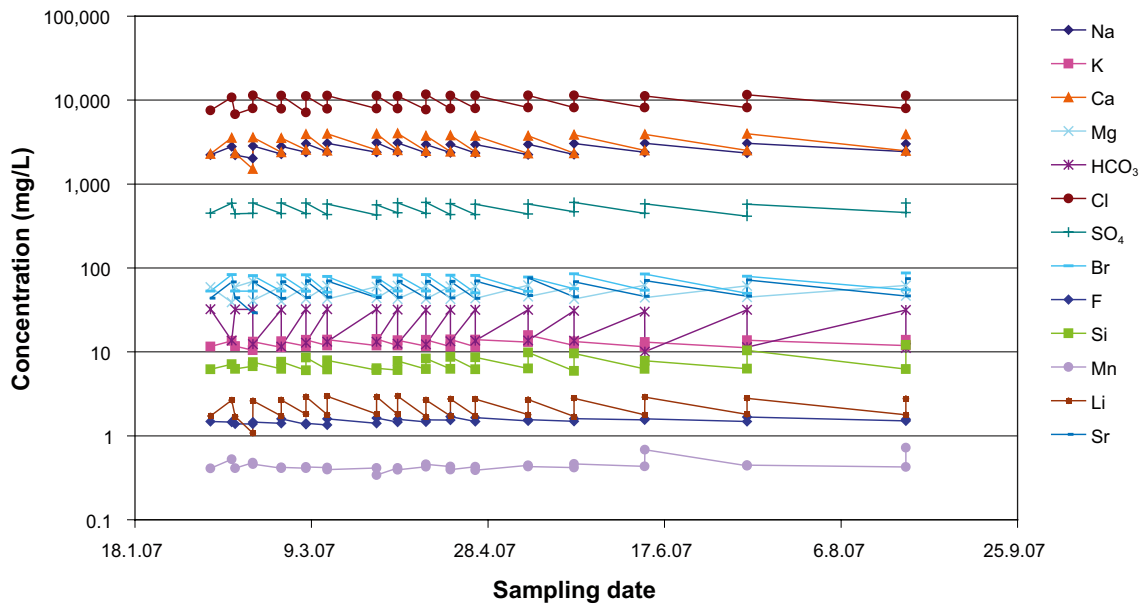




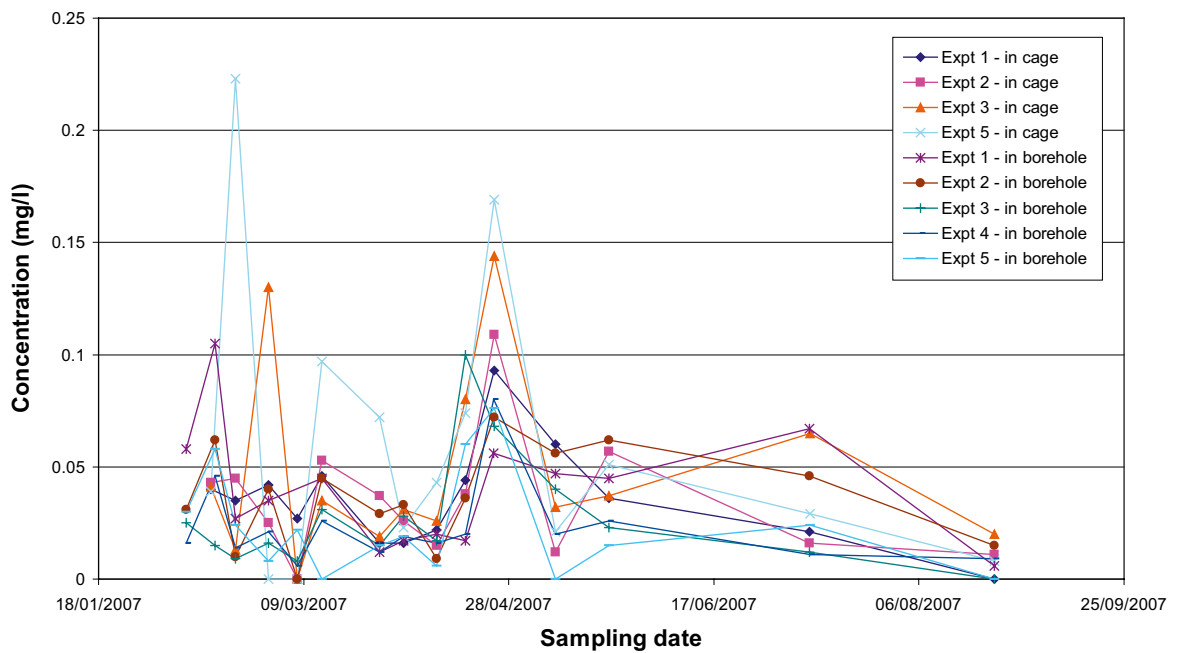
**Figure 4-3.** Summary of water analyses: Experiment 3. For any given sampling date the first concentration shown when approaching along the line from the left hand side of the diagram refers to the analysis in the borehole, but outside the support cage, and the point on the right hand side, but on the same date, refers to the concentration on the inside of the support cage. The results of the iron analyses are shown in Figure 4-7.



**Figure 4-4.** Summary of water analyses: Experiment 4. It was not possible to remove any water from inside the support cage for analysis, so all data refer to a water sample taken from the borehole outside the support cage. The results of the iron analyses are shown in Figure 4-7.



**Figure 4-5.** Summary of water analyses: Experiment 5. For any given sampling date the first concentration shown when approaching along the line from the left hand side of the diagram refers to the analysis in the borehole, but outside the support cage, and the point on the right hand side, but on the same date, refers to the concentration on the inside of the support cage. The results of the iron analyses are shown in Figure 4-7.



**Figure 4-6.** Summary of sulphide concentration in water samples in 2007.

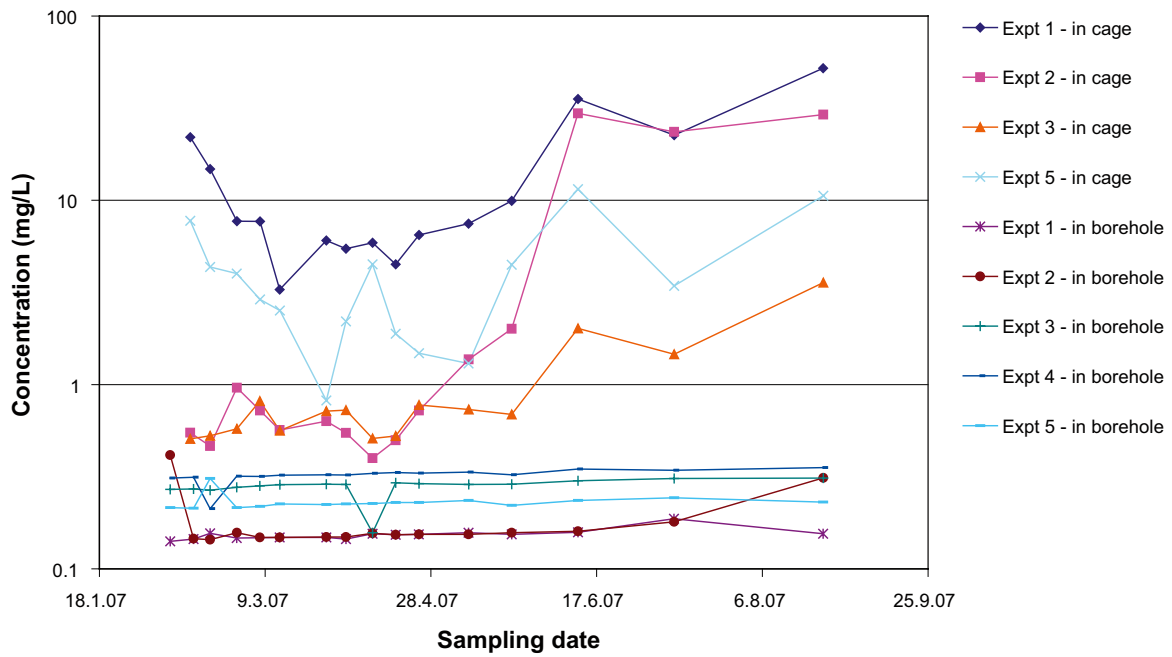


Figure 4-7. Summary of iron analysis in water samples in 2007.

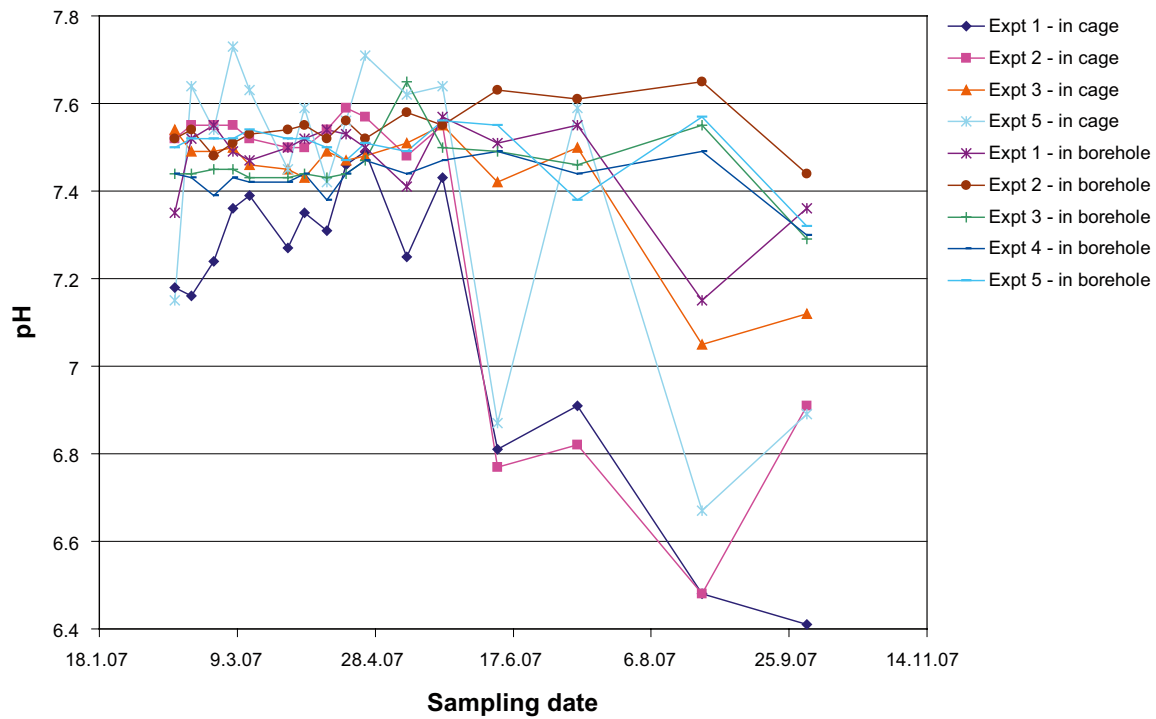


Figure 4-8. pH of water samples taken from model canister experiments in 2007.

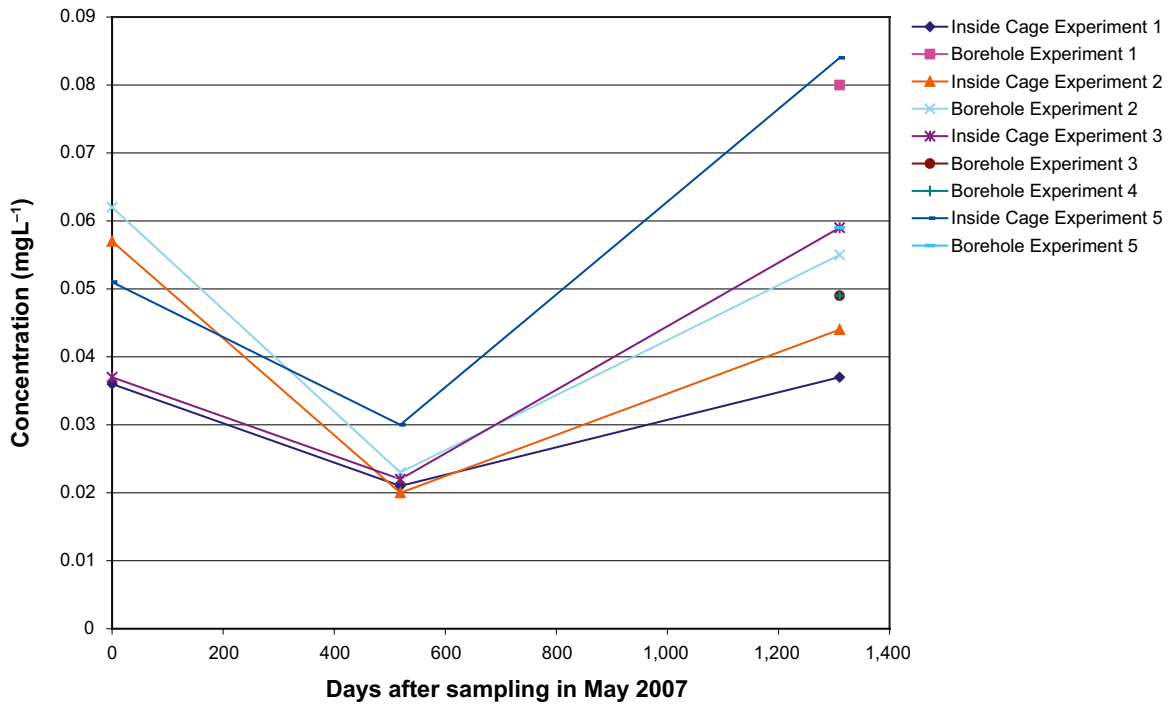


Figure 4-9. Variation of sulphide concentration with time since the sampling in May 2007 (see Table 4-1).

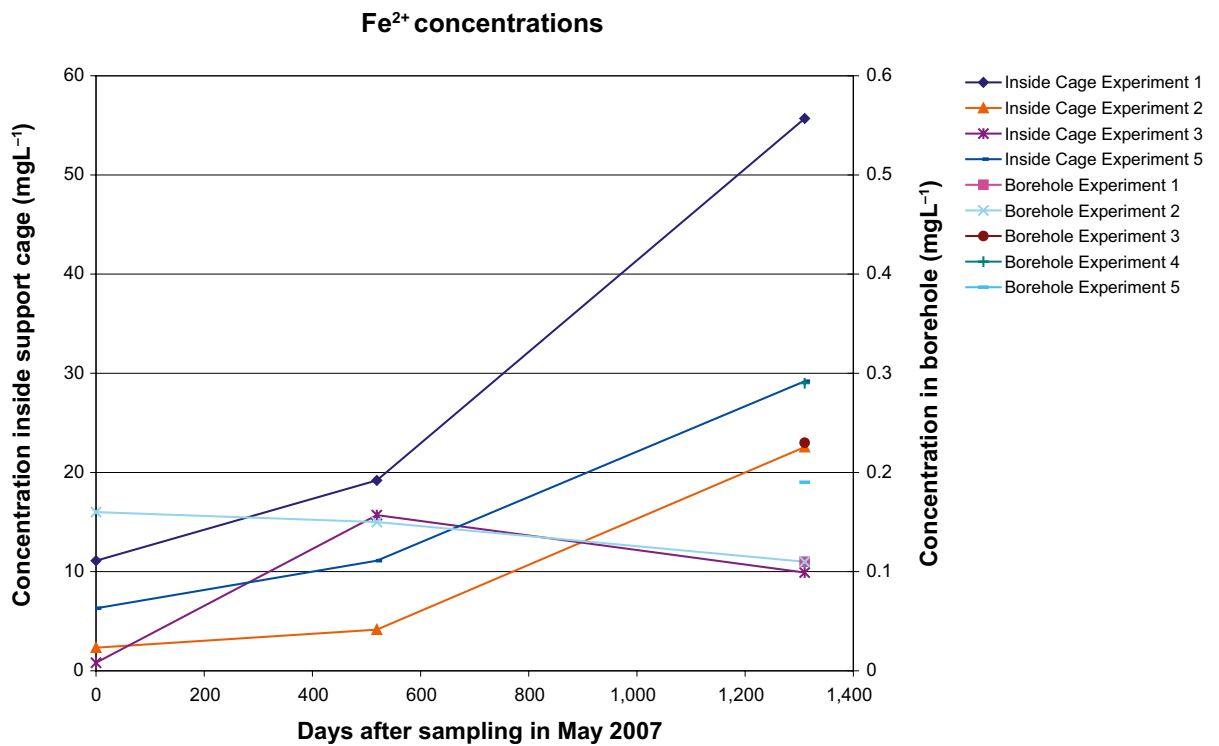


Figure 4-10. Variation of iron concentration with time since sampling in May 2007 (see Table 4-1).

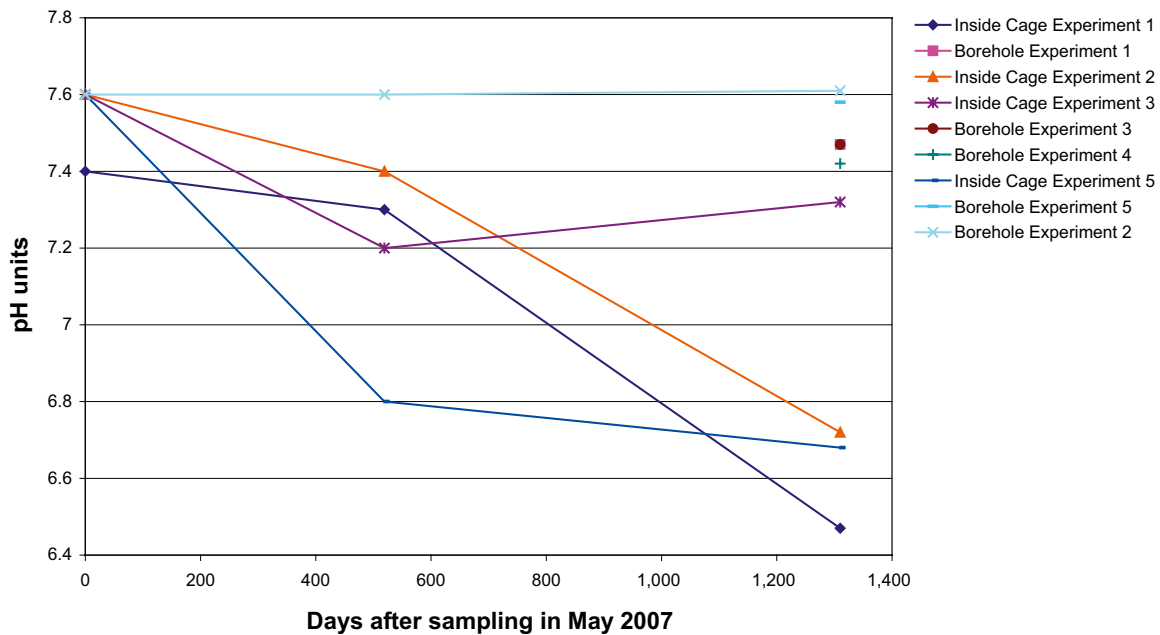


Figure 4-11. Variation of pH with time since sampling in May 2007 (see Table 4-1).

#### 4.1.1 Sulphide

The sulphide concentrations over the complete monitoring period were in the range 0 to 0.22 mgL<sup>-1</sup>, with the greatest range observed in the 2007 data. The values measured in 2008 were lower than the values measured in 2007, in some experiments by a factor of two. The overall sulphide concentrations were generally low (at least three orders of magnitude less than the sulphate concentration). The data obtained in 2010 show that the sulphide concentrations had generally increased since 2008 (Figure 4-9), reaching a maximum value of 0.084 mgL<sup>-1</sup> inside the experiment with no bentonite at all (Experiment 5). In some experiments the sulphide concentration was higher in the borehole compared to the concentration inside the support cage in the 2010 measurement (e.g. in Experiments 1 and 2), whereas in Experiments 3 and 5 the concentration was higher inside the support cage than in the borehole water. For comparison the most recent sulphide concentration value for the interior of Experiment 3 taken in August 2011 (~1,600 days after sampling in May 2007) prior to removal of the canister for analysis was 0.045 mgL<sup>-1</sup> [7].

#### 4.1.2 Iron concentrations

The greatest variation between the internal and external ion concentrations (Figure 4-10) was found in the dissolved iron analyses, with values ranging in the 2010 analysis from a minimum value of 0.11 mgL<sup>-1</sup> external to the support cage (e.g. in boreholes 1 and 2) compared to a maximum value of 55.69 mgL<sup>-1</sup> inside the support cage in experiments with low density bentonite (Experiments 1 to 3) or no bentonite at all (Experiment 5). Similar variation was noted previously in 2007 and 2008. For example in 2008 there was a minimum Fe<sup>2+</sup> concentration of 0.15 mgL<sup>-1</sup> external to the support cage compared to values up to 19.2 mgL<sup>-1</sup> inside the support cage. For comparison, the most recent iron concentration value for Experiment 3 taken in August 2011 (~1,600 days after sampling in May 2007) prior to removal of the canister for analysis was 39.17 mgL<sup>-1</sup> [7], which represents a further increase since the 2010 analysis. Overall the Fe<sup>2+</sup> concentrations inside the support cages have increased significantly since 2008, as shown in Figure 4-10, and the rate of release appears to be increasing with increasing time.

### 4.1.3 pH

The pH values of the water samples taken from inside and outside the support cages are also shown in Table 4-1 and Figure 4-11. These data show a continued decrease in the pH of water inside the support cages compared to the water in the boreholes. The data show pH values of below 7 inside the support cage in the experiments with low density bentonite in the support cage, with Experiment 1 exhibiting a minimum pH of 6.47, compared to the borehole pH value of 7.4–7.6. The most recent pH value for Experiment 3 taken in August 2011 prior to removal of the canister for analysis was 6.62 or 6.96<sup>1</sup> [7].

### 4.1.4 Other elements

Table 4-2 gives the measured concentrations of a range of metallic elements and anions, including those present in trace quantities, together with the total organic content (TOC) and conductivity of the water, for the measurements made in 2008 and 2010. These results show a number of interesting features:

1. It is noticeable that chloride, sodium, calcium, bromide, silicon, total sulphur, manganese, lithium, strontium, barium, cobalt, chromium, nickel and conductivity were all significantly higher in Experiment 5 than in other experiments or in the borehole of Experiment 2. The 2010 data show some distinct differences between the interior and exterior of Experiment 5. The concentrations of nickel and chromium were at least two orders of magnitude greater than in borehole water, suggesting that in Experiment 5 (no bentonite) corrosion of the stainless steel support cage was occurring, as well as corrosion of the cast iron insert. Low concentrations of nickel and chromium were observed in Experiments 1, 2 and 3, indicating that most of the increased concentration of iron in these experiments was due to corrosion of the cast iron insert rather than the stainless steel support cage (unless any nickel and chromium released had precipitated as an insoluble corrosion product). The higher concentrations of chloride, sodium, calcium, bromide, silicon, total sulphur, manganese, lithium, strontium, barium, in Experiment 5 indicate that there are local variations in water chemistry, which are presumably due to different water flow patterns through the rock fractures.
2. There have been changes in the composition of the groundwater since it was analysed in 2008, both internally and externally to the model canister experiment. For example, where comparison is possible, it is apparent that the concentrations of the major ions namely chloride, sodium and calcium have increased significantly since 2008. This suggests that not only are there local variations in groundwater chemistry (i.e. between boreholes), but that the local composition changes as a function of time, presumably due to changes in flow patterns within the rock mass.
3. The total concentration of sulphur is equivalent to a higher concentration of sulphate than was actually measured (Table 4-1) (i.e. the mass of sulphate is 3×the mass of sulphur) and the difference cannot be accounted for by the measured low concentrations of sulphide present (Table 4-1), so some sulphur must be present in a form other than sulphate or sulphide.
4. The changes in the concentrations of the minor cations, such as magnesium, strontium, potassium and lithium, and silicon-containing ions, are small between 2008 and 2010 and probably within the error bands for the analyses. There are nevertheless significant differences between the boreholes and between the internal and external environments for each experiment.
5. Regarding the elements present in trace amounts (i.e. at  $\mu\text{gL}^{-1}$  concentrations) it is noteworthy that the concentration of manganese is higher internally than externally and that manganese is present as a component of the cast iron insert (~0.09 wt%) and the stainless steel (~2wt%), and that the dissolved concentration internally has increased in some experiments since 2008 (e.g. Experiments 1 and 2) and is higher internally than externally in Experiments 1, 2 and 5. The concentrations of nickel and chromium inside the support cage for Experiment 5 are significantly higher internally than externally and this is assumed to be due to release from the stainless steel support cage, which appears to be more of a feature for the experiment with no bentonite present in the support cage. The concentration of dissolved copper is extremely small in all experiments ( $0.0005 \mu\text{gL}^{-1}$ ) and appears to have fallen since 2008.
6. The total organic carbon content has fallen since 2008 in all measurements where comparison is possible.
7. The conductivity has increased since 2008 and this is in agreement with the increased dissolved concentration of the major ions.

<sup>1</sup> Note that two different measurements are given in the analytical data.

**Table 4-2. Chemical composition of the water from inside and outside the support cage around the model canister experiments, as sampled in October 2008 and December 2010 (measurement uncertainty  $\sim\pm 12\%$ ).**

	Date	Experiment 1	Experiment 1 (borehole)	Experiment 2	Experiment 2 (borehole)	Experiment 3	Experiment 3 (borehole)	Experiment 4	Experiment 5	Experiment 5 (borehole)
<b>Cl (mgL<sup>-1</sup>)</b> ( $\pm 5\%$ )	2008	7,887		7,674	7,926	6,895			11,362	
	2010	8,599.0	8,524	8,373	8,572	7,968	7,973	7,656	11,420	8,905
<b>Na (mgL<sup>-1</sup>)</b>	2008	2,350		2,350	2,330	2,130			2,930	
	2010	2,480	2,470	2,470	2,510	2,340	2,280	2,320	3,100	2,500
<b>Ca (mgL<sup>-1</sup>)</b>	2008	1,910		2,470	2,460	1,930			3,840	
	2010	2,620.0	2,640.0	2,640	2,650	2,430	2,490	2,260	3,910	2,810
<b>Total S (mgL<sup>-1</sup>)</b>	2008	129		186	188	157	156	233		
	2010	132	184	169	182	156	160	152	223	172
<b>Br (mgL<sup>-1</sup>)</b>	2008	49.8		44.7	48.3	35.7			71.3	
	2010	53.3	52.8	53.5	48.90	48.6	48.6	45.4	75.6	55.1
<b>Mg (mgL<sup>-1</sup>)</b>	2008	47.9		51.9	51.3	76.0			42.9	
	2010	51.8	49.1	50.6	49.3	62.7	64.2	66.3	44.6	56.9
<b>Sr (mgL<sup>-1</sup>)</b>	2008	36.7		46.6	46.6	37.8			73.2	
	2010	45.7	46.5	46.6	47.2	41.8	42.9	40.4	66.9	48.6
<b>K (mgL<sup>-1</sup>)</b>	2008	9.0		11.6	11.4	11.0			13.5	
	2010	10.6	10.7	10.8	11.2	10.7	11.3	10.9	12.4	10.9
<b>Si (mgL<sup>-1</sup>)</b>	2008	4.01		6.00	6.04	5.91			9.28	
	2010	4.07	5.8	5.01	5.83	5.96	6.10	6.39	6.95	5.89
<b>F (mgL<sup>-1</sup>)</b>	2008	1.83		1.83	1.75	1.23			1.87	
	2010	1.35	1.53	1.43	1.48	1.43	1.48	1.46	1.56	1.49
<b>Li (<math>\mu</math>gL<sup>-1</sup>)</b>	2008	1410		1820	1750	1360			2670	
	2010	1,860	1,880	1,920	1,850	1,660	1,670	1,530	2,830	1,960
<b>Mn (<math>\mu</math>gL<sup>-1</sup>)</b>	2008	362		387	370	490			678	
	2010	691	351	468	349	452	455	485	525	408
<b>Ba (<math>\mu</math>gL<sup>-1</sup>)</b>	2008	89.0		80.3	78.3	89.8			101	
	2010	135	80.5	89.7	80.6	90.9	85.6	85.2	86.8	100
<b>Mo (<math>\mu</math>gL<sup>-1</sup>)</b>	2008	54.0		60.1	57.4	60.5			53.4	
	2010									
<b>Zn (<math>\mu</math>gL<sup>-1</sup>)</b>	2008	1.08		4.03	1.19	<0.8			4.33	
	2010									

Note: a blank cell indicates that no measurement was made.

**Table 4-2 (cont). Chemical composition of the water from inside and outside the support cage around the model canister experiments, as sampled in October 2008 and December 2010 (measurement uncertainty  $\sim\pm 12\%$ ).**

	Date	Experiment 1	Experiment 1 (borehole)	Experiment 2	Experiment 2 (borehole)	Experiment 3	Experiment 3 (borehole)	Experiment 4	Experiment 5	Experiment 5 (borehole)
<b>Ni (<math>\mu\text{gL}^{-1}</math>)</b>	2008	0.866		2.87	< 0.2	0.971			322	
	2010	0.5830	< 0.5	1.33	< 0.5	< 0.5	< 0.5	< 0.5	74.6	< 0.5
<b>Cu (<math>\mu\text{gL}^{-1}</math>)</b>	2008	0.251		0.767	< 0.2	< 0.2			0.283	
	2010	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
<b>V (<math>\mu\text{gL}^{-1}</math>)</b>	2008	0.199		0.275	0.291	0.215			0.0455	
	2010	0.010	0.1600	0.2240	0.0533	0.1810	0.1440	0.3620	0.1430	0.0854
<b>Pb (<math>\mu\text{gL}^{-1}</math>)</b>	2008	0.179		0.383	0.152	0.174			0.220	
	2010									
<b>Cr (<math>\mu\text{gL}^{-1}</math>)</b>	2008	0.169		1.80	0.159	0.191			248	
	2010	0.1	0.1	0.100	0.100	0.1000	0.1980	0.1000	55.70	0.1000
<b>Co (<math>\mu\text{gL}^{-1}</math>)</b>	2008	0.0391		0.152	0.0526	0.022			8.12	
	2010									
<b>NO<sub>2</sub><sup>-</sup> (mgL<sup>-1</sup>)</b>	2008	0.0013		0.0006	< 0.0002	0.0008			0.0012	
	2010	0.0003	0.0002	0.0002	0.0002	0.0003	0.0002	0.0002	0.0003	0.0003
<b>NO<sub>3</sub><sup>-</sup> (mgL<sup>-1</sup>)</b>	2008	0.0010		< 0.0003	0.0015	0.0021			0.0006	
	2010	0.0007	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	0.0006	< 0.0003
<b>PO<sub>4</sub><sup>3+</sup> (mgL<sup>-1</sup>)</b>	2008	< 0.0005		< 0.0005	< 0.0005	< 0.0005			< 0.0005	
	2010	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	0.0007	< 0.0005	0.0010	< 0.0005
<b>TOC (mgL<sup>-1</sup>)</b>	2008	3.2		1.9	1.3	3.6			1.2	
	2010	1.7	1.1	1.2	1.1	1.5	1.5	1.4	1.0	1.1
<b>Conductivity, mS m<sup>-1</sup></b>	2008	2,230		2,178	2,197	1,975			2,960	
	2010	2,347	2,353	2,336	2,342	2,196	2,193	2,115	3,033	2,422

Note: a blank cell indicates that no measurement was made.



**Table 4-3. Dissolved gas in the water from the model canister experiments sampled in September 2007 and October 2008 (bd = below detection level).**

Gases	Date	Experiments				
		1	2	2 G	3	5
Gas/water (mL L <sup>-1</sup> )	09-07	68	128	76	69	112
	10-08	90	109	103	53	86
	8-10	69.7	74.4	70.2	67.9	83.5
H <sub>2</sub> (μL L <sup>-1</sup> )	09-07	0.22	0.52	0.22	0.10	215
	10-08	90.1	0.57	0.52	0.55	7.3
	8-10	> 18.5	4.5	1.1	17.2	> 54.1
CO (μL L <sup>-1</sup> )	09-07	0.58	1.08	3.39	0.72	1.14
	10-08	0.52	0.53	0.70	0.69	6.8
	8-10	0.28	0.26	0.26	0.25	0.43
CH <sub>4</sub> (μL L <sup>-1</sup> )	09-07	326	317	210	245	117
	10-08	500	593	344	215	216
	8-10	329	387	271	167	183
CO <sub>2</sub> (μL L <sup>-1</sup> )	09-07	913	786	186	1,850	843
	10-08	338	284	338	568	394
	8-10	664	799	66.1	465	679
C <sub>2</sub> H <sub>6</sub> (μL L <sup>-1</sup> )	09-07	0.33	0.20	0.09	0.12	0.65
	10-08	bd	018	bd <sup>a</sup>	0.28	1.08
	8-10	0.24	0.32	0.04	0.1	0.44
C <sub>2</sub> H <sub>2-4</sub> (μL L <sup>-1</sup> )	09-07	0.14	0.17	bd	0.02	bd
	10-08	bd	bd	bd	bd	bd
	8-10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
C <sub>3</sub> H <sub>8</sub> (μL L <sup>-1</sup> )	09-07	bd	bd	bd	bd	bd
	10-08	bd	bd	bd	0.05	0.05
	8-10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
C <sub>3</sub> H <sub>6</sub> (μL L <sup>-1</sup> )	09-07	bd	bd	bd	bd	bd
	10-08	bd	bd	bd	bd	bd
	8-10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ar (μL L <sup>-1</sup> )	09-07	838	1,060	649	849	710
	10-08	1,110	1,190	740	185	bd
	8-10	626	425	589	773	1,120
He (μL L <sup>-1</sup> )	09-07	7,980	8,420	8,110	4,920	14,200
	10-08	9,990	9,100	9,070	6,600	14,900
	8-10	8,670	9,180	8,800	7,030	12,500
N <sub>2</sub> (μL L <sup>-1</sup> )	09-07	57,800	118,000	67,100	61,100	95,600
	10-08	77,400	91,900	98,200	44,900	71,200
	8-10	59,400	63,600	60,400	59,500	68,900
O <sub>2</sub> (μL L <sup>-1</sup> )	09-07	bd	bd	bd	bd	bd
	10-08	bd	bd	bd	bd	bd

#### 4.1.5 Gas analysis

The results of the dissolved gas analyses are shown in Table 4-3 and more detail about the results from analyses in 2007, 2008 and 2010 are given in reference [12]. The dissolved oxygen concentration in the groundwater was essentially zero [3]. The dominant dissolved gas is nitrogen, with significant quantities of helium, argon, carbon dioxide and methane also present. The concentration of hydrogen was particularly high in Experiment 5 in 2007 ( $215 \mu\text{L L}^{-1}$ ) but much lower ( $7.3 \mu\text{L L}^{-1}$ ) in 2008 but it increased again in 2010. The levels of both carbon dioxide and the alkalinity were lower in 2008 but increased again inside Experiments 1, 2 and 5. Further interpretation of the results of the gas analysis is presented in [12].

#### 4.1.6 Microbial analysis

The results of the microbial analyses for sulphate-reducing bacteria and autotrophic acetogens are summarised in Table 4-4 and 4-5 and a further set of analyses was performed in 2010. The details of the experimental measurement and the analyses, which were provided by Microbial Analytics AB, are given in [12]. The data from the sample taken in October 2008 show that the autotrophic acetogens were the dominant species but that sulphate-reducing bacteria were also present in significant numbers. By 2010 the balance of the microbial population had changed and the relevant proportion of SRB had increased (see [12]). No other types of microbes were analysed in detail, because these two varieties were believed to be significant in relation to corrosion, but the possibility that other species could be present cannot be excluded. The results of the following measurements are included in Table 4-4 and Table 4-5:

- Most probable numbers (MPN) and metabolites produced by sulphate-reducing bacteria and autotrophic acetogens (AA),
- biomass measured as adenosine-tri-phosphate (ATP) content,
- total number of cells,
- number of cultivable heterotrophic aerobic bacteria (CHAB), and
- molecular biology analyses which investigate the RNA and DNA pools in the samples.

The total number of cell levels remained unchanged in 2008 but the ATP level increased by almost 10-fold inside the model canister, where the water was in contact with cast iron. The concentration of ATP was found to have decreased inside the experiments in 2010 compared to 2008. Further details and discussion of the results are given in [12]. A further set of microbial analyses was carried out for Experiment 3 in 2011 and the results from these measurements are presented in reference [7].

#### 4.1.7 Pressure

The results from the pressure gauges in the boreholes are shown in Figure 4-12. Unfortunately there was a loss of data due to a fault with the datalogging system during the Winter of 2007/8 and due to breakdown of the computer during the winter of 2011. The data show that there is a general tendency for the pressure to fall with time, although the rate of decrease has fallen and the pressures have stabilised and increased slightly in recent months. The low pressure is mainly due to water loss through the rock face surrounding the boreholes.

**Table 4-4. The microbial composition inside and the outside (2G) the model canister experiments sampled in 05-2007.**

Experiment	ATP (amol mL <sup>-1</sup> ) <sup>a</sup>	TNC (mL <sup>-1</sup> ) <sup>a</sup>	Q-PCR 16S DNA (mL <sup>-1</sup> )	CHAB (mL <sup>-1</sup> ) <sup>a</sup>	MPN SRB (mL <sup>-1</sup> ) <sup>c</sup>	Q-PCR active SRB (relative activity)	Q-PCR total SRB (mL <sup>-1</sup> )	MPN AA (mL <sup>-1</sup> ) <sup>c</sup>	Q-PCR AA (relative activity)	Acetate (mgL <sup>-1</sup> )
1	2,400 ± 450	130,000 ± 16,000	na <sup>b</sup>	227 ± 42	5,000 (2,000 – 17,000)	10	na <sup>b</sup>	30,000 (2,000 – 17,000)	631	8.5
2	2,800 ± 240	95,000 ± 39,000	na <sup>b</sup>	200 ± 57	1,400 (600 – 3,600)	2	na <sup>b</sup>	50,000 (20,000 – 200,000)	10	8
2 G	3,300 ± 710	31,000 ± 11,000	na <sup>b</sup>	20 ± 35	3 (1 – 12)	3	na <sup>b</sup>	3 (1 – 12)	3	6.9
3	15,500 ± 810	150,000 ± 61,000	na <sup>b</sup>	530 ± 28	230 (90 – 860)	2	na <sup>b</sup>	7,000 (3,000 – 21,000)	336	6.9
5	3,000 ± 680	13,000 ± 4,900	na <sup>b</sup>	17 ± 12	300 (100 – 1,100)	1	na <sup>b</sup>	bd	1	11

<sup>a</sup> ± standard deviation <sup>b</sup> not analysed <sup>c</sup> 95% confidence interval).

**Key**

ATP	adenosine triphosphate
TNC	total number of cells
CHAB	number of cultivable heterotrophic aerobic bacteria
MPN	most probable numbers
AA	autotrophic acetogens
SRB	sulphate-reducing bacteria
Q-PCR	quantitative real time polymerase chain reaction
DNA	deoxyribonucleic acid

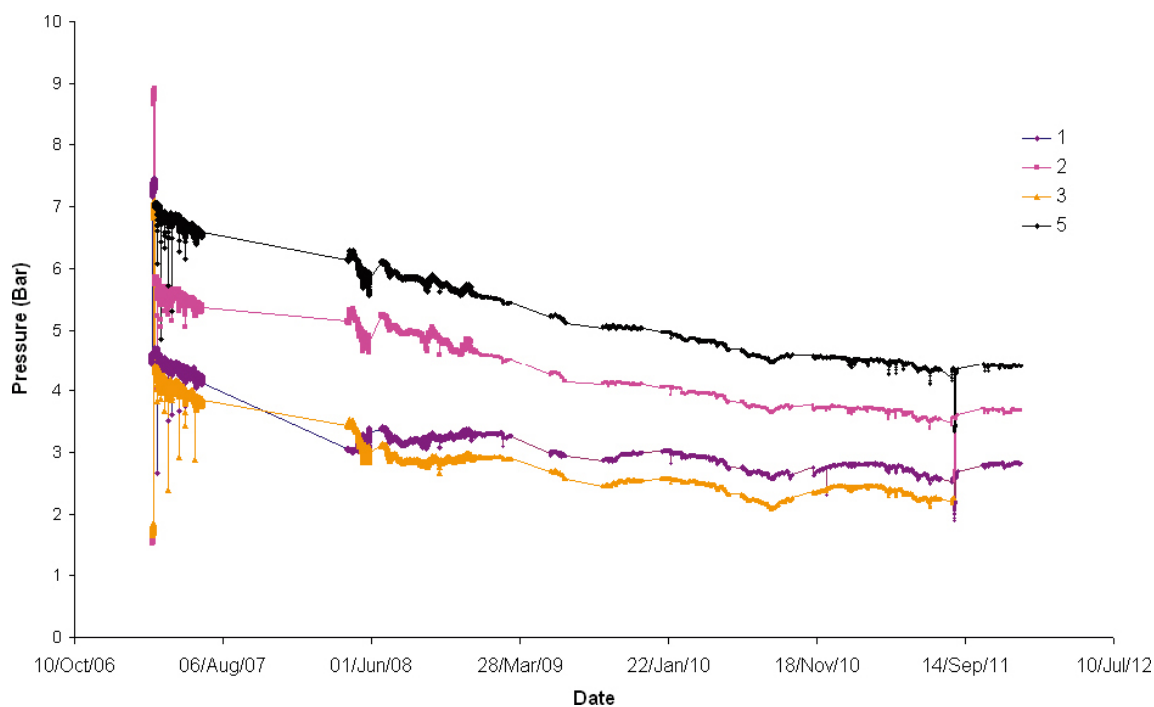
**Table 4-5. The microbial composition inside and outside (2G) the model canister experiments sampled in October 2008.**

Experiment	ATP (amol mL <sup>-1</sup> ) <sup>a</sup>	TNC (mL <sup>-1</sup> ) <sup>a</sup>	Q-PCR 16S DNA (mL <sup>-1</sup> )	CHAB (mL <sup>-1</sup> ) <sup>a</sup>	MPN SRB (mL <sup>-1</sup> ) <sup>c</sup>	Q-PCR active SRB (mL <sup>-1</sup> )	Q-PCR total SRB (mL <sup>-1</sup> )	MPN AA (mL <sup>-1</sup> ) <sup>c</sup>	Q-PCR active AA (mL <sup>-1</sup> )	Acetate (mgL <sup>-1</sup> )
1	17,400 ± 2,500	180,000 ± 4,600	6,700,000	bd <sup>b</sup>	5,000 (2,000 – 17,000)	5,500	540,000	1.7 (0.7 – 4)	bd <sup>b</sup>	1.7
2	10,400 ± 690	180,000 ± 18,000	4,500,000	3 ± 6	800 (300 – 2,500)	31	37,000	17 (7 – 48)	bd <sup>b</sup>	1.6
2G	4,400 ± 570	2,500 ± 880	8,000,000	3 ± 6	2.3 (0.9 – 8.6)	bd <sup>b</sup>	bd <sup>b</sup>	0.4 (0.1 – 1.7)	bd <sup>b</sup>	2.9
3	27,400 ± 1,820	200,000 ± 22,000	5,000,000	20 ± 17	70 (30 – 210)	350	74,000	90 (30 – 290)	bd <sup>b</sup>	1.8
5	18,600 ± 1,270	71,000 ± 11,000	14,000,000	bd <sup>b</sup>	110 (40 – 300)	bd <sup>b</sup>	11,000	2,700 (1,200 – 6,700)	bd <sup>b</sup>	2.3

<sup>a</sup> ± standard deviation <sup>b</sup> below detection limit <sup>c</sup> 95% confidence interval).

**Key**

ATP	Adenosine triphosphate
TNC	Total number of cells
CHAB	Number of cultivable heterotrophic aerobic bacteria
MPN	Most probable numbers
AA	Autotrophic acetogens
SRB	Sulphate-reducing bacteria
Q-PCR	Quantitative real time polymerase chain reaction
DNA	Deoxyribonucleic acid



**Figure 4-12.** Pressure reading for borehole 1 to 5 (pressure inside support cage, no measurements possible for Experiment 4 because of presence of compacted bentonite).

## 4.2 Electrochemical potential measurements

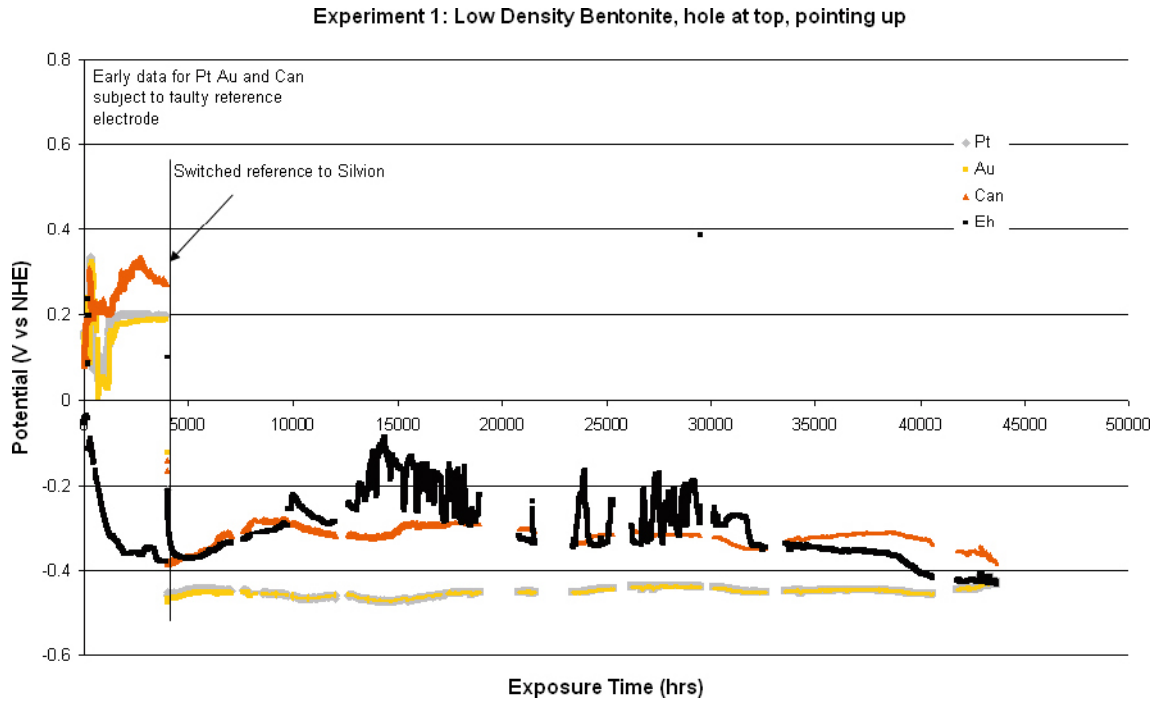
This section presents the electrochemical potential measurements for each of the model canister experiments. Some of the figures also include the results of corrosion rate measurements (see Section 4.3). The exposure period for all experiments up to the end of the data shown in this report was ~45,000 hours (i.e. ~5.1 years).

### 4.2.1 Experiment 1: Low density bentonite

In this experiment the defect in the outer copper shell (located near the top cap weld), is pointing vertically upwards. Figure 4-13 shows the results from the potential measurements for gold, platinum,  $E_h$  probe and the miniature canister. These data show the  $E_h$  values using gold and platinum, which are inside the support cage, and the  $E_h$  measured using the mixed-metal oxide electrode outside the support cage. Initially the internal silver-silver chloride reference electrodes were used for the Au and Pt electrodes, but these failed and it was necessary to switch to the Silvion reference electrode, which was mounted in the borehole outside the support cage (see change at 4,000 hours). The Au, Pt and MiniCan potential data up to 4,000 hours should be discounted. It is not clear why the Ag-AgCl disc electrodes failed in these experiments, since they had behaved satisfactorily during the laboratory autoclave tests [3]; however recent examination of Experiment 3 [7] has shown that the electrodes had become covered with a layer of black deposit (iron sulphide) which had probably disabled the reference electrodes. To date, the Silvion reference electrodes have performed satisfactorily.

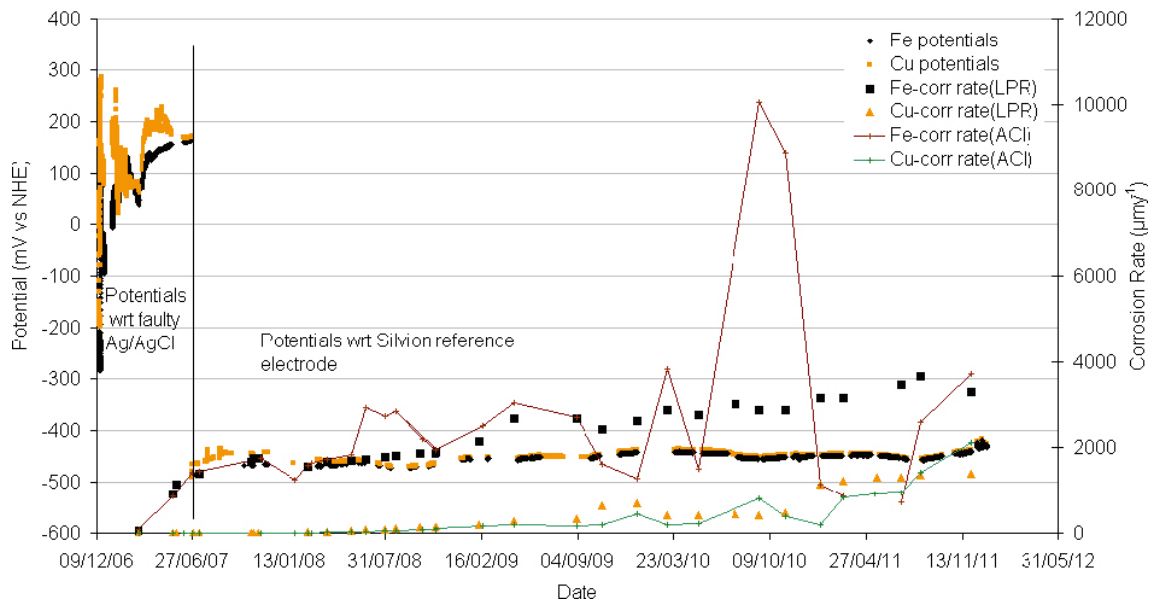
The mixed-metal oxide  $E_h$  values are reliable and show a decrease in the  $E_h$  with time. This is expected, since oxygen is consumed by microbial activity, mineral reactions and corrosion. The  $E_h$  value is lower inside the cage than outside, indicating more reducing conditions, possibly due to the ongoing corrosion reactions. In 2010 there were some fluctuations in the  $E_h$  values measured using the metal-oxide probe; the reasons for these are not clear at present but during 2011 the potentials stabilised and the  $E_h$  value became more negative so that they are now similar to the values measured on the gold and platinum electrodes inside the MiniCan support cage.

The electrochemical potential for the model canister represents a mixed potential for the copper canister itself and the inner cast iron insert, which would have been partially wetted by water passing through the 1 mm defect in the outer copper canister.



**Figure 4-13.** Results of  $E_n$  and canister potential measurements from Experiment 1 (low density bentonite).

Figure 4-14 shows the potentials for the iron and copper coupons inside Experiment 1, up to the end of 2011. Again there was a problem with the reference electrodes up to 27 June 2007, but after that date the measurements were changed to be with respect to the Silvion reference electrode, at which point reasonable values of about  $-450$  mV vs NHE<sup>2</sup> were obtained, for both iron and copper. The iron and copper potentials are consistent with anoxic conditions existing in the boreholes. These potentials have now been stable for a period of approximately five years.



**Figure 4-14.** Results of corrosion potential and corrosion rate measurements for cast iron and copper electrodes in Experiment 1 (low density bentonite).

<sup>2</sup> NHE = normal hydrogen electrode, which in this report is assumed to be equivalent to the SHE, standard hydrogen electrode. The two terms are used interchangeably.

#### 4.2.2 Experiment 2: Low density bentonite

In this experiment the defect in the outer copper shell is at the top end of the canister (i.e. near the lid) but pointing downwards. Figure 4-15 shows the results from the potential measurements for gold, platinum,  $E_h$  probe and the model canister.

With Experiment 2, as for Experiment 1, there was a problem with the small Ag-AgCl reference electrodes mounted inside the support cages, but when the measurements were carried out against the external Silvion reference electrode reasonable values were obtained. The  $E_h$  value is again slightly more reducing inside the support cage than outside. The Eh values measured in this experiment were slightly lower than in Experiment 1.

The electrochemical potential values for iron and copper are shown in Figure 4-16. As for Experiment 1 it was necessary to measure the values against the Silvion reference electrode because the internal silver-silver chloride electrodes failed. This correction was made after June 2007. The potentials have been stable since the reference electrode system was changed; they are consistent with anoxic reducing conditions.

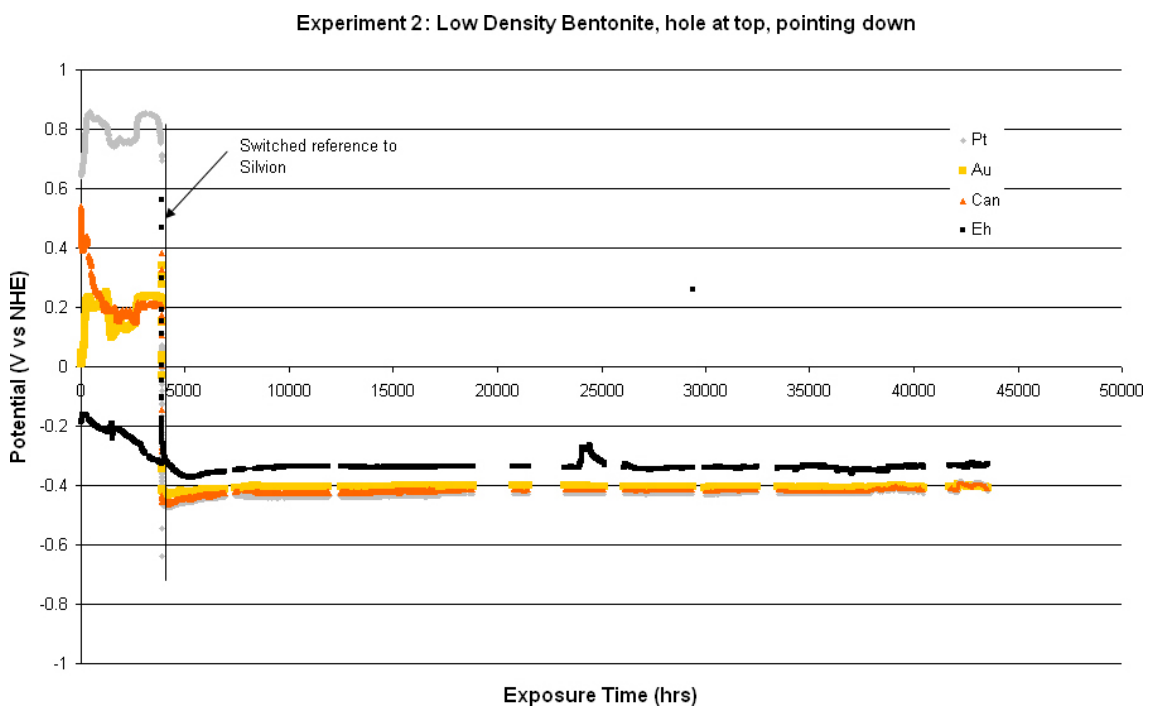
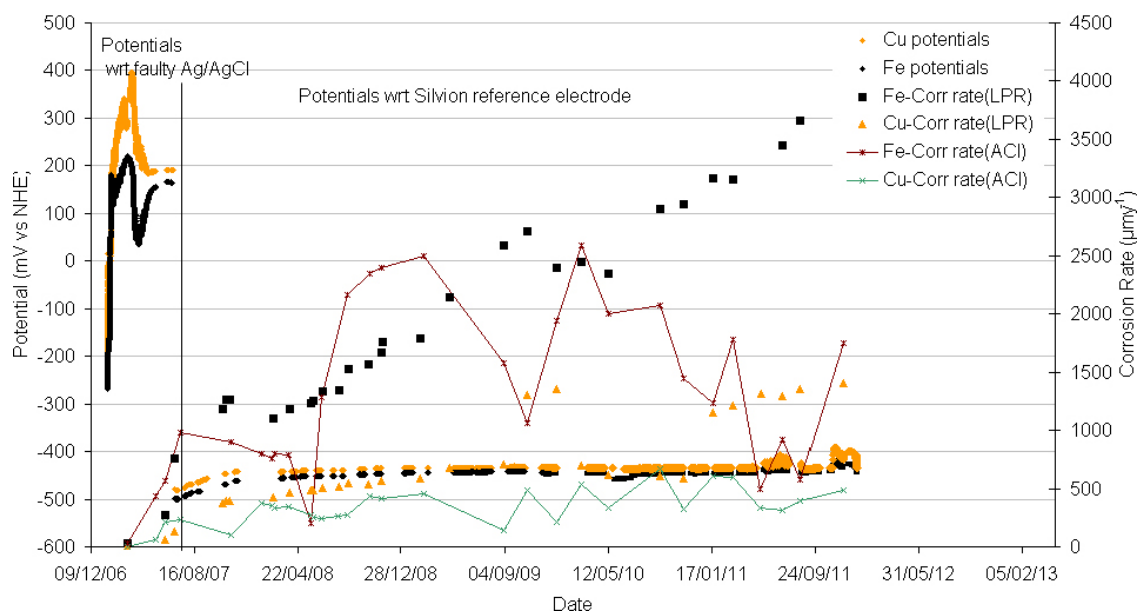


Figure 4-15. Results of  $E_h$  and can potential measurements from Experiment 2 (low density bentonite).



**Figure 4-16.** Results of corrosion potential and corrosion rate measurements for cast iron and copper electrodes in Experiment 2 (low density bentonite).

#### 4.2.3 Experiment 3: Low density bentonite

In this experiment there are two defects present in the outer copper shell; the defect near the top lid is pointing upwards, while the defect near the bottom cap is pointing downwards. Figure 4-17 shows the results from the potential measurements for gold, platinum,  $E_h$  probe and the model canister. In Experiment 3 the internal Ag-AgCl electrodes worked properly until approximately 8,000 hours had elapsed, when it was necessary to change to the Silvion reference electrode outside the support cage. As mentioned previously this failure of the internal reference electrodes appears to have been due to the build up of deposit on the surface of the reference electrodes [7]. The early fluctuations in  $E_h$  inside the support cage appear to be genuine. The  $E_h$  value external to the support cage stabilised at  $\sim -300$  mV after 3,500 hours.

The electrochemical potential values for iron and copper in Experiment 3 are shown in Figure 4-18. These data show a decrease in the corrosion potential of the copper initially, stabilising at highly negative values. The potentials were subsequently measured against Silvion after failure of the internal silver-silver chloride reference electrodes after approximately 7,500 hours. The potentials have been stable for the last 26 months but have attained more positive values than initially ( $\sim -430$  mV NHE). This experiment was removed in August 2011 for analysis and the results of the examination are reported separately [7].

#### 4.2.4 Experiment 4: Compacted bentonite

In Experiment 4 the defect in the outer copper shell is near the top lid but pointing downwards. The whole model canister is surrounded by compacted bentonite, with the test electrodes placed in slots cut into the compacted bentonite. Figure 4-19 shows the results from the potential measurements for gold, platinum,  $E_h$  probe and the model canister. The potentials for the platinum exhibited a considerable amount of noise. It was necessary to use the external Silvion reference electrodes to measure the potentials after about 3,500 hours. It is noticeable that the  $E_h$  values are not as negative as in the fully saturated bentonite tests.

The electrochemical potential values for copper and iron in Experiment 4 are shown in Figure 4-20 and 4-21 respectively. Contact has now been lost with the iron electrode in this experiment (it appears that both iron electrodes and the auxiliary electrode are shorted to the stainless steel flange). This may have been caused by expansion of the compact bentonite leading to crushing of the electrical connections. The data for the iron electrode are included for completeness, but the data should be treated with caution (i.e. they are not valid and are only included for completeness).



Experiment 3: Low Density Bentonite, 2 holes, bottom facing down, top facing up

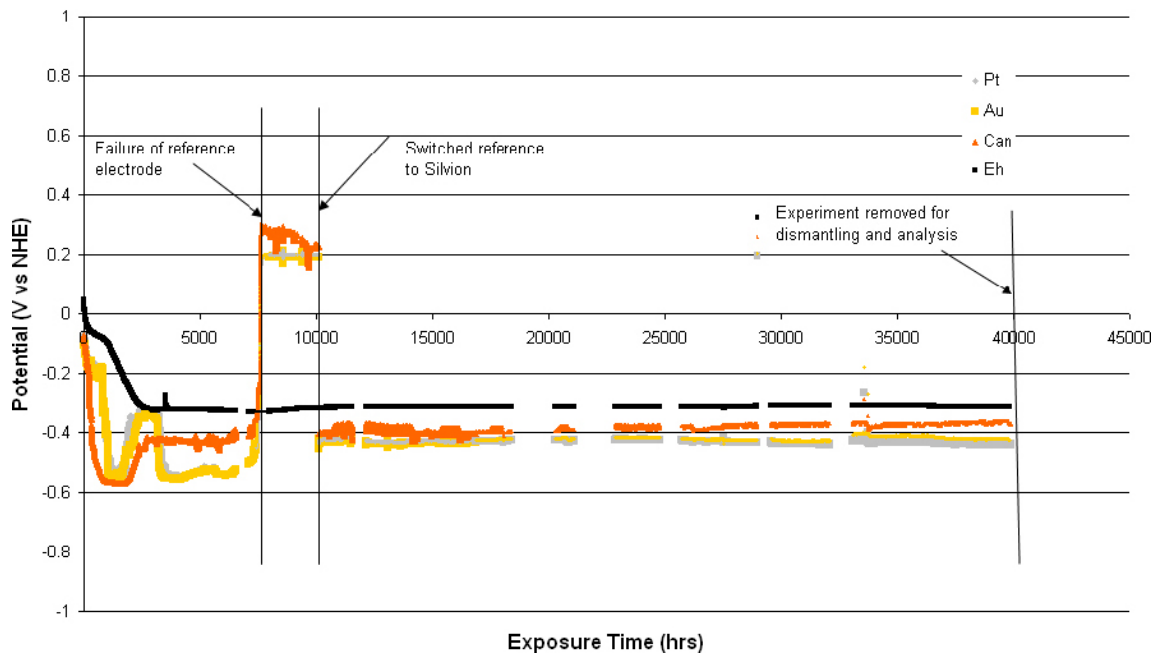


Figure 4-17. Results of  $E_h$  and can potential measurements from Experiment 3 (low density bentonite).

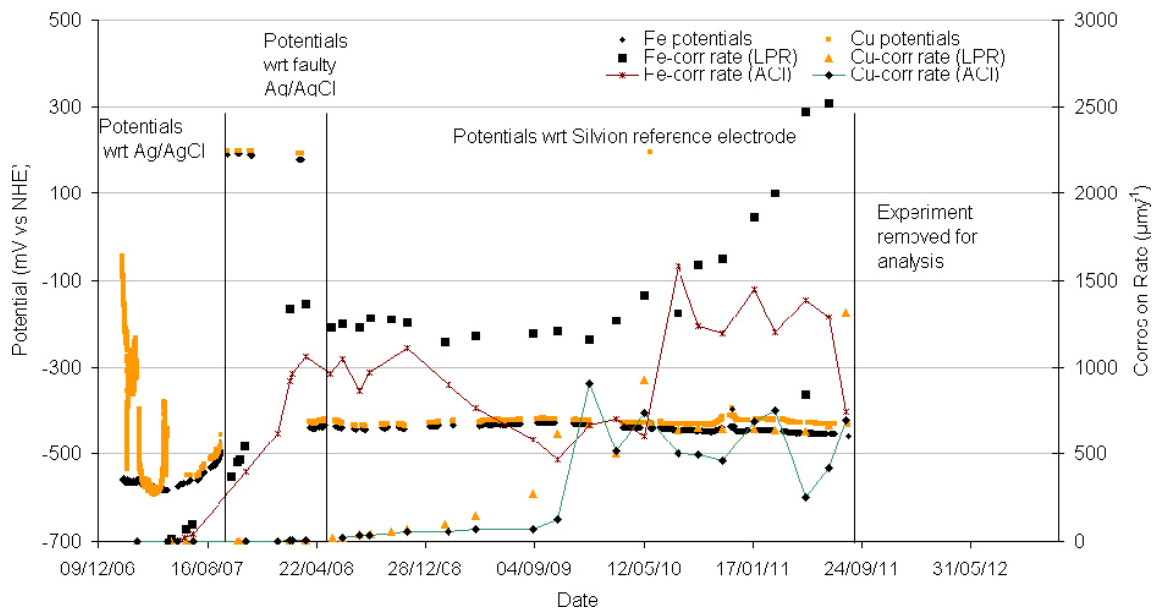


Figure 4-18. Results of corrosion potential and corrosion rate measurements for cast iron and copper electrodes in Experiment 3 (low density bentonite).

Experiment 4: Compacted bentonite

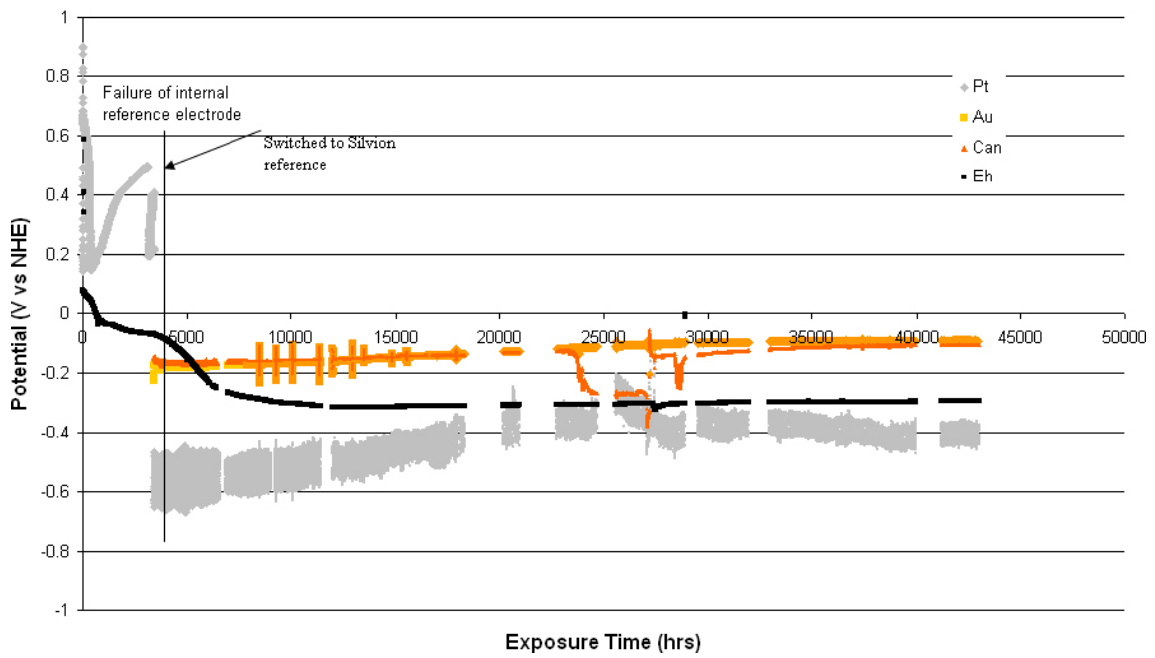


Figure 4-19. Results of  $E_h$  and can potential measurements from Experiment 4 (compact bentonite).

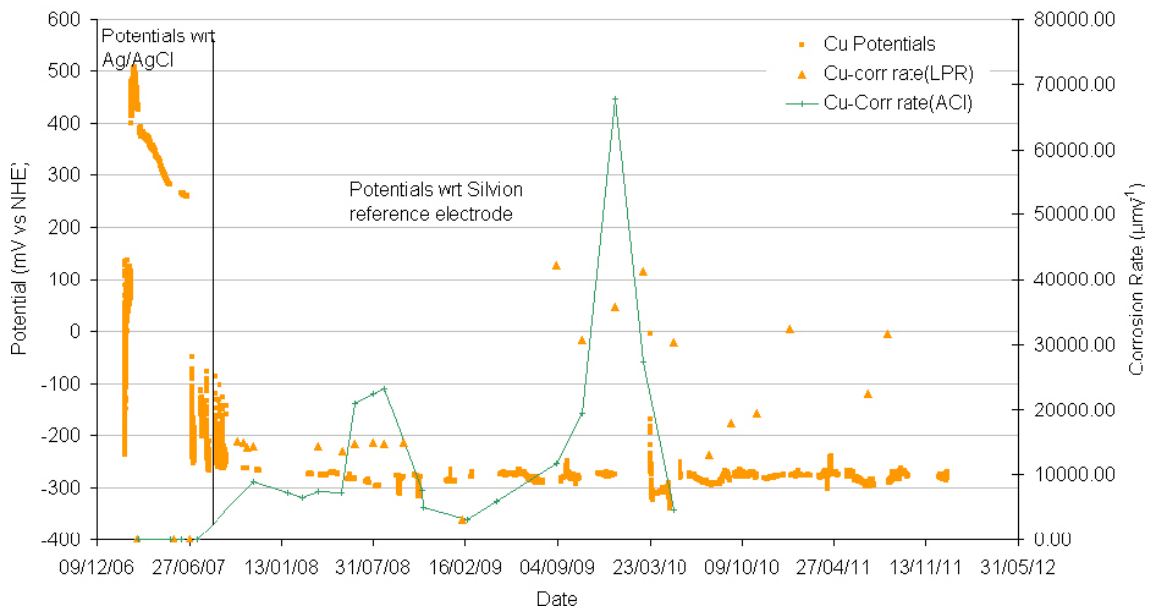
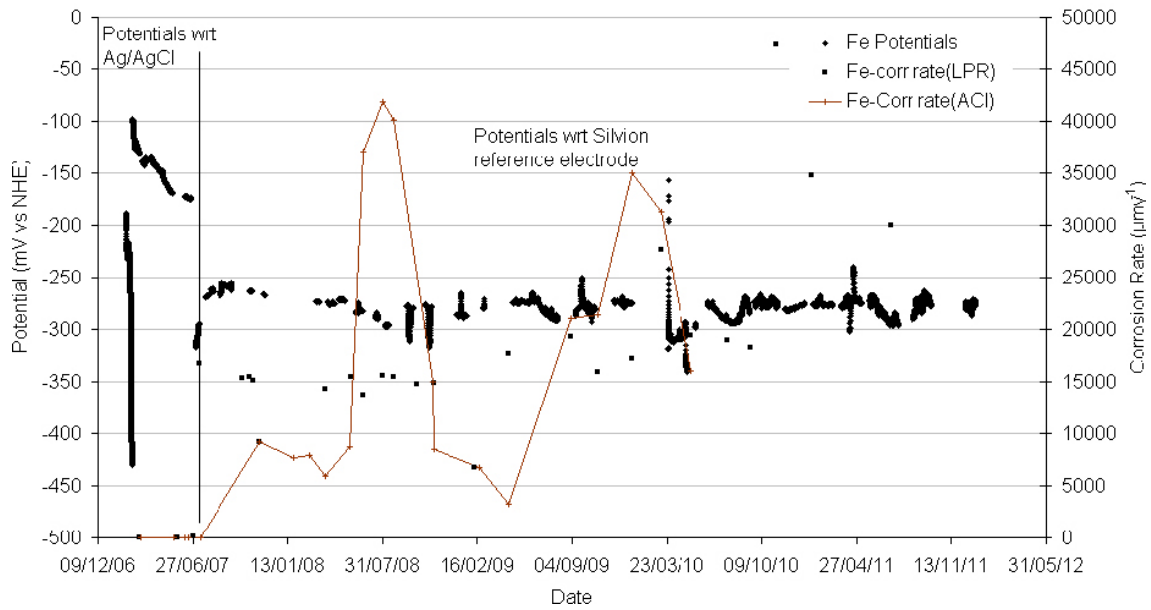


Figure 4-20. Results of corrosion potential and corrosion rate measurements for copper electrodes in Experiment 4 (compacted bentonite).



**Figure 4-21.** Results of corrosion potential and corrosion rate measurements for cast iron electrodes in Experiment 4 (compacted bentonite).

#### 4.2.5 Experiment 5: No bentonite

In this experiment there are two defects in the outer copper shell, both of which are near the top lid. One defect is pointing vertically upwards, the other is pointing downwards. In this experiment there is no bentonite around the model canister (i.e. it is in direct contact with the Äspö groundwater). Figure 4-22 shows the results from the potential measurements for gold, platinum,  $E_h$  probe and the model canister. In this experiment there was a problem with both the internal silver-silver chloride reference electrodes and the external  $E_h$  probe and the Silvion electrode and so it was necessary to set up an external reference electrode and  $E_h$  probe, mounted on the borehole flange. The iron and copper potentials in this experiment are shown in Figure 4-23. Again there were problems with the small internal Ag-AgCl reference electrodes up to June 2007, after which it was necessary to switch to using the stainless steel flange as a pseudo reference electrode and then to an external reference electrode. The  $E_h$  probe data and the recent iron and copper potentials are unusually high and there was some doubt about the reliability of this reference electrode system, using a Clarke's silver-silver chloride reference electrode system. In May 2010 the external reference electrode was replaced with a Silvion external reference electrode and this appears to be operating satisfactorily, although it is noticeable that there appeared to be an equilibration period after the new reference electrode was installed (see Figure 4-22), for the  $E_h$  potentials, and the copper and iron potentials. This probably corresponds to a period when there was a spike of oxygen entering the borehole after the external reference electrode was changed. It is also noticeable that this corresponded to an increase in the electrochemically measured corrosion rate.

Experiment 5: No bentonite, 2 holes at top, 1up, 1down

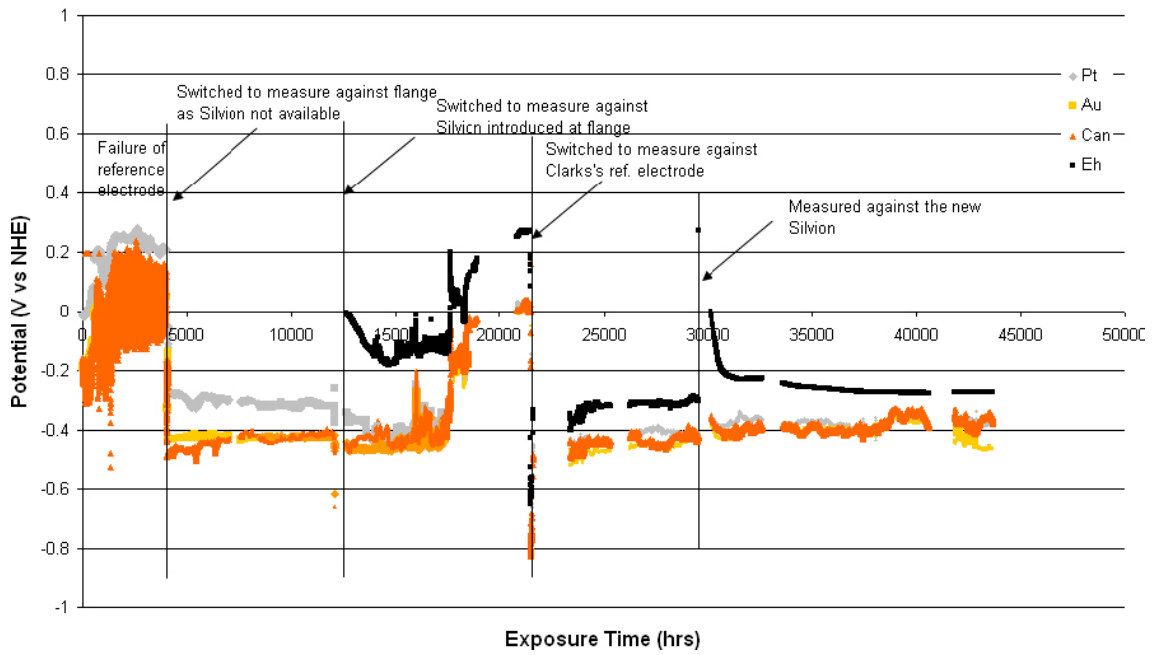


Figure 4-22. Results of  $E_n$  and can potential measurements from Experiment 5 (no bentonite).

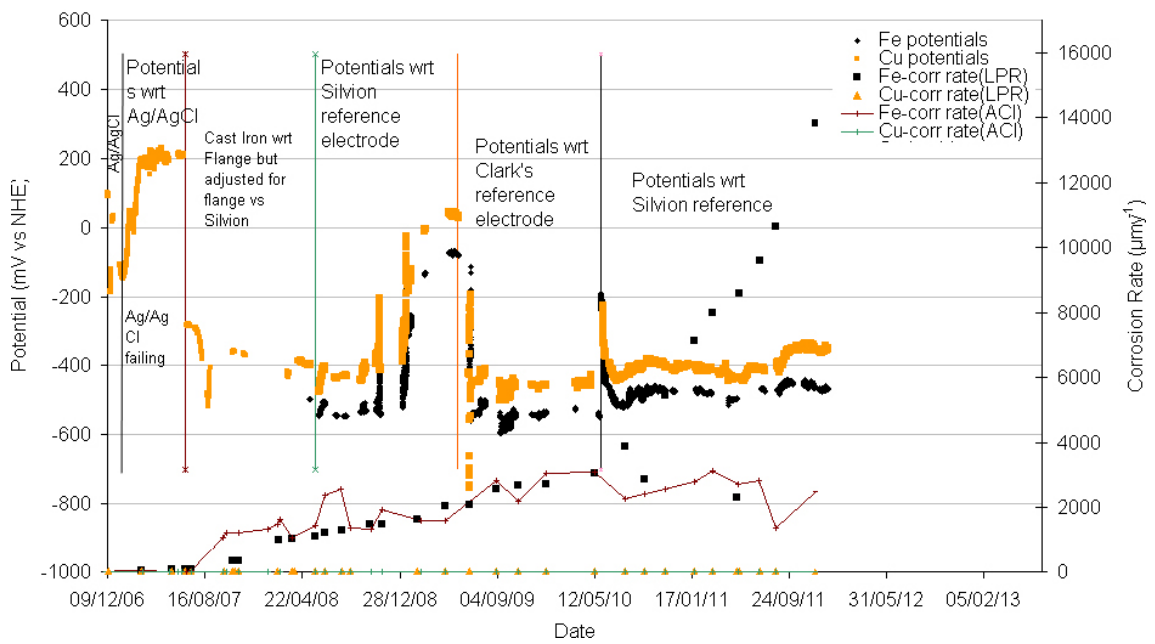
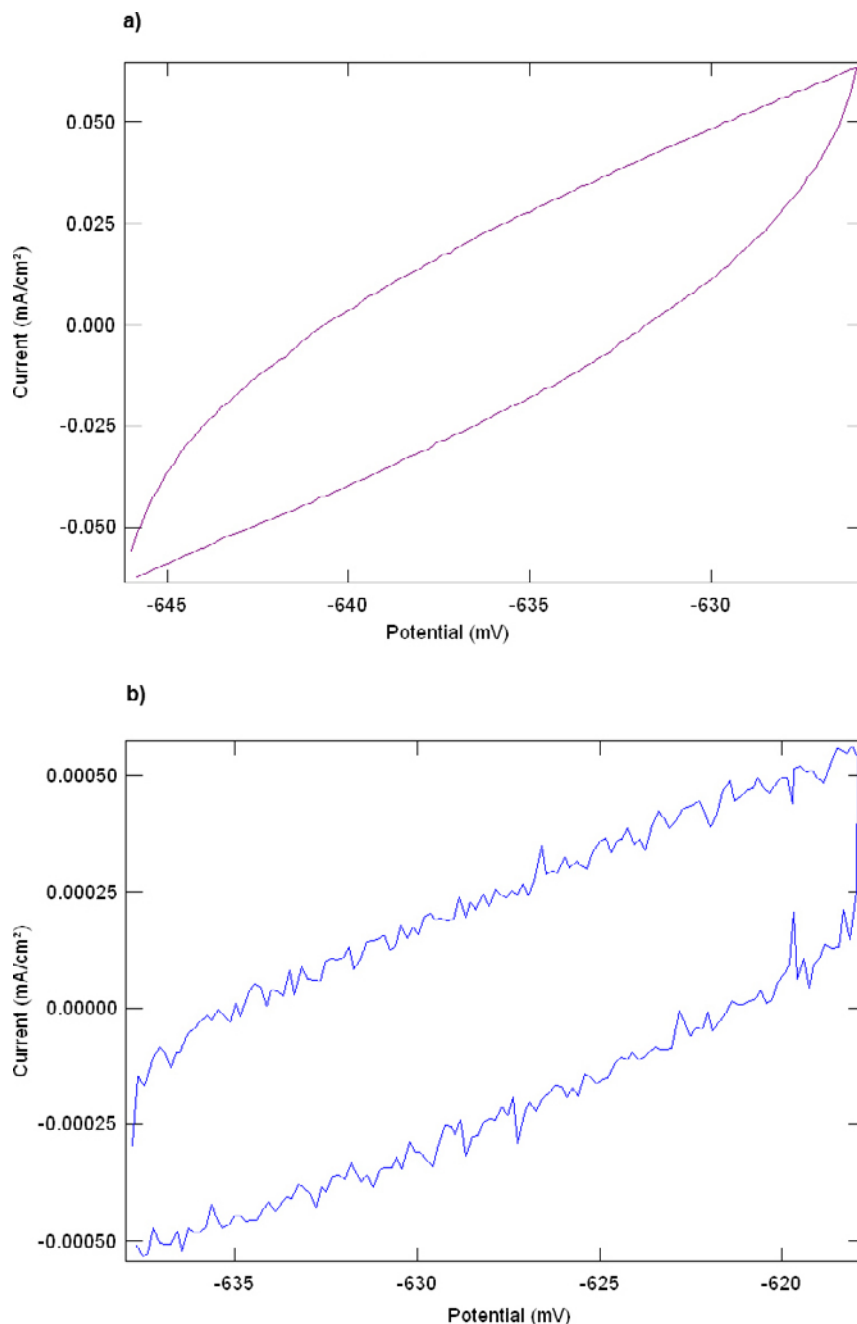


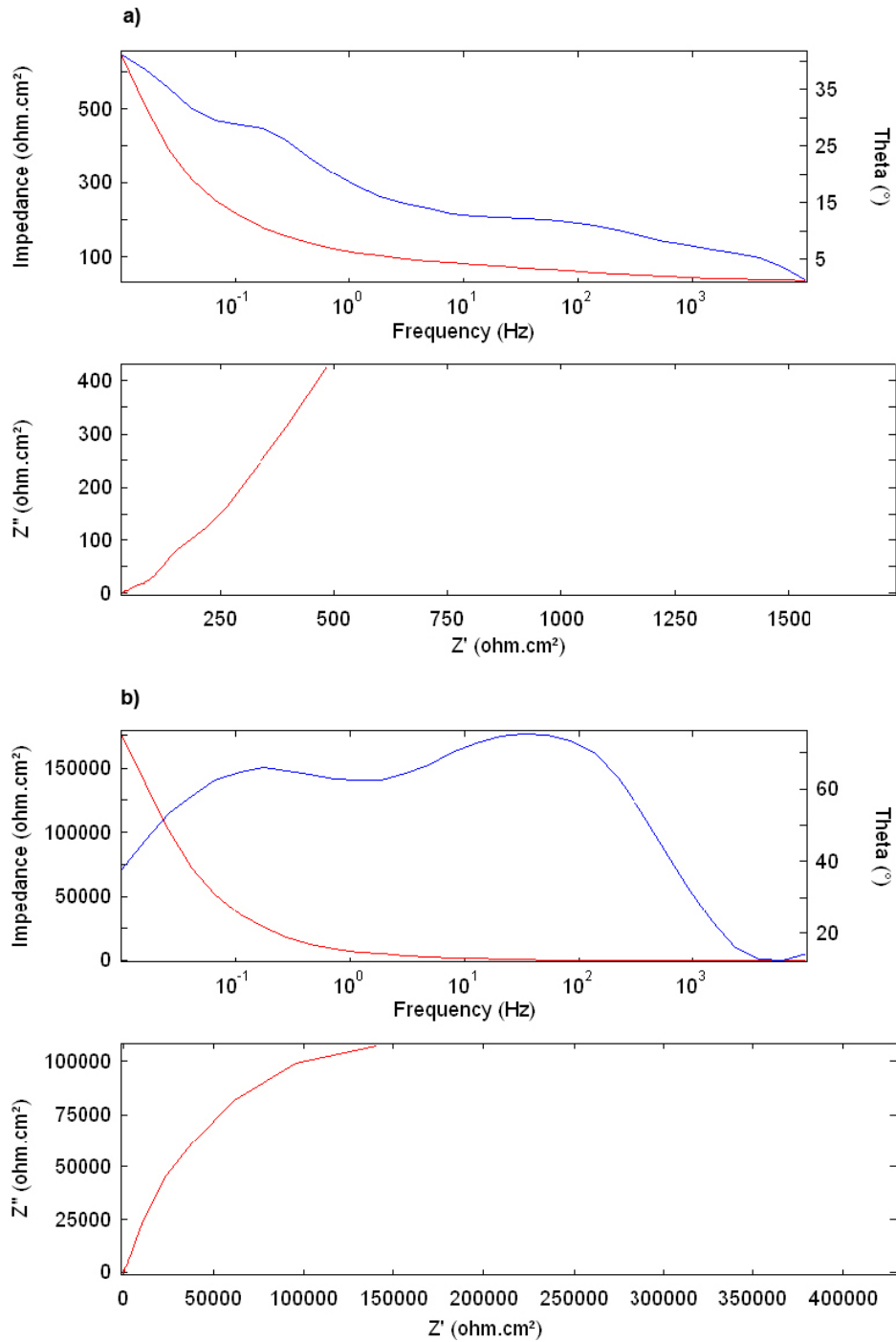
Figure 4-23. Results of corrosion potential and corrosion rate measurements for cast iron and copper electrodes in Experiment 5 (no bentonite).

### 4.3 Electrochemical corrosion rate measurements

Corrosion rate measurements were carried out using the following electrochemical techniques: linear polarisation resistance, LPR, AC impedance (ACI) and electrochemical noise (ECN). The LPR measurements were carried out over a potential range of  $\pm 10$  mV with respect to the corrosion potential at a scan rate of  $10 \text{ mV min}^{-1}$  (starting with the electrode polarised to  $-10$  mV). The corrosion rate is obtained by measuring the slopes of the plots and applying the Stern-Geary approximation [13], with a Stern-Geary constant of 26 mV. The AC impedance measurements were carried out using a perturbation of  $\pm 10$  mV, starting at an initial frequency of 10 kHz start and a final frequency of 10 mHz finish, with 100 readings taken per test. The electrochemical noise measurements were carried out at a sampling rate of ten readings per second for a period of one hour. Examples of typical LPR and AC impedance measurements for copper and iron electrodes in Experiment 1 are shown in Figure 4-24 and 4-25. All the raw data obtained during 2011 are given in Appendix 1 and the raw data acquired during previous reporting periods are presented in reference [6]. The plots in these



**Figure 4-24.** Typical examples of linear polarisation resistance (LPR) measurements on Experiment 1: (a) cast iron, (b) copper.



**Figure 4-25.** Typical examples of AC impedance measurements (ACI) on Experiment 1: (a) cast iron, (b) copper. Top figure: blue line = theta plot; red line = impedance plot.

two appendices show how the LPR data and the AC impedance data in Nyquist and Bode format have evolved with exposure time. An increasing slope in the LPR plots corresponds to an increasing corrosion rate. Similarly a decrease in the diameter of the AC impedance Nyquist plots corresponds to an increase in corrosion rate. It is possible to see some fine structure in the Nyquist plots at the high frequency end of the scans, which probably represent the development of features in the surface films rather than instrumental artefacts.

Summaries of the measured corrosion rate data for copper and cast iron are presented in Figure 4-26 to Figure 4-29. The measured corrosion rates are also shown on the plots of corrosion potential against time for each of the five experiments (i.e. Figure 4-14, 4-16, 4-18, 4-20 and 4-22). Generally speaking, good agreement was obtained between the corrosion rates derived from the two techniques, although it should be noted that they essentially measure the same parameter (i.e. charge transfer resistance) so that agreement does not necessarily mean that the corrosion rates are accurate. There is a peculiarity about the corrosion rate data for cast iron from Experiment 4 because it appears that the electrode is currently in contact with the stainless steel flange. Figure 4-29 shows that up to June 2006 the corrosion rate was less than  $100 \mu\text{m yr}^{-1}$  but thereafter there was a sudden change in behaviour. This seems unlikely to be a genuine change in corrosion rate and the most likely explanation is that swelling of the bentonite clay caused damage to the electrical connections and forced the electrodes up into contact with the stainless steel flange. This would have had the effect of producing a much larger electrode surface area and hence the measured currents would have increased sharply.

The corrosion rate values obtained for copper in Experiments 1, 2, 3 and 5 are summarised in Figure 4-26 and the values from electrochemical measurements on cast iron in Experiments 1, 2, 3 and 5 are shown in Figure 4-28. The corrosion rate data for copper in Experiment 4 are plotted separately for copper in Figure 4-27 because it yielded considerably higher corrosion rate values. The corrosion rates measured for copper in Experiment 4 (Figure 4-27) are impossibly high because if such corrosion rates had actually occurred there would not be any electrode material left to measure (the original dimensions of the copper electrodes were  $5 \times 10 \times 20 \text{mm}$ ). This suggests that, at least for Experiment 4, the corrosion rates after November 2007 were not being measured accurately and that there must be some kind of experimental artefact affecting them. It is possible that there has been some disruption of the electrodes and the connections due to the swelling pressure exerted by the compacted bentonite. Prior to the step change in the corrosion rate at the end of 2007 the measured corrosion rate of the copper in compacted bentonite was of the order of  $1 \mu\text{m yr}^{-1}$  (Figure 4-27). Data obtained after this date are not credible. There is also an unresolved question about whether the high pressure exerted by the swelling bentonite in Experiment 4 could affect the electrochemical response of any corrosion product films.

The data in Figure 4-26 show that initially the measured corrosion rate of copper in Experiments 1 to 3, with low density bentonite was  $<10 \mu\text{m yr}^{-1}$ , but after an incubation period, which varied in duration between the experiments, the electrochemically measured corrosion rate increased by several orders of magnitude. The measured corrosion rate of copper in Experiment 5, where no bentonite was present, has remained at  $<6 \mu\text{m yr}^{-1}$  based on LPR measurements and  $<3 \mu\text{m yr}^{-1}$ , based on AC impedance measurements for the duration of the experiment. This indicates that the presence of low density bentonite has either (i) increased the corrosion rate of the copper, or (ii) changed the surface of the copper electrode so that the electrochemical properties indicated an increased, but inaccurate, corrosion rate. One possible explanation is that the microbial activity is enhanced in the presence of low density bentonite, leading to a greater production of sulphide by SRB activity, which is known to increase the corrosion rate of copper [18]. Analysis of Experiment 3 [7] has shown that all the surfaces inside the support cage were covered in a black layer of iron sulphide and, since this material is conductive, this could have increased the measured current and produced a misleadingly high value of corrosion rate. This is supported by the fact that the corrosion rate measured using the weight loss technique gave a much lower corrosion rate for the copper in Experiment 3 ( $0.15 \mu\text{m yr}^{-1}$ ). It is interesting to note that the lowest corrosion rates for both iron and copper, corresponded to the time when water samples were being extracted most frequently (e.g. see Figure 4-1 for dates of water sampling) and it is possible that the increase in corrosion rate corresponded to the time when microbial activity was least disturbed by drawing water out of the support cage. In situ studies by Hallbeck and Pedersen at a location near to the MiniCan experiment in the Äspö laboratory have shown that closure of a groundwater test loop can lead to an increase in the concentration of sulphide in the groundwater [14] due to SRB activity. It should be noted that these experiments did not contain any bentonite in the test loop, showing that the SRB activity can be sustained even in the absence of an additional source of nutrients such as the organic material in bentonite.

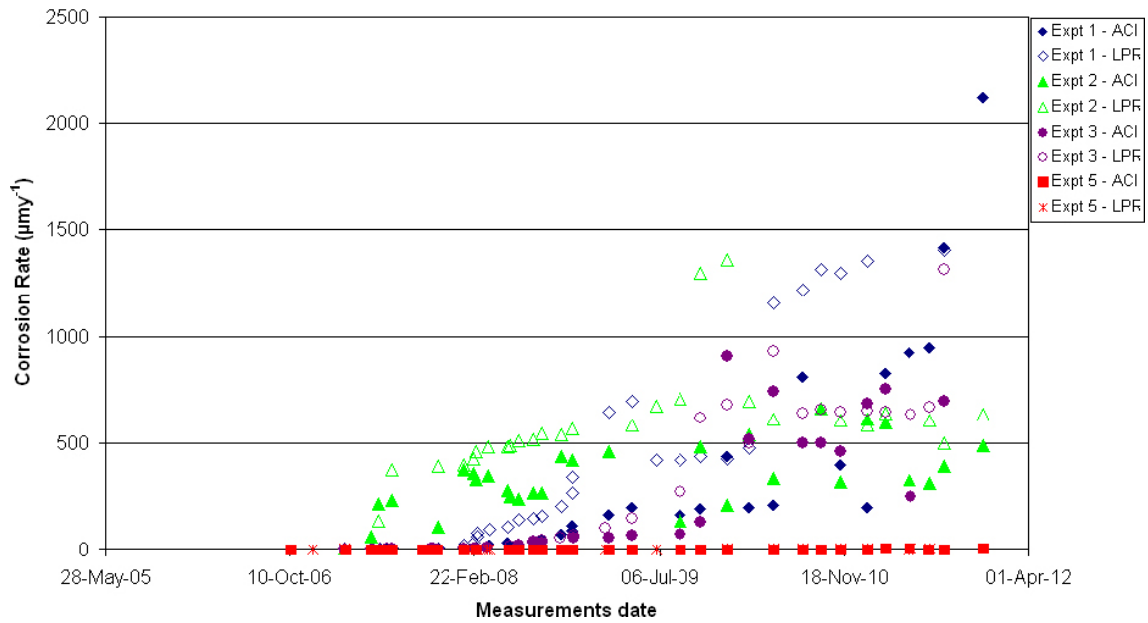


Figure 4-26. Summary of copper corrosion rates obtained by AC impedance and LPR measurements.

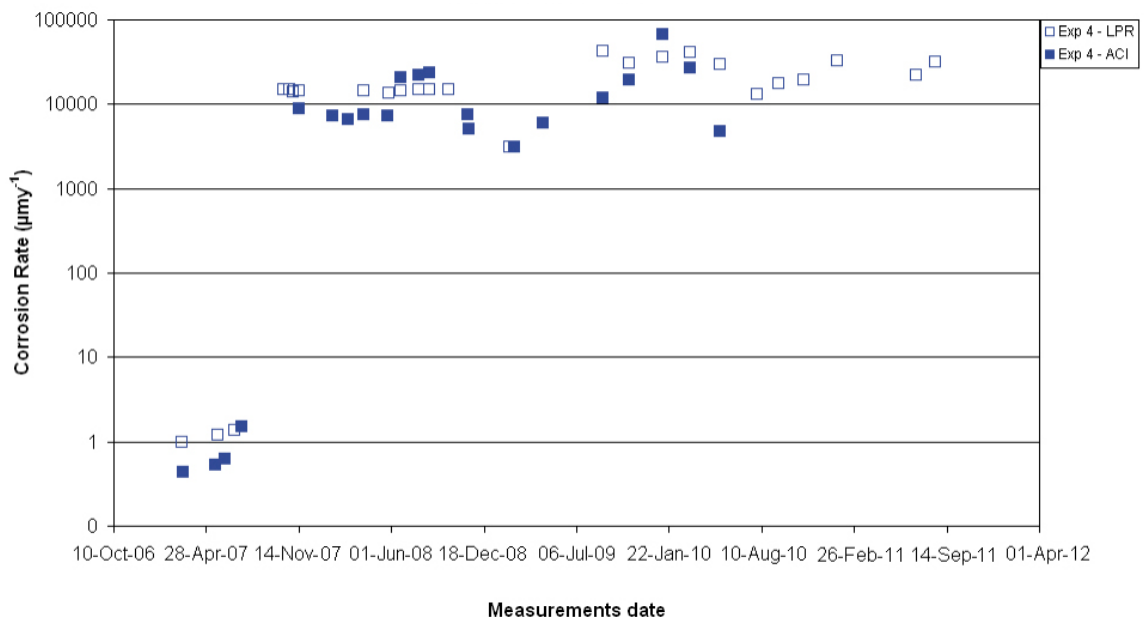
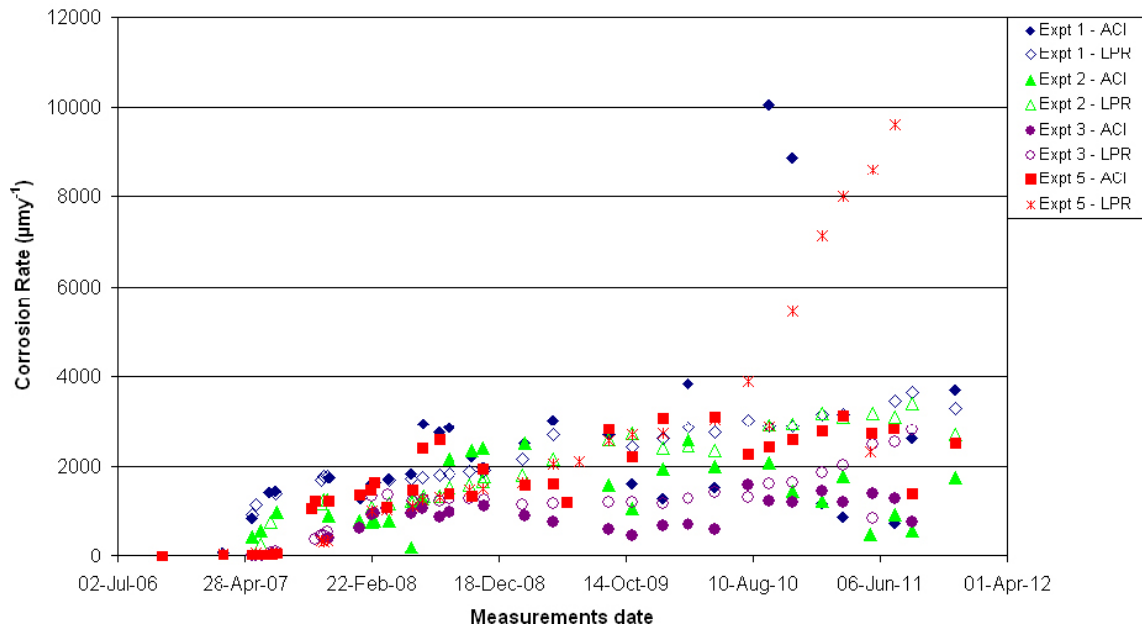
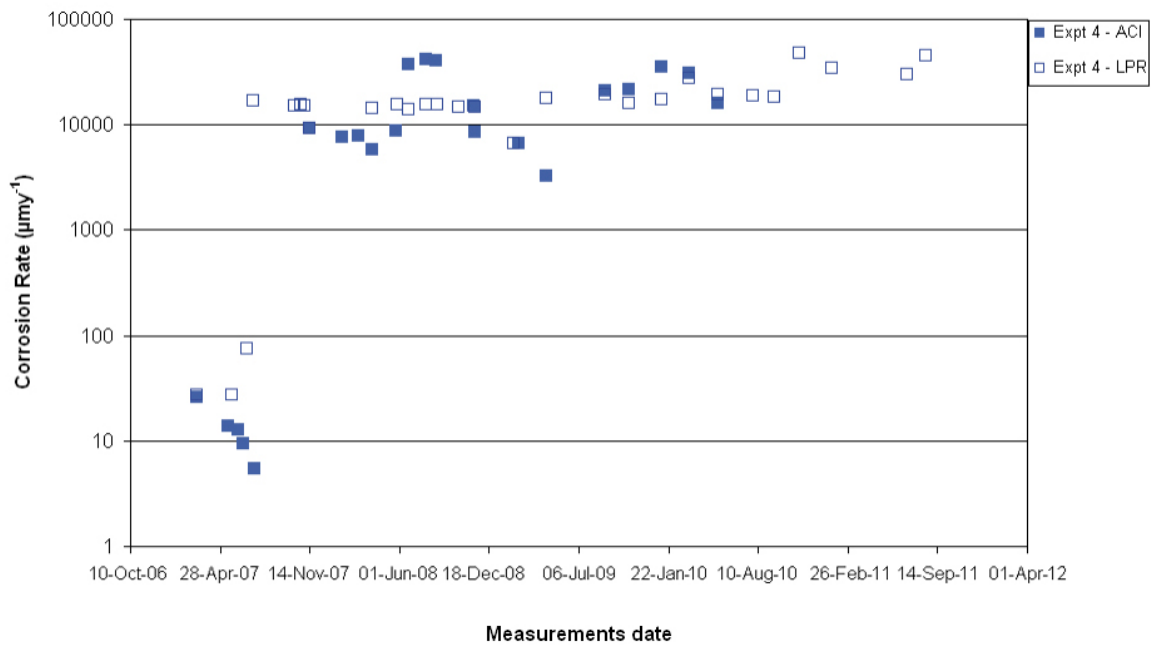


Figure 4-27. Summary of copper corrosion rates obtained by AC impedance and LPR measurements (Experiment 4). Note that these data are included for completeness, but it is unlikely that the measurements after mid 2007 are valid (i.e. the point at which there is a step change in the measured corrosion rate).





**Figure 4-28.** Summary of cast iron corrosion rates obtained by AC impedance and LPR measurements.



**Figure 4-29.** Summary of cast iron corrosion rates obtained by AC impedance and LPR measurements (Experiment 4). Note that these data are included for completeness, but the iron electrode is touching the stainless steel flange and it is unlikely that the measurements after mid 2007 are valid (i.e. the point at which there is a step change in the measured corrosion rate).

The data in Figure 4-28 indicate that the measured corrosion rate of the cast iron in Experiments 1, 2, 3 and 5 has increased but then stabilised at values of several thousand  $\mu\text{m yr}^{-1}$ . However, based on values published in the literature there is reason to believe that the corrosion rate measured using electrochemical methods may overestimate the true value because of the nature of the iron sulphide film formed in the presence of SRB activity; this is discussed further in Section 5.3. On the other hand results from analysis of Experiment 3 [7] show that the corrosion rate of cast iron, based on examination of the weight loss coupon, was indeed very high and of the order of at least  $500 \mu\text{m yr}^{-1}$ , which is approximately the value measured electrochemically for the cast iron electrodes (e.g. see October 2009 measurements in Figure 4-28).

During 2010 the possibility that changes in the reference electrode configuration might have affected the corrosion rate measurements was investigated. Normally, in an electrochemical cell, the reference electrode would be placed near to the working electrode to minimise any potential drop effects (known as IR drop effects) caused by the resistance of the solution to the current passing through it during the electrochemical measurement. However, because of the failure of the internal; Ag-AgCl electrodes it was necessary to use an external Silvion reference electrode which was further from the working electrode and so the IR drop would have been greater. The groundwater has a high conductivity and so this effect is unlikely to be large, but in order to be able to eliminate the possibility a series of experiments was carried out in which the gold electrode was used as a pseudo-reference electrode. The gold electrode was close to the working electrode and so this would have reduced any IR drop effects. The results from this set of measurements are given in Table 4-6. The results indicate that the measured corrosion rates were not significantly affected by the choice of reference electrode. This view is supported by the fact that the measured corrosion rates did not exhibit a step change when the reference electrode was changed (e.g. see Figure 4-18). Other possible reasons considered for the measured increased corrosion rates are that localised attack is occurring on the electrodes, or that crevice corrosion has occurred around the polymeric sheathing on the electrodes. These issues are considered further in a separate companion report [7] on the removal and analysis of Experiment 3.

**Table 4-6. Comparison of the LPR corrosion rate data ( $\mu\text{m yr}^{-1}$ ) obtained on the copper and cast iron coupons using different reference electrodes: Reference electrode A (external Silvion electrode) and Reference electrode B (gold as pseudo-reference electrode inside compacted bentonite).**

Experiment	Cast Iron	Copper	Cast Iron	Copper
	Reference Electrode A		Reference Electrode B	
1 (low density bentonite)	1,519	211	2,800	407
2 (low density bentonite)	2,000	337	2,960	586
3 (low density bentonite)	604	741	1,500	1,009
4 (compacted bentonite)	16,000	4,742	8,900	7,005
5 (no bentonite)	3,097	1.5	2,400	1.3

Note: the iron electrode in Experiment 4 is shorted to the outer flange.

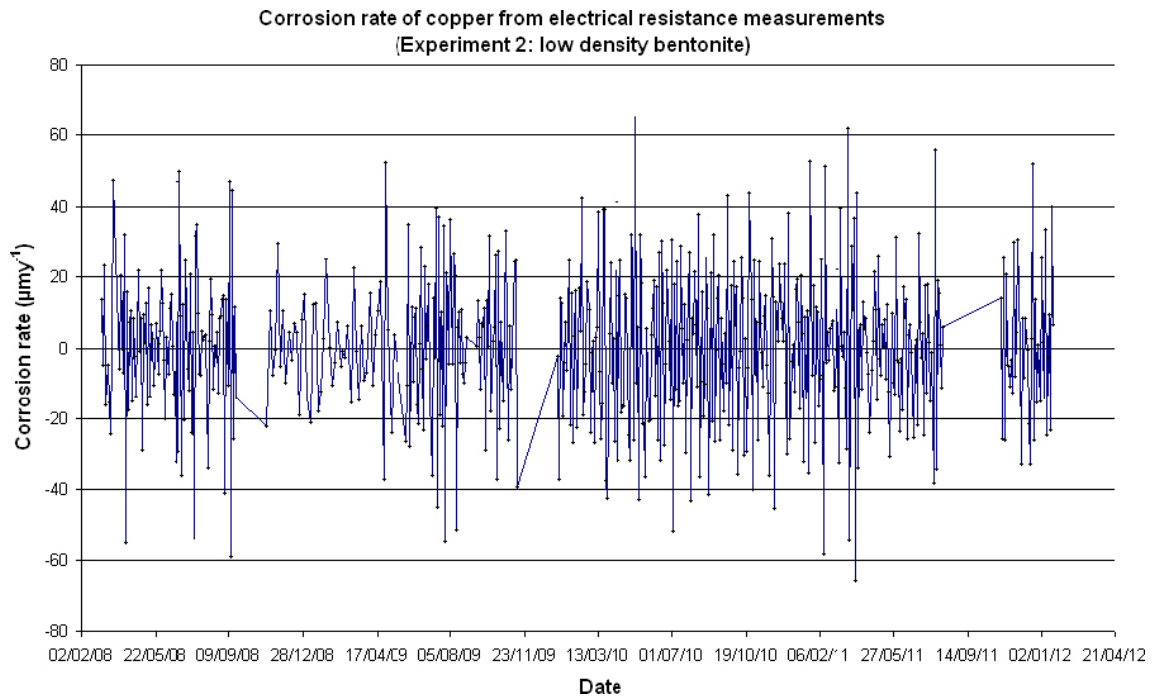
## 4.4 Copper wire resistance measurements

The results from the electrical resistance measurements on coils of copper wire are shown in Figure 4-30 (Experiment 2) and Figure 4-31 (Experiment 5). The resolution of these measurements is expected to increase with increasing measurement duration. It appears that the long-term corrosion rate for copper is close to zero in these measurements, but the signal is rather noisy. The manufacturers of the measuring equipment (ACM instruments) advised that an average value for the corrosion rate from the electrical resistance data should be taken. It is also possible to smooth the data, as shown in Figure 4-32. The averaged values based on the electrical resistance data for copper are  $0.25 \mu\text{m yr}^{-1}$  for Experiment 2 (low density bentonite) and  $0.39 \mu\text{m yr}^{-1}$  for Experiment 5 (no bentonite). These values did not change during 2011.

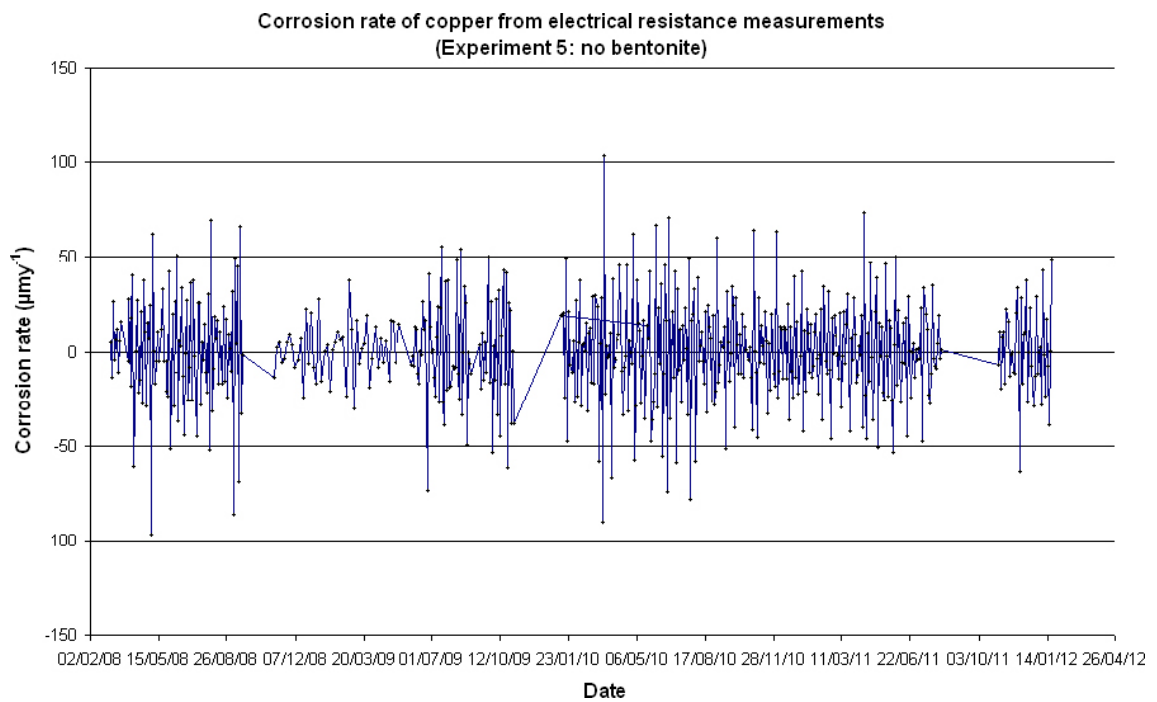
## 4.5 Strain gauge data

The strain gauge results for Experiments 1 and 4 are shown in Figure 4-33. Element 4a failed after  $\sim 1,000$  hours and element 4b failed after  $\sim 6,000$  hours. Gauges 1a and 1b showed an initial increase in tensile strain and the explanation for this behaviour is not clear. It seems to be too early to be due to expansion caused by a corrosion process and also the gauges 1c and 1d did not show a comparable change in dimensions. This would suggest that for Experiment 1 there was a rapid, greater, non-uniform change in dimensions near the top of the canister compared to the middle of the canister, during the first few weeks after the experiment was installed. The fact that the 1a and 1c elements exhibited a larger deformation than the 1b and 1d elements indicates that there were small directional variations in the degree of deformation on Experiment 1. The most likely explanation is that there was some relaxation or 'settling' of the experiment immediately after it was installed.

It is possible that the cyclic variation in the response of the strain gauges was caused by small local temperature fluctuations, particularly as all the strain gauges show small synchronised changes which are probably due to temperature fluctuations affecting the measuring equipment, as it is unlikely that there would be any significant temperature fluctuations inside the boreholes. It is also noticeable that the peaks in the response appear to be on an annual timescale so it is possible that there is an effect of seasonal variation on the local temperatures, either the water temperature, which would affect the sensor output, and/or the air temperature which could affect the electronic instrumentation readings. A similar pattern can be seen in the water pressure measurements (Figure 4-12), which are also based on strain gauge technology. Data obtained for the variation in the air temperature in the vicinity of the MiniCan experiments (Figure 4-34) show that there is a seasonal variation in air temperature and relative humidity, which correspond with the variation in the pressure gauge and strain gauge readings. It seems most likely that this is due to the effect of temperature on the electronic control equipment (an Agilent datalogger used for both pressure and strain measurements) and the pressure sensor, rather than a genuine effect on the pressure or strain, since the electronic components were not housed in a temperature controlled environment. It is also possible that there may have been some small temperature fluctuations inside the borehole, but no data on this parameter are currently available.



**Figure 4-30.** Results of corrosion measurement from copper wire electrical resistance measurement (Experiment 2: low density bentonite).



**Figure 4-31.** Results of corrosion measurement from copper wire electrical resistance measurement (Experiment 5: no bentonite).

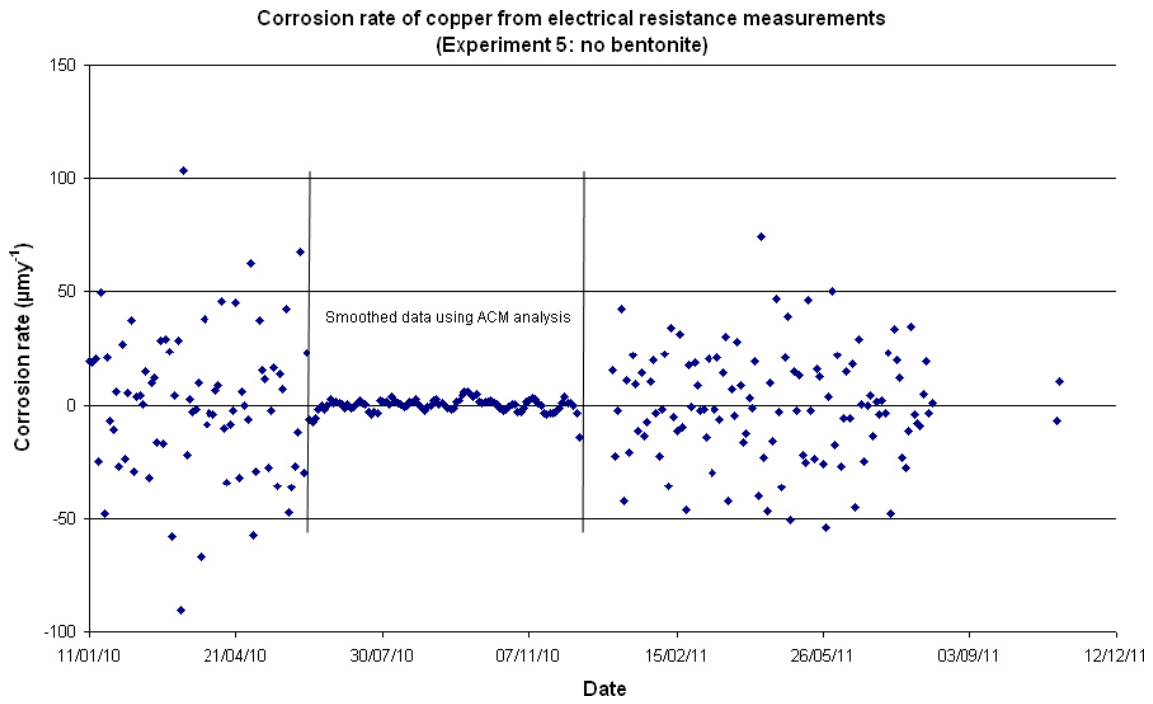


Figure 4-32. Example of smoothed corrosion rate data obtained from copper wire electrical resistance measurement.

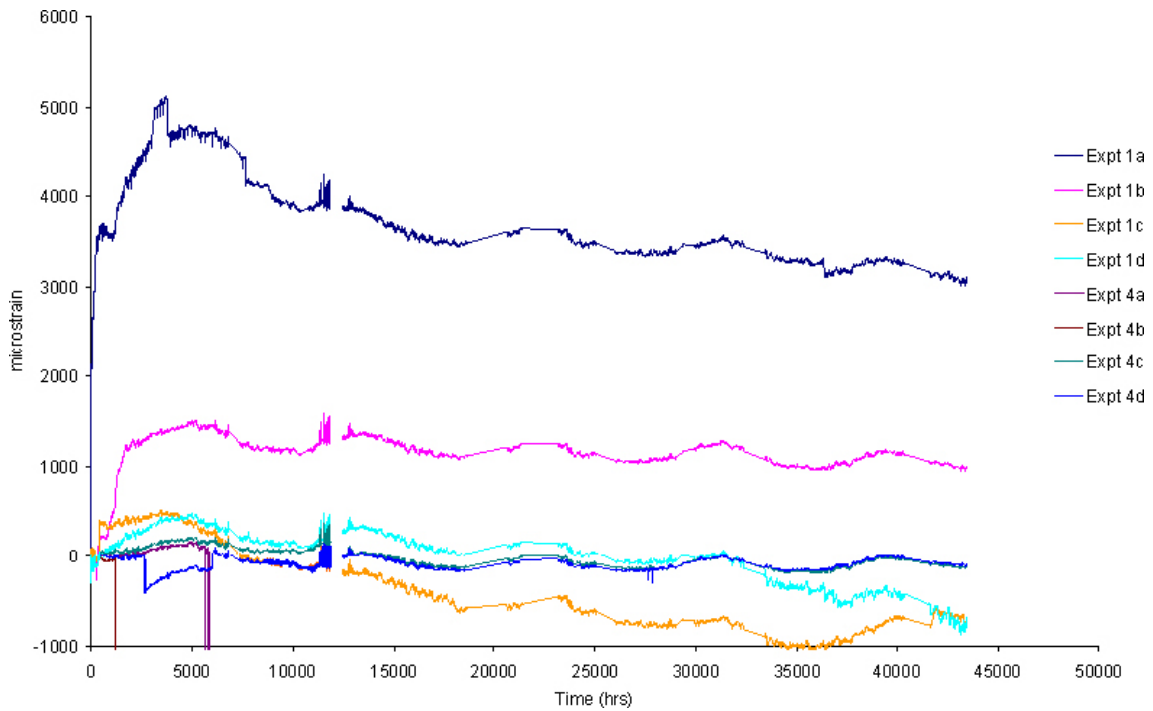
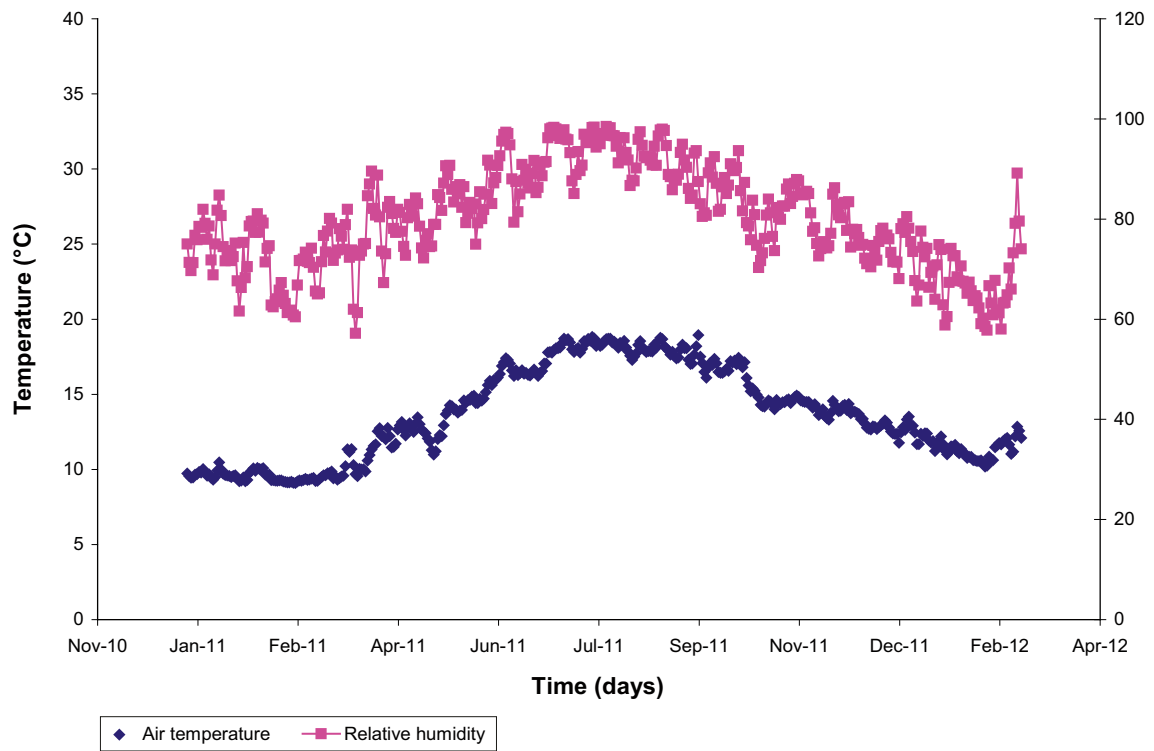


Figure 4-33. Strain gauge results from Experiments 1 and 4.

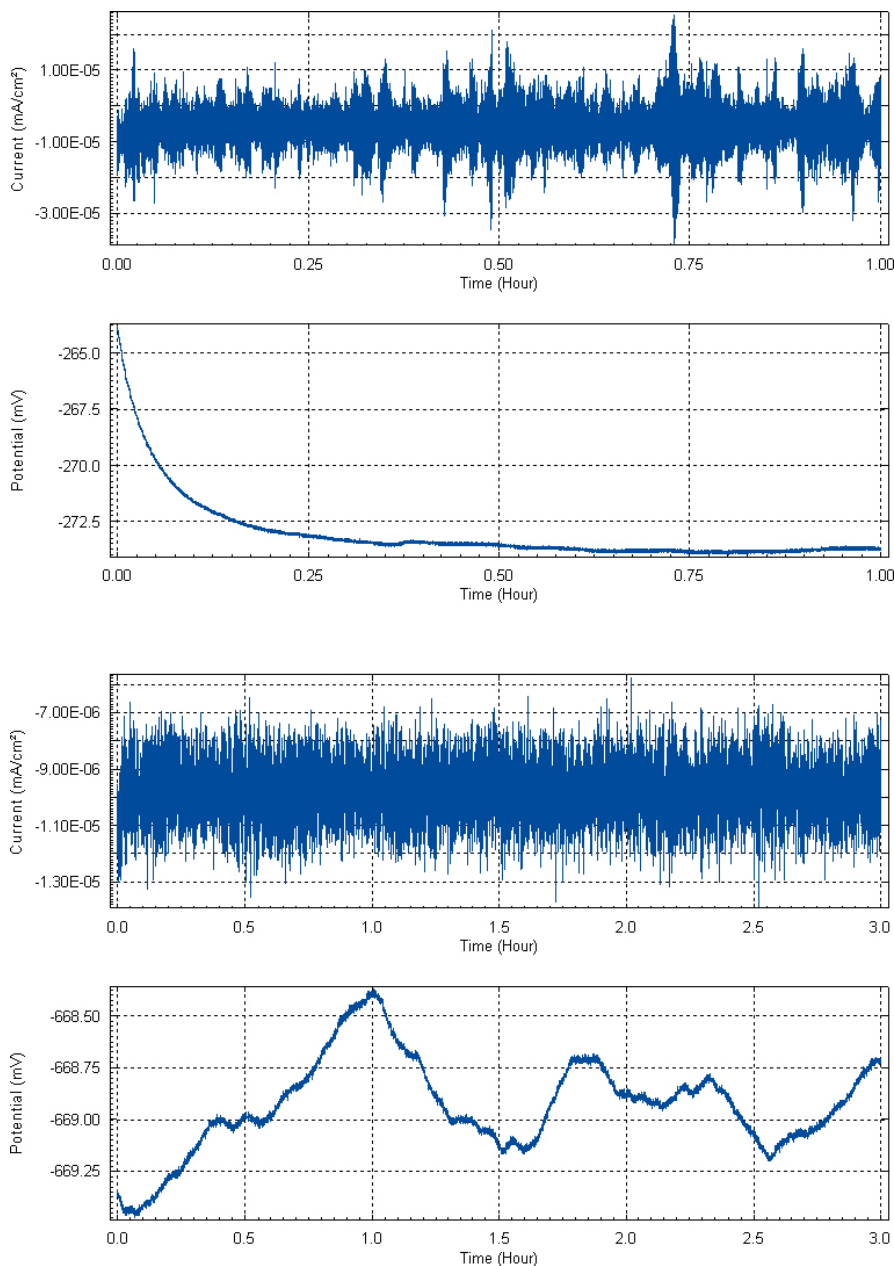
**Ambient temperature at -450 metres  
Outside lift room (25 metres from experiments)**



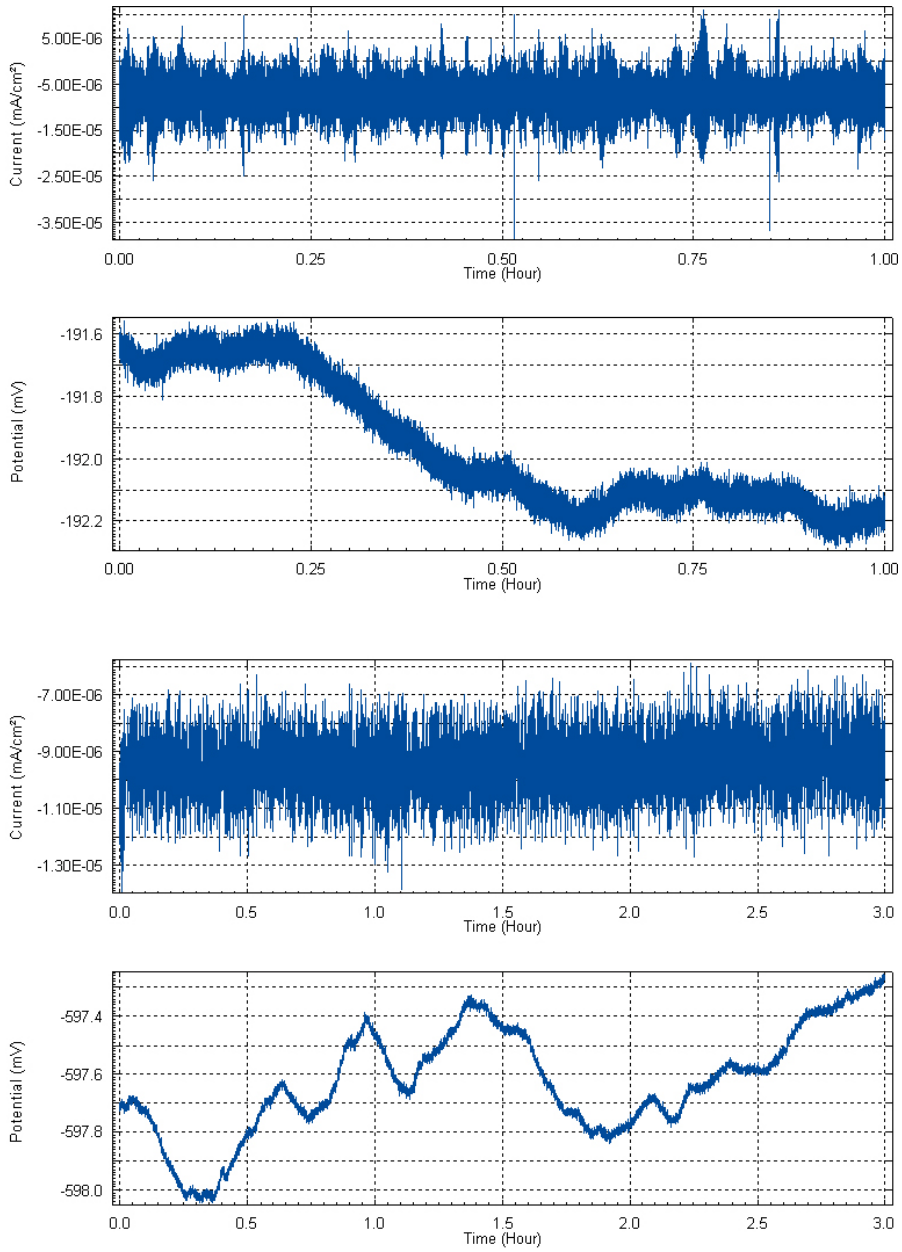
**Figure 4-34.** Variation in air temperature and relative humidity at a location 25m from the MiniCan experiments in the Äspö URL.

## 4.6 Evolution of electrochemical noise data

Electrochemical noise is a technique used to look for indications of localised corrosion; an example of the data acquired to date is shown in Figure 4-35 and 4-36. These data were obtained by coupling two copper electrodes together and measuring the current and potential noise between them. If localised corrosion were occurring transients would be expected in the results. To date, there are no indications of localised corrosion occurring on the MiniCan corrosion coupons (e.g. sharp transients lasting 10s of seconds), for either cast iron or copper. It is also possible to calculate the corrosion rate of the coupled electrodes by applying the software provided by ACM instruments Ltd. This software calculates the charge transfer resistance by dividing the root mean square of the potential noise by the root mean square of the current noise. These results were checked by exporting the raw data to a spreadsheet and carrying out further analysis. The results of the corrosion rates derived from the electrochemical noise measurements are shown graphically in Figure 4-37. It can be seen that the measured corrosion rate values are significantly lower than those measured by the LPR and AC impedance techniques.

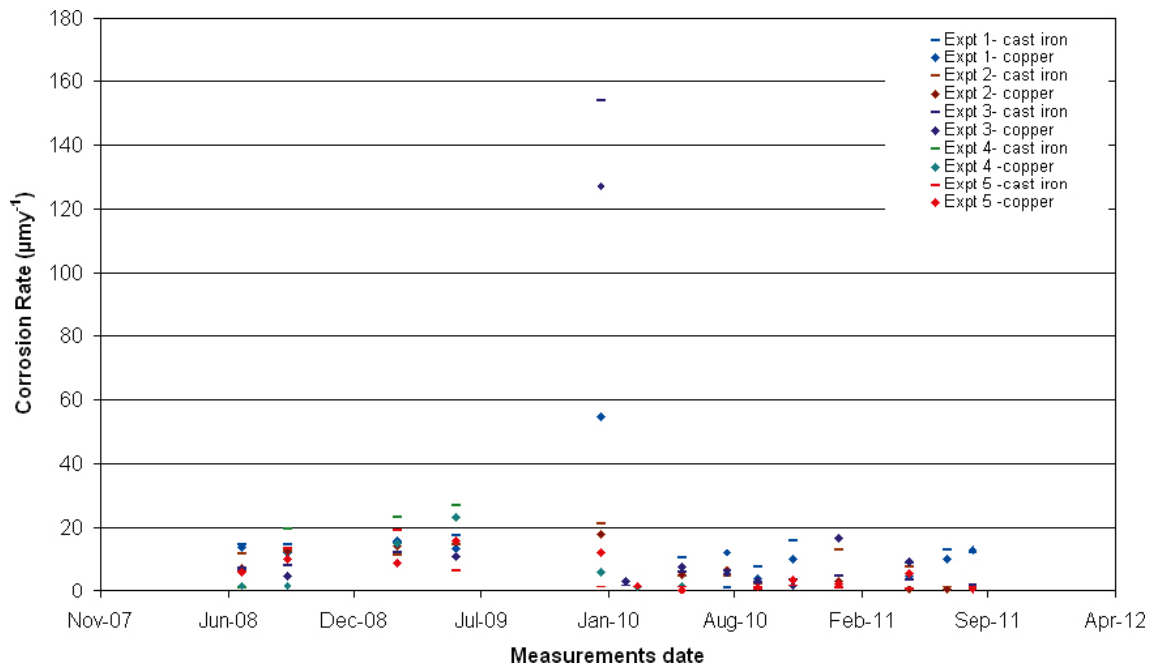


**Figure 4-35.** Results from electrochemical noise measurements for cast iron electrode in Experiment 5 (no bentonite).



**Figure 4-36.** Example of electrochemical noise data from for copper electrode in Experiment 5 (no bentonite).

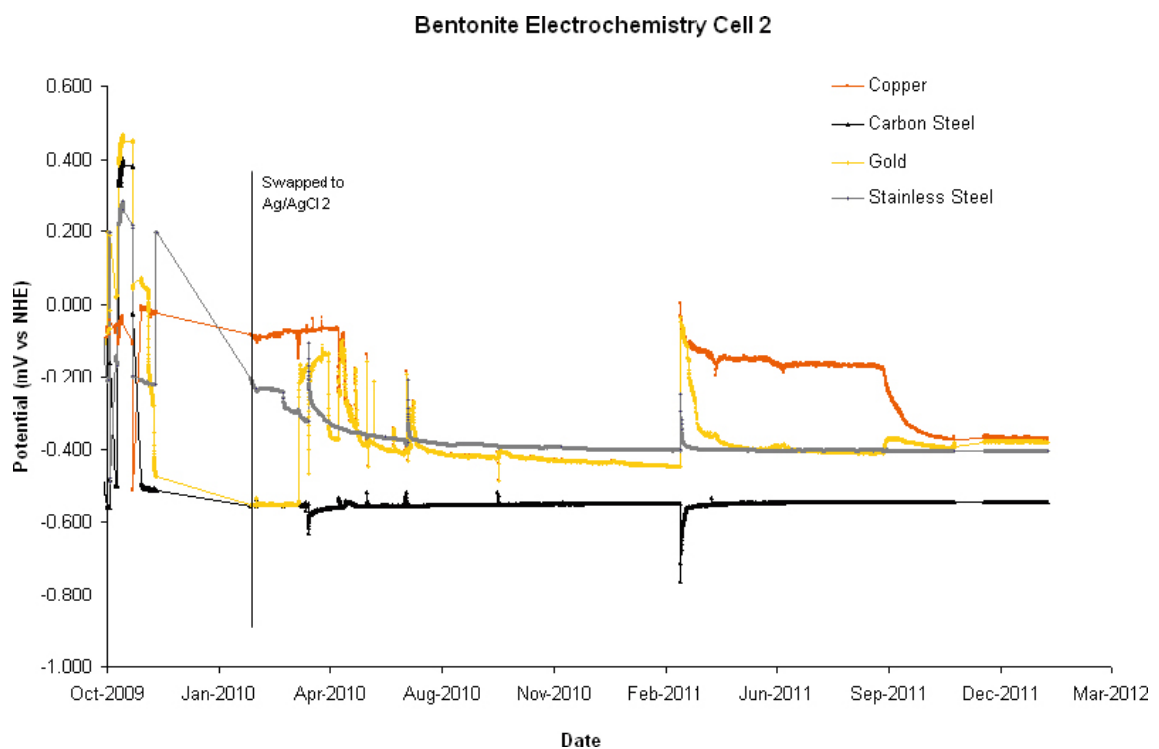




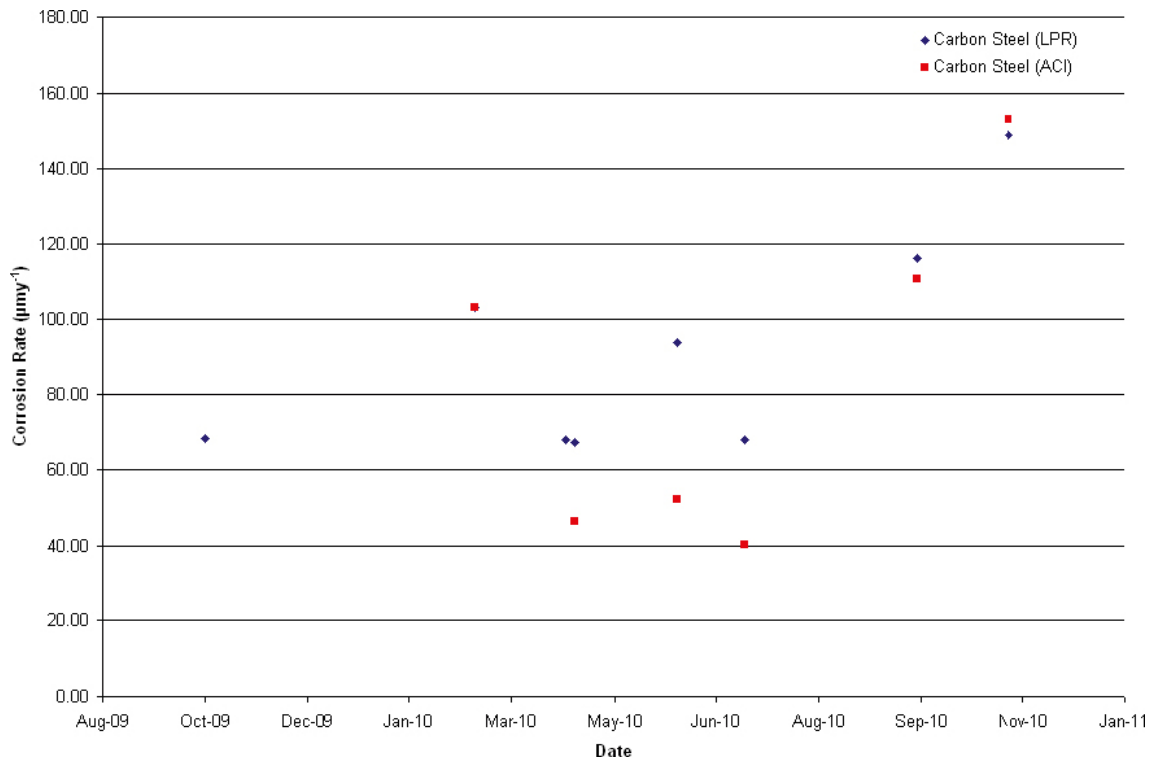
**Figure 4-37.** Corrosion rates for copper and cast iron calculated from electrochemical noise data using ACM analysis software.

## 4.7 Electrochemical cell

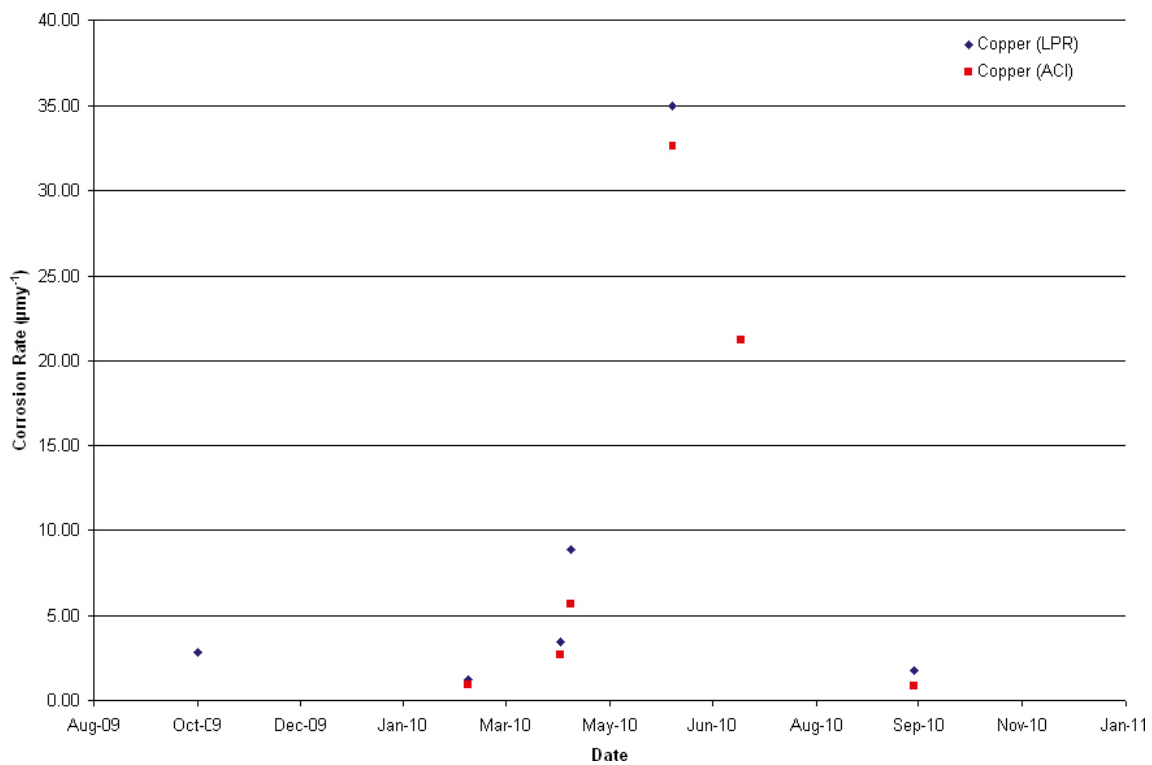
The electrochemical potential results obtained from the electrochemical cell with carbon steel, copper and gold electrodes mounted in compacted bentonite in the laboratory are shown in Figure 4-38 and the corresponding corrosion rate data for carbon steel and copper up to the end of 2010 are given in Figure 4-39 and 4-40 respectively. The initial high potentials in Figure 4-38 correspond to air ingress into the cell but when the air leaks were fixed the potentials of the copper and gold fell to values similar to those measured in the MiniCan experiments. The corrosion rate of carbon steel was measured as several tens of  $\mu\text{m yr}^{-1}$  and the corrosion rate is increasing. These values are higher than those measured by gas generation experiments but are consistent with previous electrochemical measurements in compacted bentonite [11]. The corrosion rate of copper appeared to pass through a peak before attaining a corrosion rate of  $\sim 3 \mu\text{m yr}^{-1}$ , which is a similar value measured for copper in compacted bentonite at the start of Experiment 4 (Figure 4-27). This peak in corrosion rate may correspond to the oxygen spike at the start of the experiment, but when the oxygen was consumed by corrosion of the carbon steel or copper wires the corrosion rate decreased again.



**Figure 4-38.** Summary of corrosion potential data for carbon steel and copper electrodes in compacted bentonite (Cell BE2).



**Figure 4-39.** Summary of carbon steel corrosion rates obtained by AC impedance and LPR measurements in compacted bentonite (Cell BE2).



**Figure 4-40.** Summary of copper corrosion rates obtained by AC impedance and LPR measurements for copper electrode in compacted bentonite (Cell BE2).

## 5 Discussion

### 5.1 Water analysis and microbial activity

There are a number of interesting features regarding the results of the water analysis from the model canister experiments. In general, the groundwater composition outside the support cages does not vary significantly between boreholes, although there are some small variations both between boreholes and as a function of time.

The first major observation is that there is a marked increase in the iron concentration inside the model canister support cages compared to the surrounding water in the borehole, as shown in Figure 4-10 and Table 4-1. This is accompanied by an increase in the concentration of nickel and chromium, particularly in Experiment 5, where there is no bentonite present. On the basis of the observations made when Experiment 3 was dismantled it is clear that the increase in dissolved iron concentration is predominantly due to corrosion of the cast iron coupons and the cast iron insert itself, which will be in contact with groundwater as a result of the defect in the outer copper canister. The concentration of chromium and nickel is much lower than the concentration of iron, suggesting that most of the iron results from corrosion of the cast iron, rather than stainless steel (the Fe to Cr/Ni ratio is far greater in the water analysis than in the composition of stainless steel). Figure 4-10 shows that the rate of increase in the iron concentration appears to be accelerating in Experiments 1, 2, 3 and 5. No indications of corrosion of the stainless steel components of Experiment 3 were observed when the experiment was dismantled.

Table 4-1 and Figure 4-11 show that there has been a decrease in the pH inside the support cage compared to outside the support cage. This is most likely to be a result of the microbial activity inside the support cage, as shown in Table 4-5, although the exact mechanisms for the fall in pH are not currently known. The gas analysis data (Table 4-3) show the very low oxygen content of the groundwater and the presence of helium and methane from geological sources.

The enhanced corrosion of the iron as shown by the high concentrations of dissolved metals and the results from dismantling Experiment 3 [7], would not be expected in anoxic near-neutral water at low temperature, even with the high concentrations of chloride present, based on the results of laboratory experiments in the absence of microbial activity. This result suggests that the corrosion is enhanced by microbial activity. It should be noted that the concentration of dissolved copper was very low.

The microbial analysis indicates that autotrophic acetogens and sulphate-reducing bacteria (SRB) are active in the vicinity of the model canisters. The key metabolic reactions for these species are:



The acetogens produce acetate, which can cause stress corrosion cracking of copper, and sulphur from SRB activity is detrimental to copper. In principle, hydrogen produced by the anaerobic corrosion of iron could drive the activity of the acetogens and hence there is a possibility of autocatalytic behaviour (see Appendix 1 of reference [5] for further discussion). The processes summarised above are consistent with the measured fall in pH and the increase in corrosion rate and release of iron observed during these experiments. It is noteworthy that there was a fall in the total organic content of water inside the canisters between 2008 and 2010; the reasons for this are not clear but one possibility is the consumption of organic material in the bentonite by microbial activity.

## 5.2 Electrochemical measurements

### 5.2.1 $E_h$ measurements

The potential values for the gold and platinum inside the support cages, and the  $E_h$  probe outside the support cages in the borehole, show that after sealing the boreholes the  $E_h$  fell from initial values of the order of 0 mV vs NHE, which correspond to aerated conditions in the groundwater, to values of the order of -300 mV, as any residual oxygen was consumed by reaction with rock minerals, microbial activity and/or corrosion processes. It is notable that the  $E_h$  values inside the support cages (e.g. Experiment 3 in Figure 4-17) fell more rapidly than outside the support cage, suggesting that residual oxygen was consumed more rapidly due to the increased surface area on which corrosion reactions could take place.

The long-term electrochemical potentials of the gold, platinum and the miniature canisters are indicative of very low oxygen concentrations. The electrochemical potential values obtained for the gold in the MiniCan experiments are comparable to the electrochemical potential values obtained during laboratory investigations of galvanic corrosion of iron-copper couples in anoxic conditions [10,15], and the anaerobic corrosion of iron [16,17]. They are also comparable to  $E_h$  values reported in the literature for deep Swedish groundwaters [18,19]. The data show that for Experiments 1 to 3, with low density bentonite, the long-term  $E_h$  outside the cage is slightly higher than inside the cage, whereas for Experiment 4, with compacted bentonite the situation is reversed.

It should be noted that the increase in corrosion rate for both copper and iron (for example see Figure 4-15 and 4-16 for Experiment 3), began when the  $E_h$  had reached its minimum value. Since SRB are organisms that only proliferate under anoxic conditions it is possible that the increase in corrosion rate corresponded to the time when SRB became active and started to generate sulphide, which then caused an increase in the corrosion rate of both the copper and the iron electrodes.

### 5.2.2 Corrosion potential of copper and iron

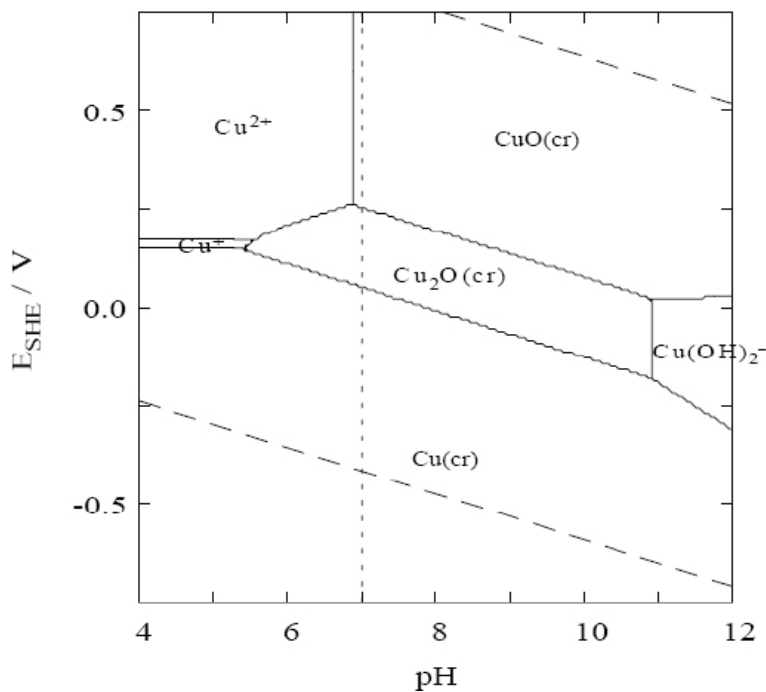
The corrosion potential of the copper and the model canisters can be compared with other measurements and modelling activities [18]; for example the predicted long-term corrosion potential of a copper canister in aerated compacted bentonite reported previously [18]. The modelling calculations showed that the predicted short-term corrosion potential for a copper canister is of the order of -300 mV vs saturated calomel electrode, SCE (i.e.  $\sim$ -50 mV vs NHE). This is more positive by approximately 100 mV than the value measured in Experiment 4 for the model canister embedded in compact bentonite under anoxic conditions (Figure 4-19). However, it should be noted that the corrosion potential of copper is a strong function of chloride concentration, oxygen concentration and mass-transport conditions [18] and direct comparisons with the results from the MiniCan experiment are not therefore possible because the environmental conditions considered in the modelling were not necessarily the same as those in the MiniCan experiment. The rest potential of the canister became more negative towards the end of 2009. The potential of the copper electrode in the same experiment was similar to that of the copper canister (Figure 4-20).

The long-term corrosion potentials of the copper electrodes in Experiments 1-3 (low density bentonite) generally fell in the range -400 to -500 mV vs NHE. The corrosion potential for copper in Experiment 4 (compact bentonite) was  $\sim$ -300 mV vs NHE and the potential for Experiment 5 (no bentonite) was approximately -500 mV vs NHE. The corrosion potentials of the model canisters themselves in Experiments 1-5 were generally approximately 100 mV more positive than the potentials of the copper electrodes, but it should be noted that the potential of the copper canisters represents a mixed potential of the copper-cast iron couple, assuming that wetting of the cast iron insert had occurred by water penetration through the 1 mm defect in the copper shell. These corrosion potential values can be compared to published Pourbaix diagrams [20] for copper in pure water (Figure 5-1), in the presence of carbonate and high concentrations of chloride (Figure 5-2) and in the presence of sulphide (Figure 5-3). In pure water, copper is thermodynamically immune to corrosion at the temperature of the MiniCan experiment and the measured corrosion potentials (Figure 5-1). In high

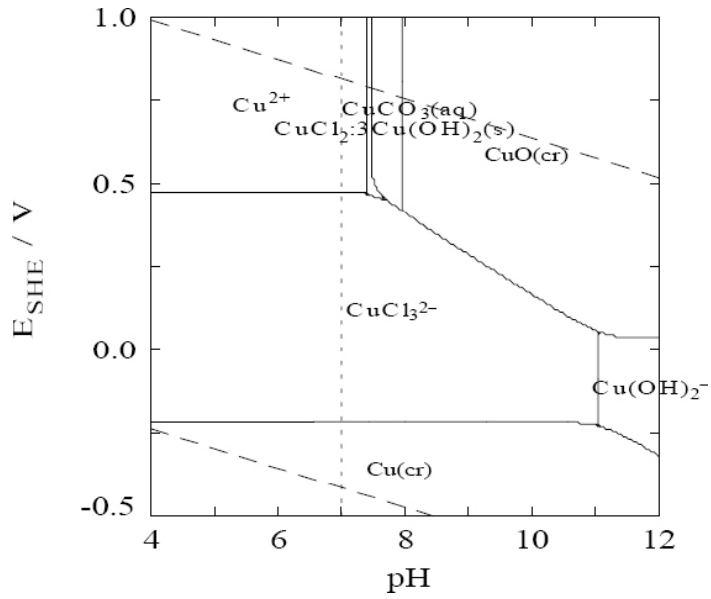
concentrations of chloride, the measured corrosion potentials for the MiniCan experiments also show that copper is immune to corrosion by the formation of copper chlorides (Figure 5-2). However, in the presence of sulphide, Figure 5-3 indicates that for Experiments 1–4 the potential of the copper is in the domain of stability of copper sulphide. Experiment 5 exhibited a more negative copper corrosion potential which was nearer the region of thermodynamic stability of copper and this may account for the lower corrosion rate measured in this experiment.

Pourbaix diagrams in Figure 5-1 to 5-3 should only be used as a guide for interpreting the MiniCan experiments, because they were calculated for a specific set of conditions (i.e. concentrations of dissolved species such as chloride, sulphur, carbonate and copper at 25°C) that were not exactly the same as those in the MiniCan experiment, which was at an ambient temperature of 15°C. The calculations of thermodynamic stability for copper could be extended to take account of the measured chemical conditions for inside the support cages of the MiniCan experiments.

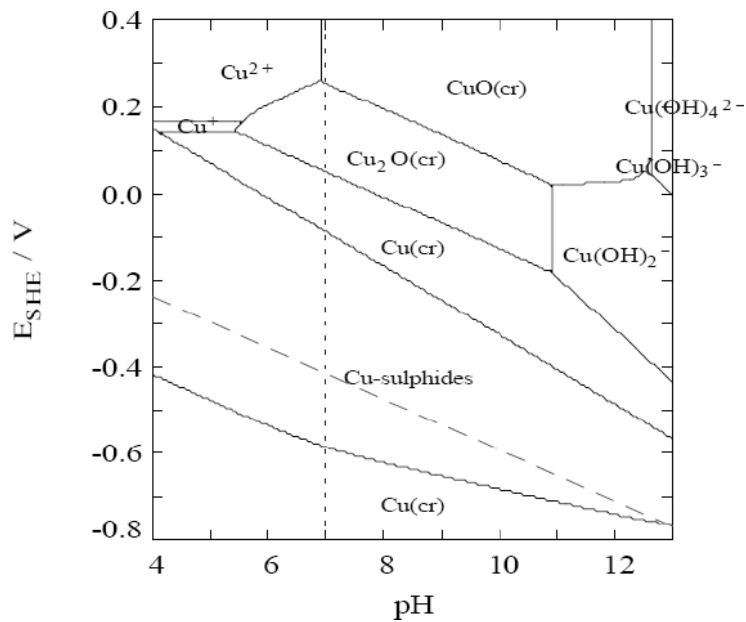
The potentials of the iron electrodes are below the hydrogen evolution potential at pH 7 and are consistent with the occurrence of anaerobic corrosion, with the resulting formation of hydrogen. The measured corrosion potentials for the cast iron electrodes are also consistent with the domain of stability of iron sulphide (Figure 5-4) [21,22].



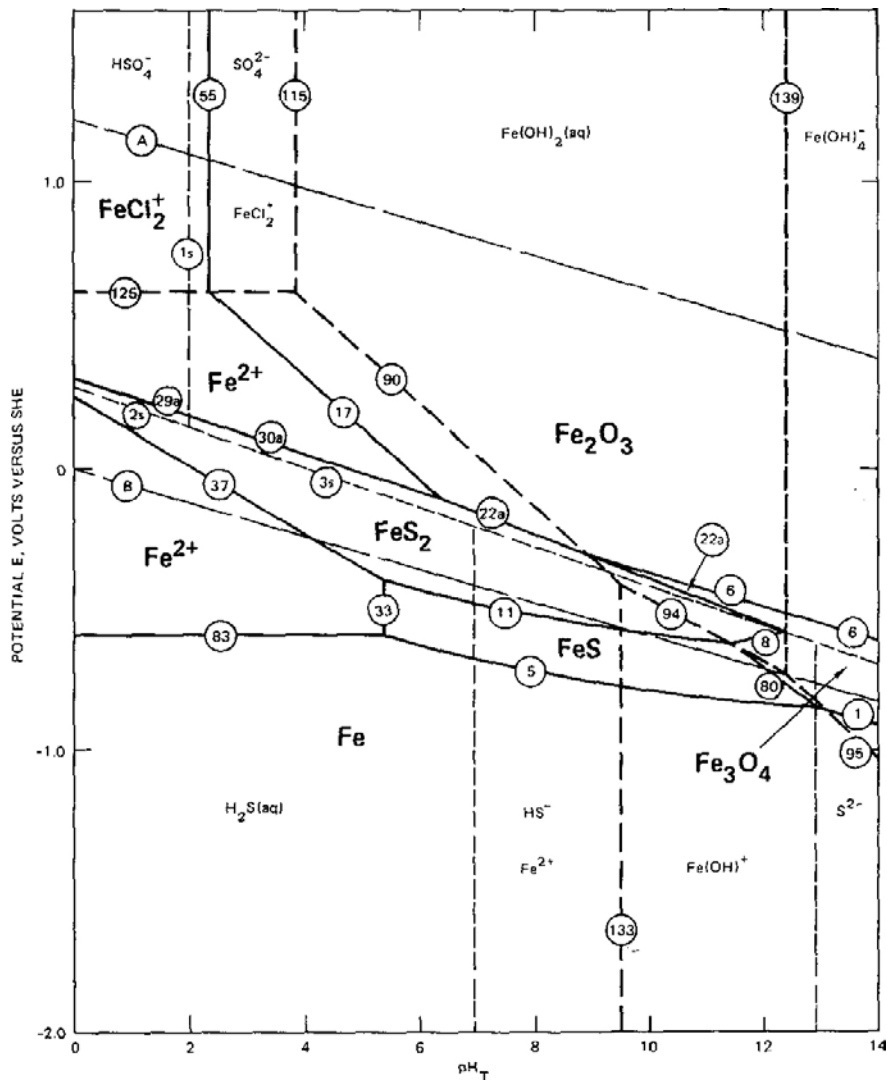
**Figure 5-1.** Pourbaix diagram for copper in pure water [ $Cu_{TOT} = 10^{-6}$  mol/kg at 25°C [20].



**Figure 5-2.** Pourbaix diagram for copper at  $[Cu]_{TOT} = 10^{-6}$  mol/kg at 25°C in solution containing  $[CO_3^{2-}]_{TOT} = 2$  mmol/kg and  $[Cl]_{TOT} = 1.7$  mol/kg [20].



**Figure 5-3.** Pourbaix diagram for copper in solutions containing  $[HS^-]_{TOT} = 0.2$  mmol/kg and  $[Cu]_{TOT} = 10^{-6}$  mol/kg at 25°C [20].



**Figure 5-4.** Potential-pH diagram for iron in high salinity brine at 25°C in the presence of 10 ppm total dissolved sulphide ( $H_2S + HS^- + S^{2-}$ ). Activities of  $HSO_4^-$  and  $SO_4^{2-} = 10^{-6}$  molal. Activities of dissolved iron species =  $10^{-4}$  molal [21].



## 5.3 Corrosion rate measurements

### 5.3.1 Iron corrosion rates

The corrosion rates for iron are high but in Experiments 1, 2, 3 and 5 they appear to have stabilised (Figure 4-28). They are considerably higher than would be expected from laboratory experiments on the anaerobic corrosion of iron [23,24]. They have to be treated with some caution as electrochemical measurements tend to overestimate the true values, since they only provide an instantaneous measure of corrosion rate, which is based on a number of assumptions about the nature of the electrochemical interface. The overall corrosion rate from the cast iron weight loss specimen from Experiment 3 (i.e. the long-term integrated measurement of corrosion rate) was at least  $500 \mu\text{m yr}^{-1}$  on the basis that the weight loss sample had been completely converted to a mass of residual graphite, silicon and oxide. It is not known at what point the weight loss sample was completely consumed but based on the initial dimensions of the sample it is possible to estimate that the minimum corrosion rate was at least  $500 \mu\text{m yr}^{-1}$ . This can be compared to an electrochemically measured value for Experiment 3 of up to  $2,500 \mu\text{m yr}^{-1}$  (Figure 4-28). Examination of the electrodes from Experiment 3 showed that there had not been crevice corrosion around the sheathing on the iron electrodes. The high corrosion rates reported here support the observation of increased iron concentrations in the water analyses and it seems most likely that the high rates are a result of microbial activity inside the support cage, particularly sulphate-reducing bacteria (see Section 4.1.6 and reference [12]).

Hilbert et al. [25] investigated the use of the LPR and ACI techniques to measure corrosion rates of steel in anoxic environments containing sulphide produced by SRB activity. Their conclusion was that under these conditions the formation of porous reactive sulphide films dominates the electrochemical response, leading to misleadingly high values of corrosion rate by a factor of 10–100 times. It is therefore probable that the high corrosion rates measured for cast iron in the MiniCan experiment by LPR and ACI are an overestimate of the true corrosion rate, but based on the weight loss measurements from Experiment 3 it appears that the overestimate is of the order of  $5\times$ . The cast iron corrosion rate for Experiment 4 (Figure 4-29) is not clear because of the probable difficulties with the connections and electrodes damaged by the swelling of the compacted bentonite. The corrosion rates derived from the electrochemical noise experiments are considerably lower than the measurements from the LPR and ACI measurements, by a factor of  $\times 100$  for the cast iron and  $\times 10$  for the copper.

### 5.3.2 Copper corrosion rates

The electrochemical measurements of the initial corrosion rate gave values for copper below  $5 \mu\text{m yr}^{-1}$  [3]. This is based on a Stern-Geary constant of 26 mV, whereas other authors (e.g. [26]) have used lower values. Thus the figures reported here are conservative values (i.e. they may exaggerate the corrosion rate). The derived corrosion rate values can be compared with values given in the literature for experiments on copper in compacted bentonite; for example values of up to  $2.5 \mu\text{m yr}^{-1}$  have been reported by Rosborg et al. [26] for measurements during the LOT experiment and  $4.7 \mu\text{m yr}^{-1}$  by Saario et al. [27] for weight loss measurements on copper in compacted bentonite in laboratory tests.

However more recent measurements (e.g. Figure 4-26) suggest that higher corrosion rates of copper may be occurring. The electrochemically measured corrosion rate for copper in Experiment 2 is much higher than that measured using the copper coil electrical resistance method (see Figure 4-26 and 4-30), which suggests that there were some experimental difficulties associated with the electrochemical corrosion rate measurements. When Experiment 3 was opened it was found that the majority of the surfaces inside the support cage were covered in a layer of black deposit, which was found by analysis to be predominantly iron sulphide. This layer is likely to have caused the high corrosion rates measured on the copper electrodes. A weight loss measurement on the copper weight loss specimen from Experiment 3 gave a corrosion rate of  $0.15 \mu\text{m yr}^{-1}$ , so it can be concluded that the later electrochemical measurements for the copper corrosion rate were a significant overestimate (particularly the AC impedance and LPR measurements; the noise measurements gave lower values) and that the electrical resistance measurements were nearer to the true corrosion rate for the copper. It is possible that the electrical resistance measurements were affected by a thin layer of copper sulphide

on the surface of the wire; copper sulphide was observed on the surface of the copper samples taken from Experiment 3. The AC impedance plots for copper (see Appendix 1) show some structure in the results that is similar to that observed for coated surfaces (e.g. [28]). It is noticeable that the ACI plots for Experiment 5 do not show the same structure.

### 5.3.3 Application of corrosion rate results to SKB repository

It should be recognised that the environmental conditions within Experiments 1, 2, 3 and 5 are not fully representative of the conditions that will be experienced in a repository because the containers are in contact with low density bentonite (Experiments 1 to 3) or raw groundwater (Experiment 5), rather than fully compacted bentonite. In both these environments it is likely that microbial activity would be different to that expected in the fully compacted bentonite that would be used in the repository situation, since fully compacted bentonite is expected to inhibit microbial activity [29]. Experiment 4 therefore represents the closest analogy to the proposed SKB design since it uses fully compacted bentonite. Unfortunately, the corrosion rates measured electrochemically in Experiment 4 appear to be unreliable, probably because the swelling of the bentonite has led to deformation or damage to the electrical connections. The true corrosion rate in compacted bentonite will not be confirmed until Experiment 4 is dismantled.

It should also be noted that in the repository situation the temperatures would be higher than in the MiniCan experiments. This could have the effect of increasing the corrosion rate, if it is due to abiotic corrosion processes, or it may affect the viability of microbial populations and hence reduce the rate of any microbially influenced corrosion processes. Conversely, the rate of corrosion may be controlled by the supply of sulphide external to the compacted bentonite so that the corrosion rate will be controlled by the rate of transport of sulphide through the bentonite layer, as discussed by King et al. [18] and the rate of production of sulphide by sulphate-reducing bacteria in the vicinity of the external surfaces of the bentonite buffer. Recent work [30] by Masurat et al. suggests that the rate of production of sulphide by microbial activity within compacted bentonite is very limited and that the amount of sulphide that can be produced by microbial activity is insufficient to sustain significant degrees of corrosion of the copper canister. This work also showed that the rate of growth of SRB is two orders of magnitude higher in lower density bentonite ( $1.5 \text{ g cm}^{-3}$ ) compared to that in compacted bentonite with a density of  $2 \text{ g cm}^{-3}$ . For comparison, the density of the bentonite used in Experiments 1 to 3 of the MiniCan project was 1.16 to  $1.36 \text{ g cm}^{-3}$ , whereas the density of the compacted bentonite in Experiment 4 was  $\sim 2 \text{ g cm}^{-3}$ .

The results from Experiment 5 (no bentonite) indicate that the corrosion rate of copper in raw groundwater is significantly lower than in the experiments with low density bentonite present and this is probably due to the lower concentration of sulphide present in a system with less organic material present in bentonite to support microbial activity and the lower corrosion potential, which may indicate that the copper is within its thermodynamic domain of stability in this experiment. The corrosion rate of the iron in Experiment 5 is similar to the values recorded in the presence of low density bentonite and significantly higher than those values measured in laboratory experiments under anoxic conditions, in the absence of sulphur. The dissolved iron concentrations in Experiment 5 are the highest measured for any of the experiments. This suggests that even if the available sulphide concentration is lower than in Experiments 1 to 3 there is still sufficient sulphide present in Experiment 5 for iron sulphide production to occur. This could be a result of SRB activity supported by the metabolism of hydrogen produced by the anaerobic corrosion of the cast iron components of the experiment [30]. Based on the results of analysing Experiment 3 it is probable that the inside of Experiment 5 is also covered by iron sulphide, but for some reason this did not lead to an increase in the electrochemically measured corrosion rate of the copper. One explanation for this may be that the flow of water through the support cage is greater because there are no restrictions from bentonite in the annulus of the support cage and therefore the iron precipitate is distributed differently with less on the surface of the copper electrodes, but this remains speculation until Experiment 5 is examined in more detail.

## 5.4 Strain gauge measurements

It is clear that the small fluctuations in the responses from the strain gauges attached to Experiments 1 and 4 (Figure 4-33) are most probably due to seasonal changes in the local temperatures in the vicinity of the experiments.

Since an unexplained increase in tensile strain for one of the sensors on Experiment 1 (strain gauge elements 1a and 1b near the top of the canister), there has been a slow decrease in the strain, suggesting a slow compression of the canister. The largest fall in the measured strain occurred on sensors 1a and 1c, which exhibited a change of ~1,000–1,500 microstrain over a 5-year period. The other sensors exhibited changes of a few hundred microstrain over a five year period. Over the complete length of the model canister (i.e. 300 mm length) a microstrain of 1,000 (i.e. 1 milli-strain) corresponds to a change in length of the canister of 300  $\mu\text{m}$ . This is well within the elastic region for the deformation of copper under load.

Strain gauge measurements are very sensitive to small changes in dimensions and the results show that no significant expansion of Experiment 1 (low density bentonite) or Experiment 4 (compacted bentonite) had occurred as a result of corrosion of the cast iron insert. This is consistent with the observations made on Experiment 3 when it was dismantled [7] and no changes were found when the external dimensions of the canister were measured and compared to the original machined dimensions.

## 6 Future work

The following suggestions are made for future activities on the MiniCan experiment:

- Consider dismantling other MiniCan experiments to confirm the observations from Experiment 3 under different operating conditions, for example for fully compacted bentonite (Experiment 4).
- Consider placing a new experiment in Borehole for Experiment 3, to investigate other parameters that may affect corrosion behaviour (e.g. higher temperatures).
- Carry out thermodynamic calculations to define Pourbaix diagrams for copper and iron in the environments measured for the interior of the support cages in the MiniCan experiments.
- Carry out hydrogen evolution measurements for copper in the environments determined for the interior of the support cages in the MiniCan experiments, to obtain instantaneous values for the corrosion rate of copper by an independent measuring technique. This could be done using the techniques used previously for characterising the anaerobic corrosion of iron in anoxic conditions [24]. It should be conducted in pure water, to establish whether hydrogen is generated by anaerobic corrosion of copper, as suggested by Hultquist and co-workers [31–35], and also in Äspö groundwater, with and without the presence of additional sulphide to simulate SRB activity.
- Continue with the electrochemical laboratory measurements in compacted bentonite, but add sulphide to the water surrounding the compacted bentonite to simulate the activity of SRB on the surface of the bentonite buffer.

## 7 Conclusions

The main conclusions from the project to date are as follows:

1. Water analysis has shown that there are compositional differences between the water inside the support cages compared to the external borehole water. These can be explained on the basis of enhanced corrosion of the iron and microbial activity inside the support cages. There has been a large increase in the concentration of dissolved iron, which is mainly present in the form of  $\text{Fe}^{2+}$ , and a parallel decrease in the pH from the groundwater pH value of  $\sim 7.6$  to a value inside the support cage of  $\sim 6.6$ .
2. Microbial analysis has demonstrated that SRB are active in the experimental boreholes.
3.  $E_h$  measurements have shown that the test conditions within the support cages around the MiniCan experiments became reducing over a period of a few thousand hours at the start of the experiments.
4. The corrosion potentials of the copper and iron electrodes in the experiments with low density bentonite (Experiments 1 to 3) are consistent with the formation of copper sulphide and iron sulphide corrosion products.
5. The electrochemically measured corrosion rates have increased for both copper and iron. Analysis of the weight loss sample in Experiment 3 has confirmed that the corrosion rate for iron is at least  $500 \mu\text{m yr}^{-1}$ . The corrosion rates measured for iron by LPR and ACI are overestimated due to the electrochemical properties of the sulphide films formed on the surface by SRB activity by a factor of approximately  $\times 5$ .
6. The corrosion rate of copper in compacted bentonite (Experiment 4) was initially of the order of  $1 \mu\text{m yr}^{-1}$  but it appears that later measurements are not valid, possibly because the swelling pressure exerted by the bentonite has disrupted the electrical connections.
7. High corrosion rates have been measured electrochemically for copper in low density bentonite and unconditioned groundwater, but these values are an overestimate caused by the surface precipitation of iron sulphide produced by corrosion of cast iron in the vicinity. The measured values are considerably higher than that measured by weight loss in Experiment 3, where a value of  $0.15 \mu\text{m yr}^{-1}$  was obtained.
8. Strain gauge measurements showed that no expansion of the copper canister had occurred as a result of corrosion of the cast iron insert.
9. It should be recognised that these test conditions are not directly comparable with the proposed repository conditions. It appears that the low density bentonite is conducive to microbial activity, particularly that of SRB, and this has led to an increase in the corrosion rate of the cast iron. However, the copper corrosion rates measured by the electrical resistance method in low density bentonite and raw groundwater are considerably lower ( $< 1 \mu\text{m yr}^{-1}$ ). In fully compacted bentonite microbial activity will be limited by the low activity of water and the corrosion rate is likely to be determined by the rate of diffusion of sulphide through the bentonite buffer.

## 8 Acknowledgments

The authors gratefully acknowledge assistance provided by the following during the reporting period:

- SKB: Christina Lilja, Lars Werme, Richard Bäck, Mats Lundqvist, Teresita Morales, Siren Bortelid Moen, SKB chemistry laboratory staff at Äspö.
- Microbial Analytics: Karsten Pedersen and Sara Eriksson.

The authors also gratefully acknowledge financial support provided by SKB for conducting this project.

## 9 References

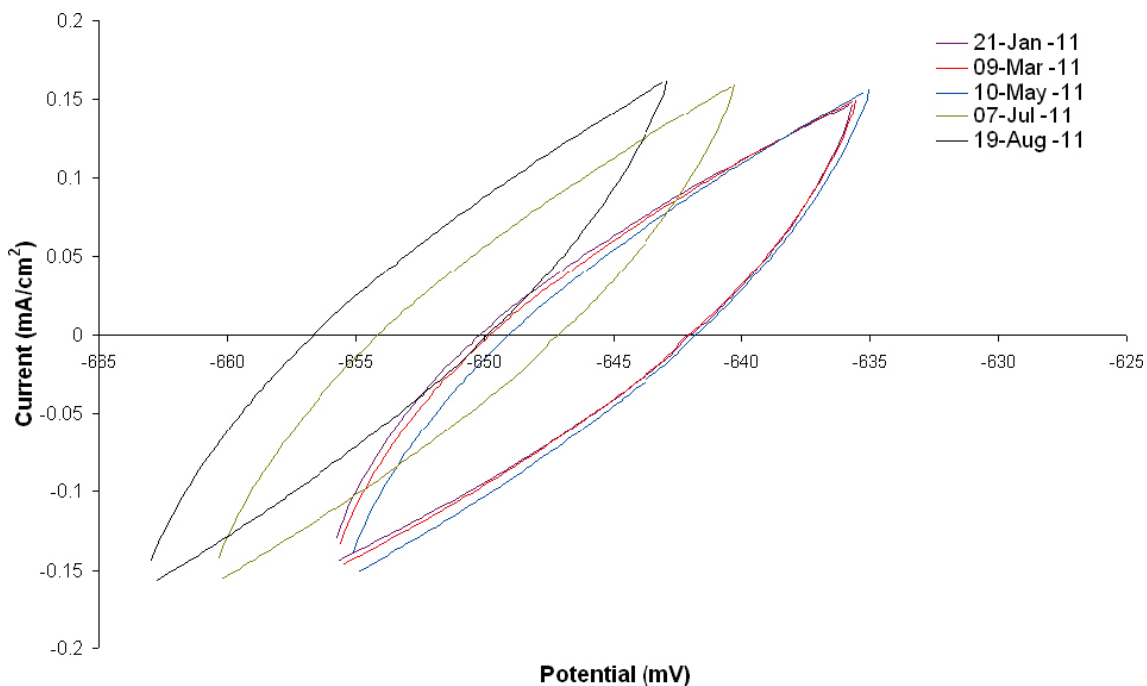
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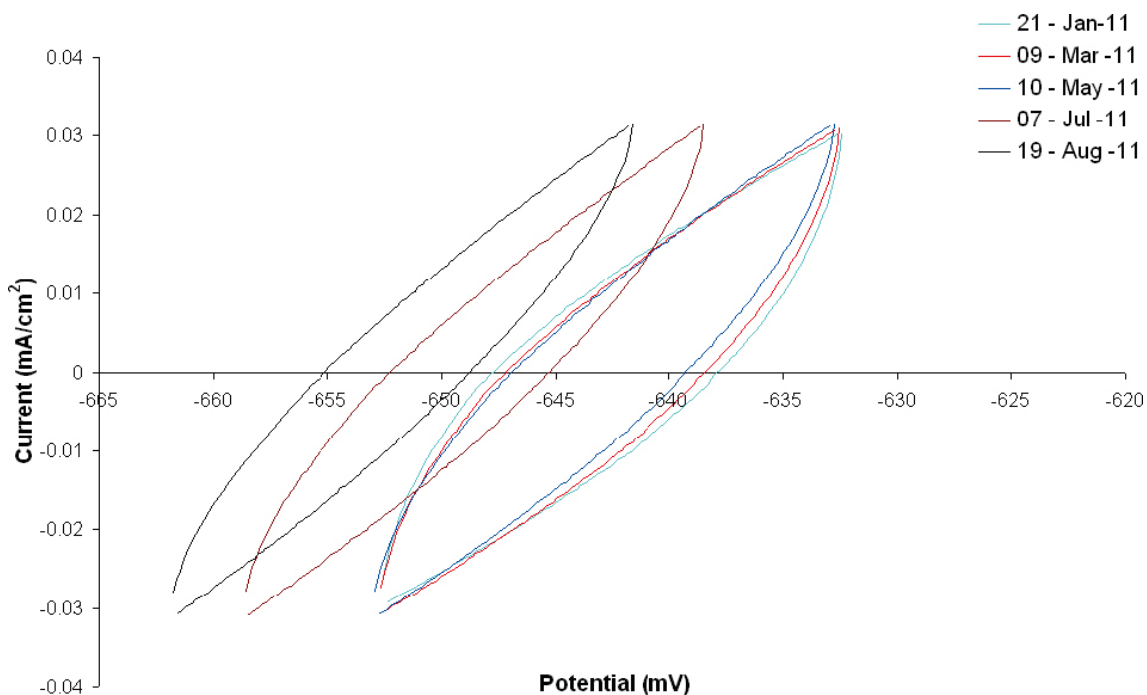


**Electrochemical corrosion rate measurements January to December 2011**

Please note that all potentials shown in the electrochemical measurements are with respect to the reference electrode (i.e. Ag/AgCl), not NHE.



*Figure A1-1. LPR plots of cast iron in Experiment 1 (low density bentonite).*



*Figure A1-2. LPR plots of copper in Experiment 1 (low density bentonite).*

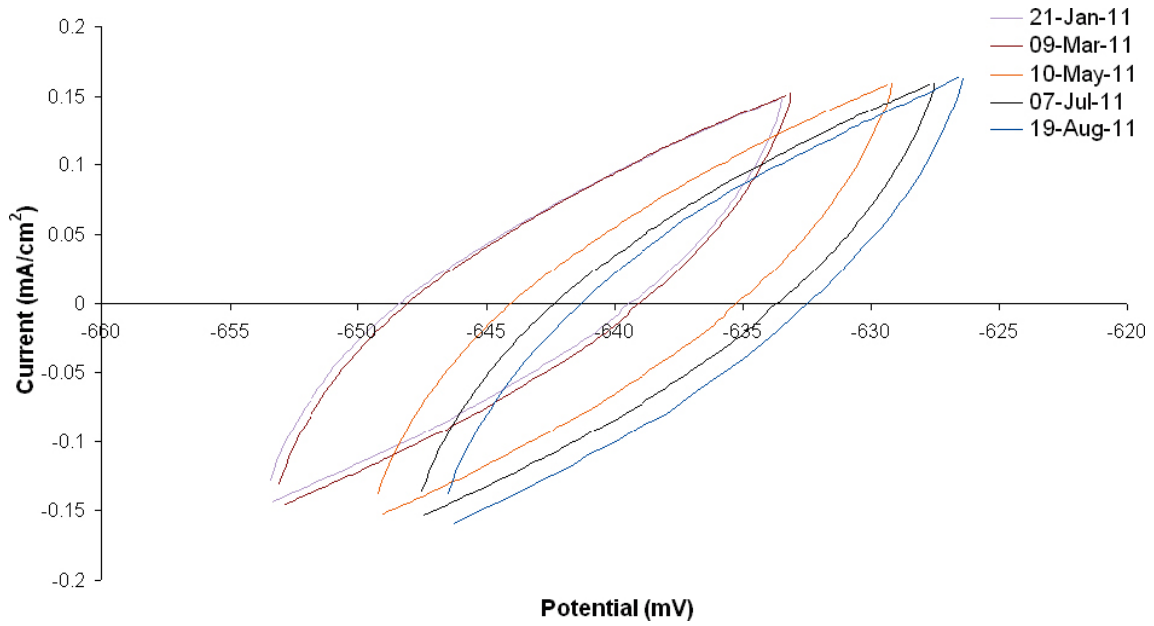


Figure A1-3. LPR plots of cast iron in Experiment 2 (low density bentonite).

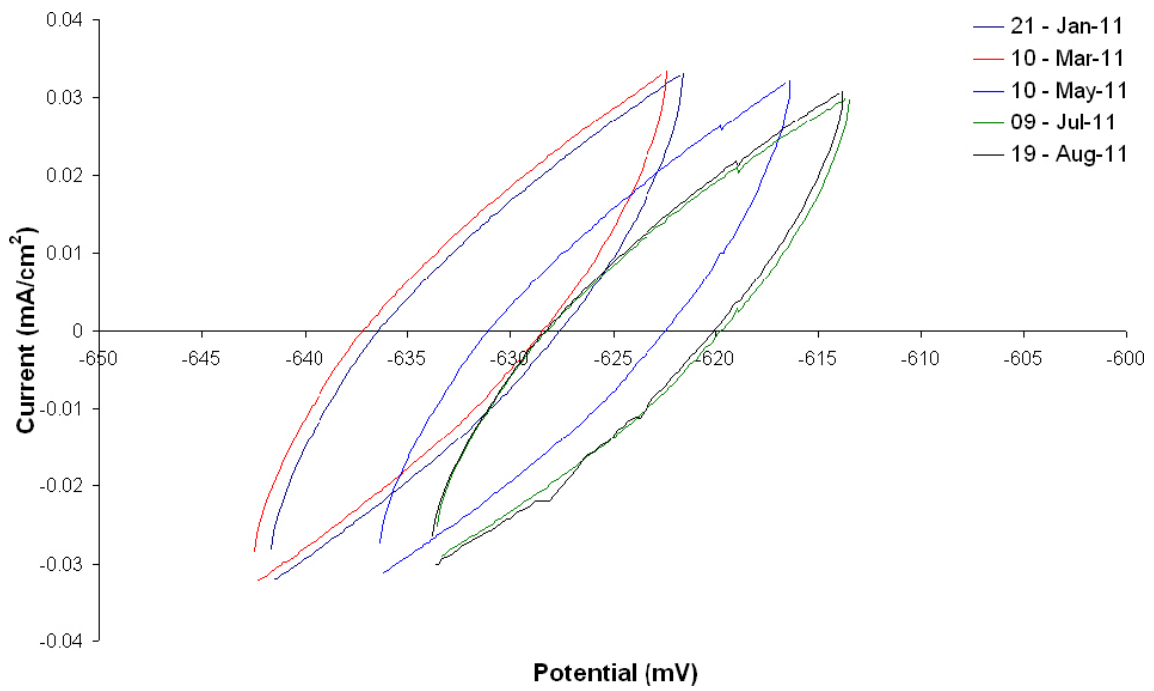


Figure A1-4. LPR plots of copper in Experiment 2 (low density bentonite).

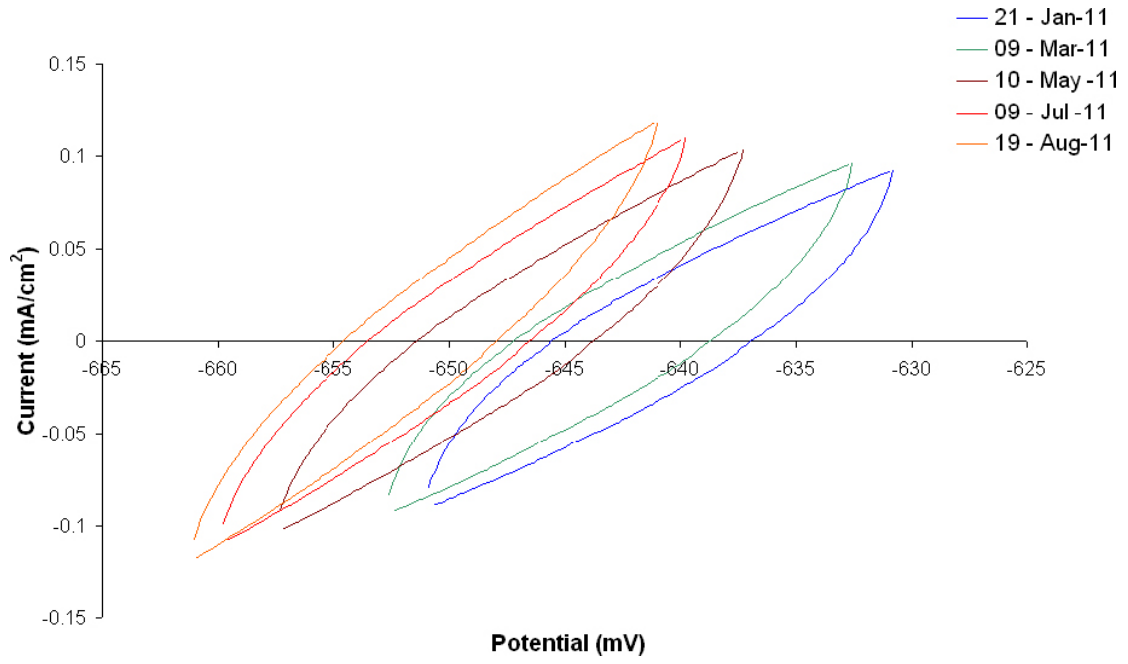


Figure A1-5. LPR plots of cast iron in Experiment 3 (low density bentonite).

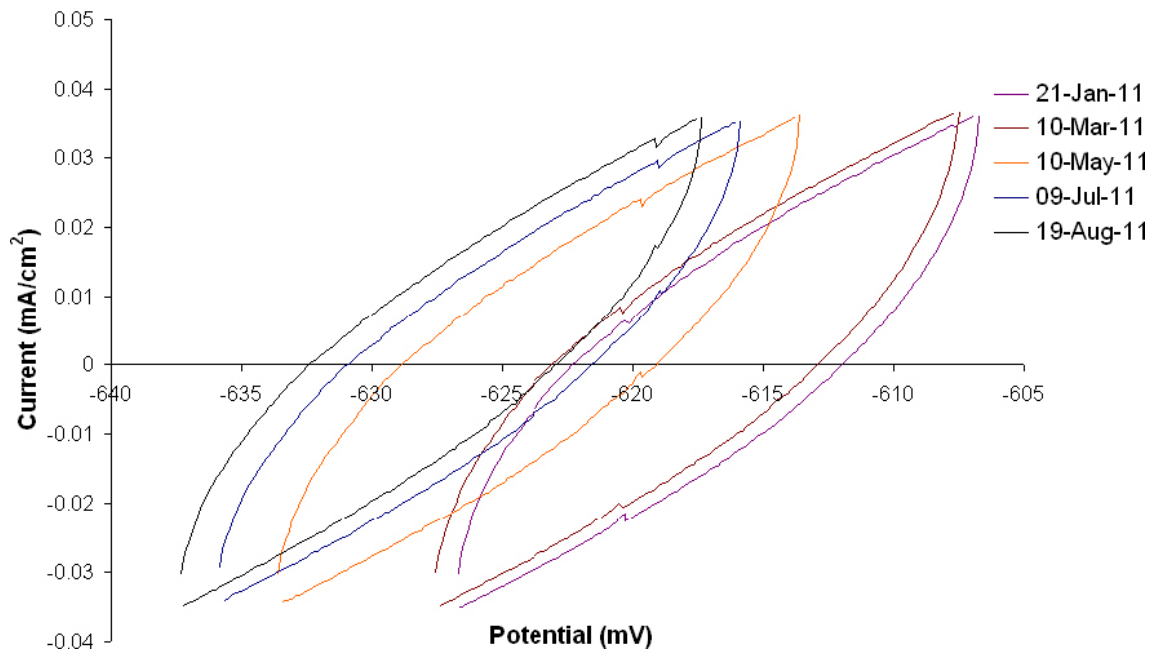
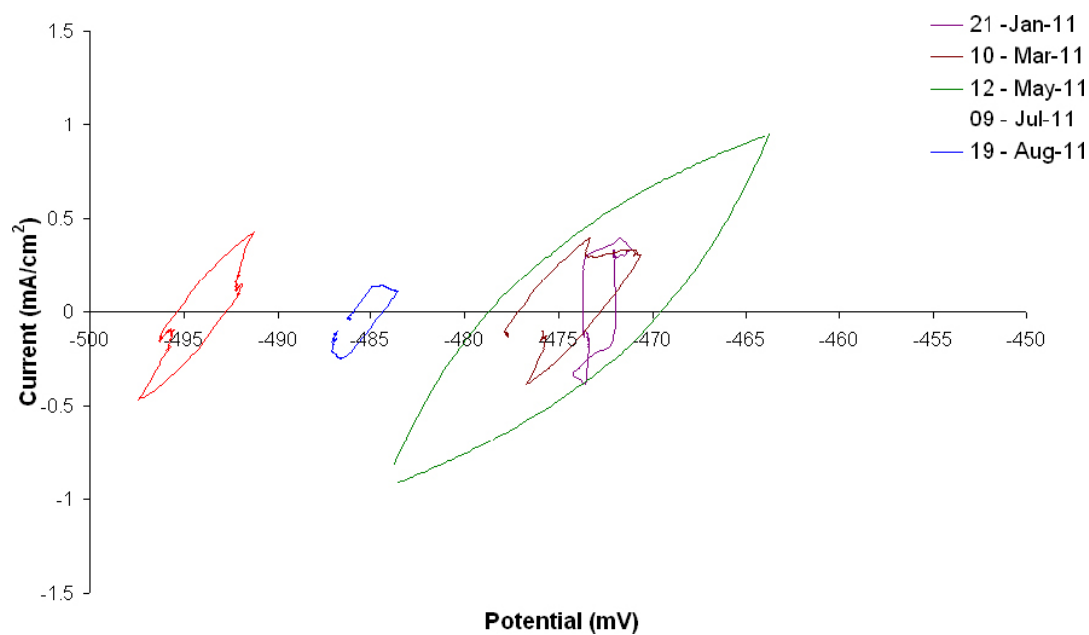
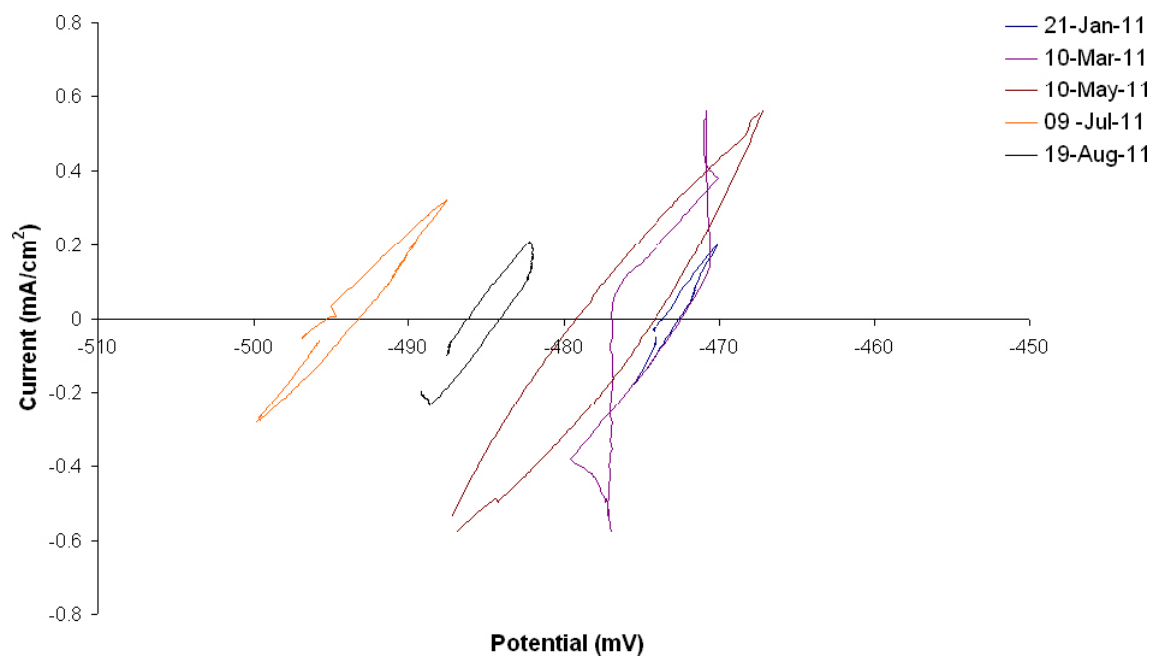


Figure A1-6. LPR plots of copper in Experiment 3 (low density bentonite).



**Figure A1-7.** LPR plots of iron in Experiment 4 (compacted bentonite) Note: It is likely that the iron electrode was in contact with the stainless steel flange of the support cage for these measurements).



**Figure A1-8.** LPR plots of copper in Experiment 4 (compacted bentonite).

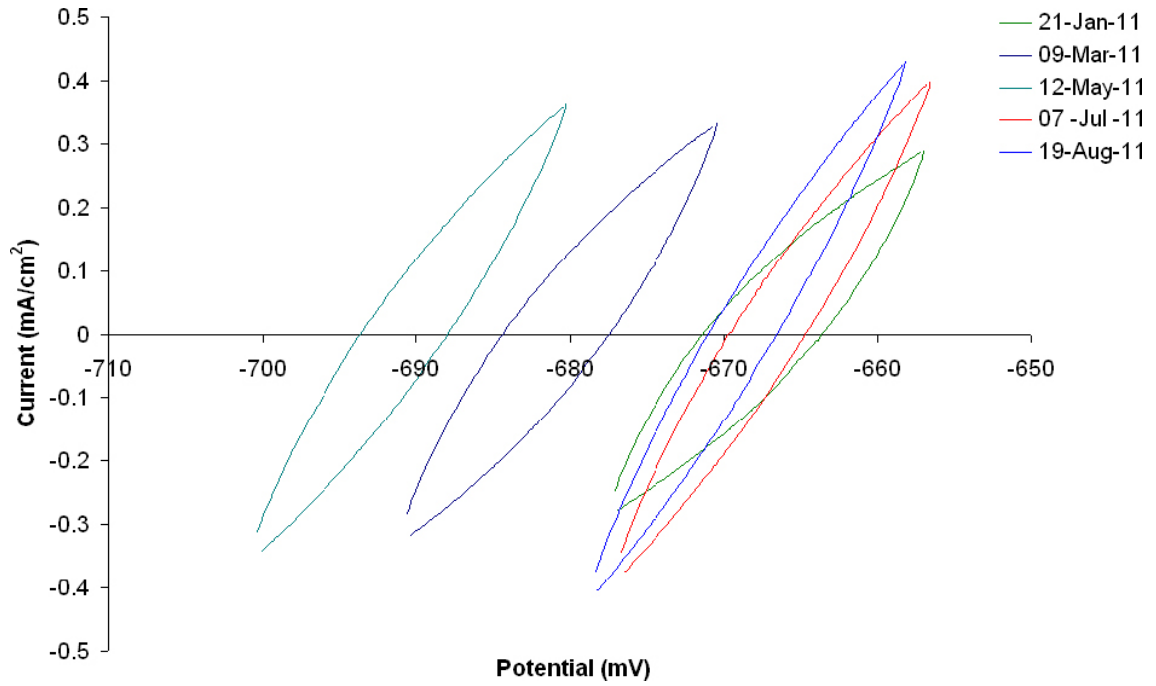


Figure A1-9. LPR plots of cast iron in Experiment 5 (no bentonite).

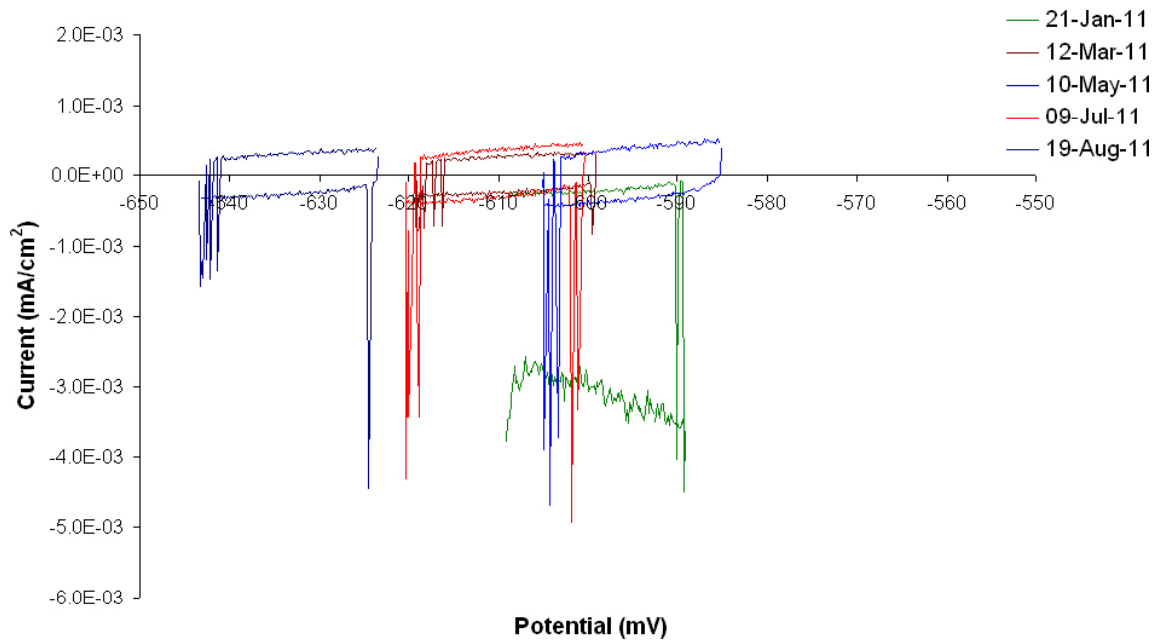


Figure A1-10. LPR plots of copper in Experiment 5 (no bentonite).

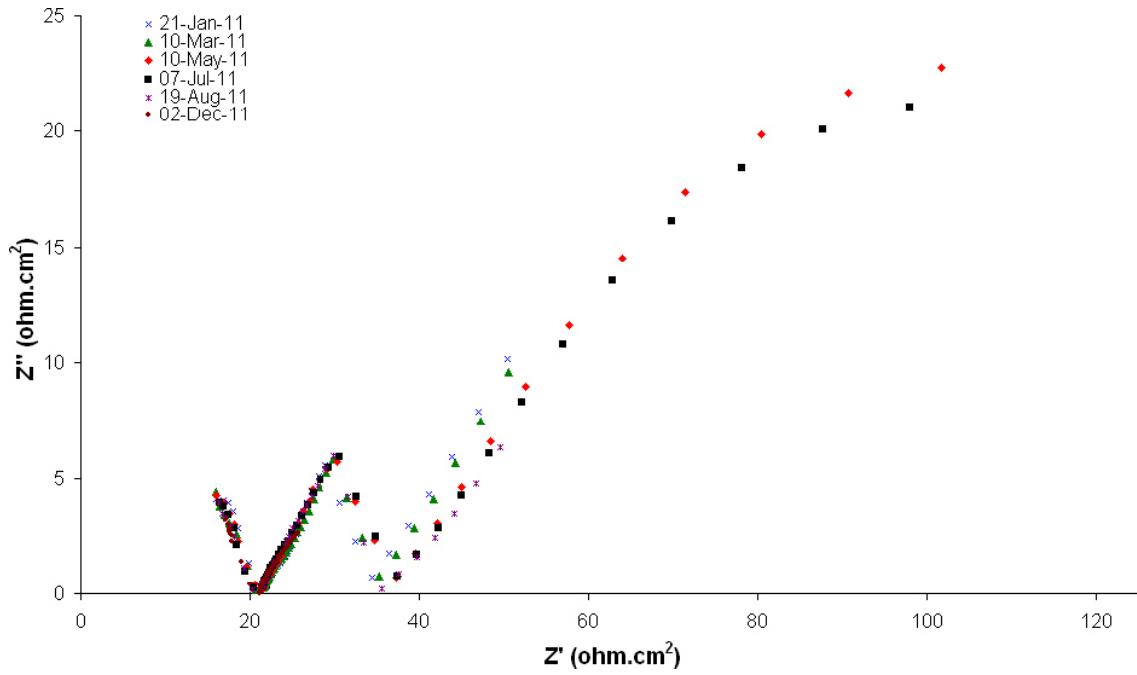


Figure A1-11. ACI plots of cast iron in Experiment 1 (low density bentonite).

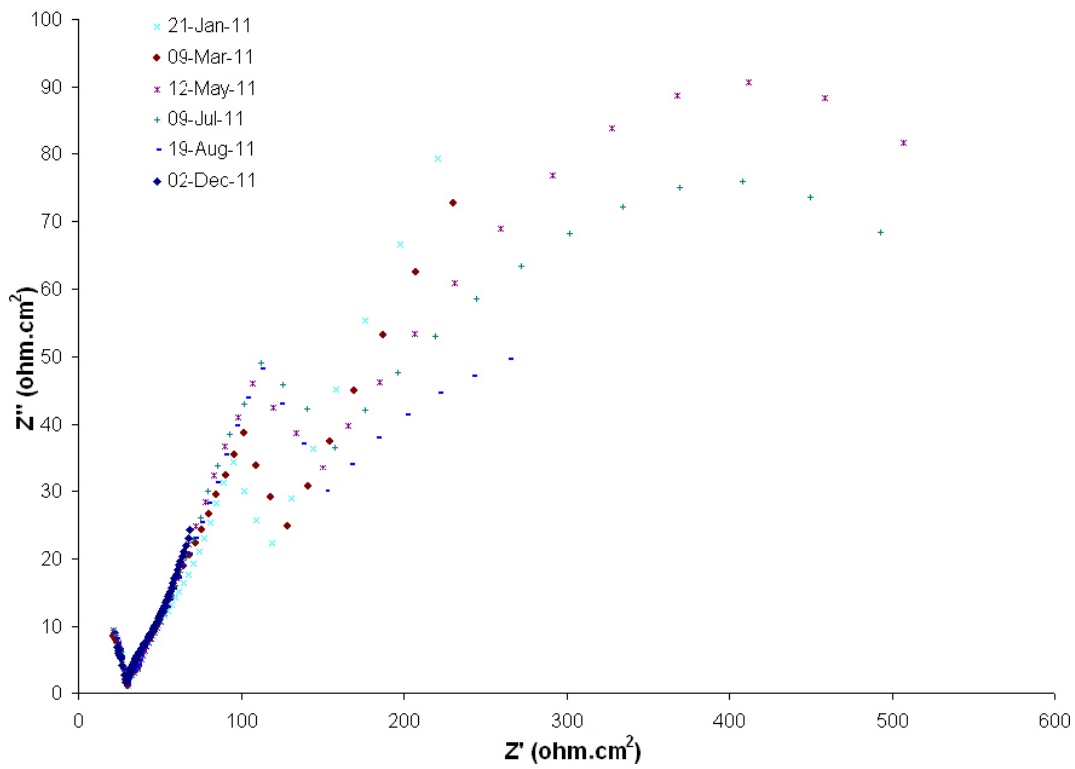


Figure A1-12. ACI plots of copper in Experiment 1 (low density bentonite).

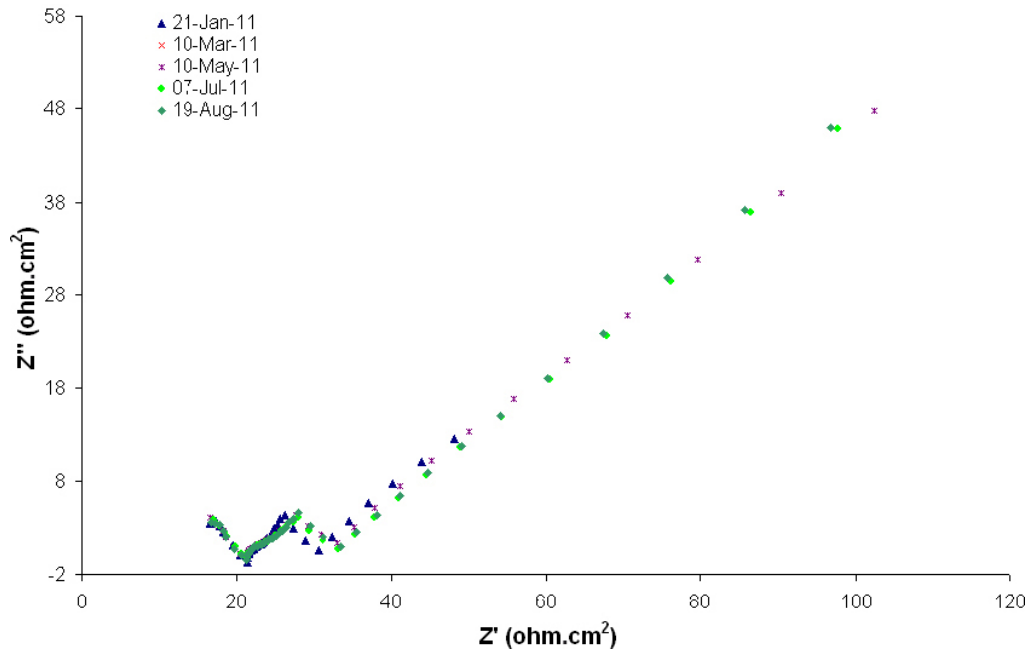


Figure A1-13. ACI plots of cast iron in Experiment 2 (low density bentonite).

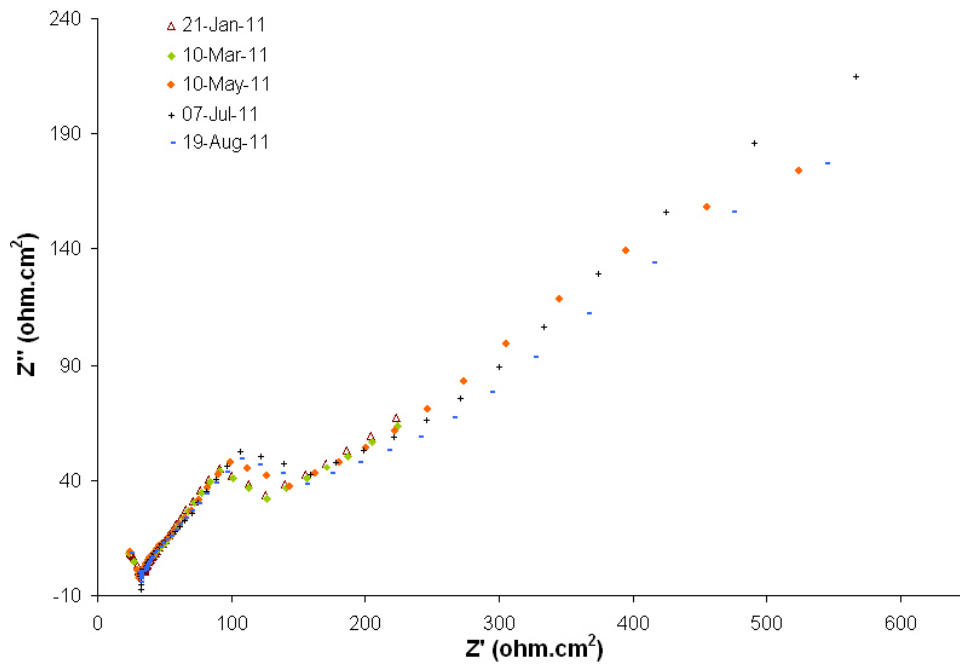


Figure A1-14. ACI plots of copper in Experiment 2 (low density bentonite).

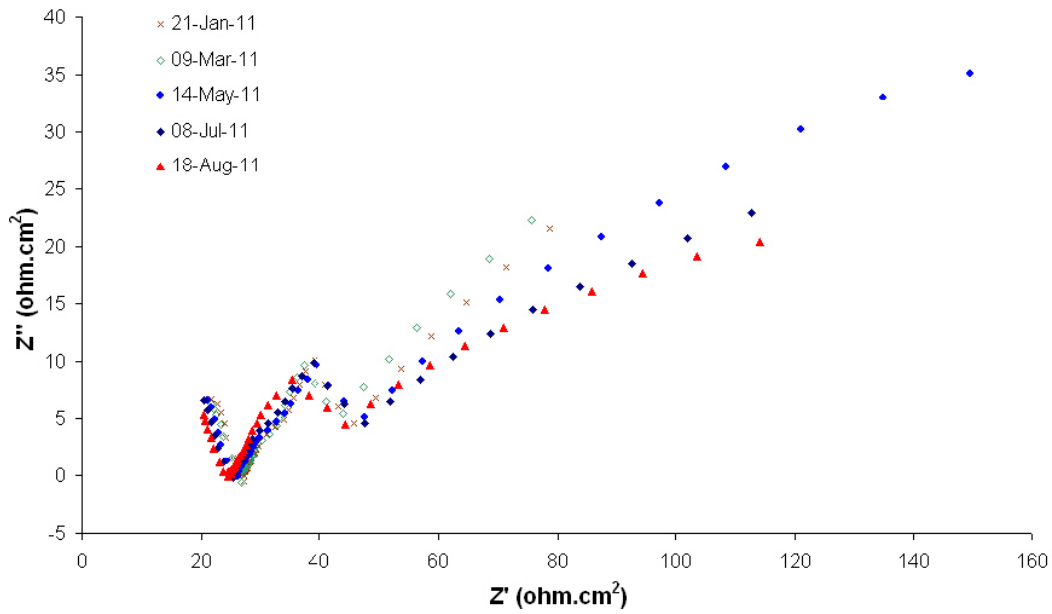


Figure A1-15. ACI plots of cast iron in Experiment 3 (low density bentonite).

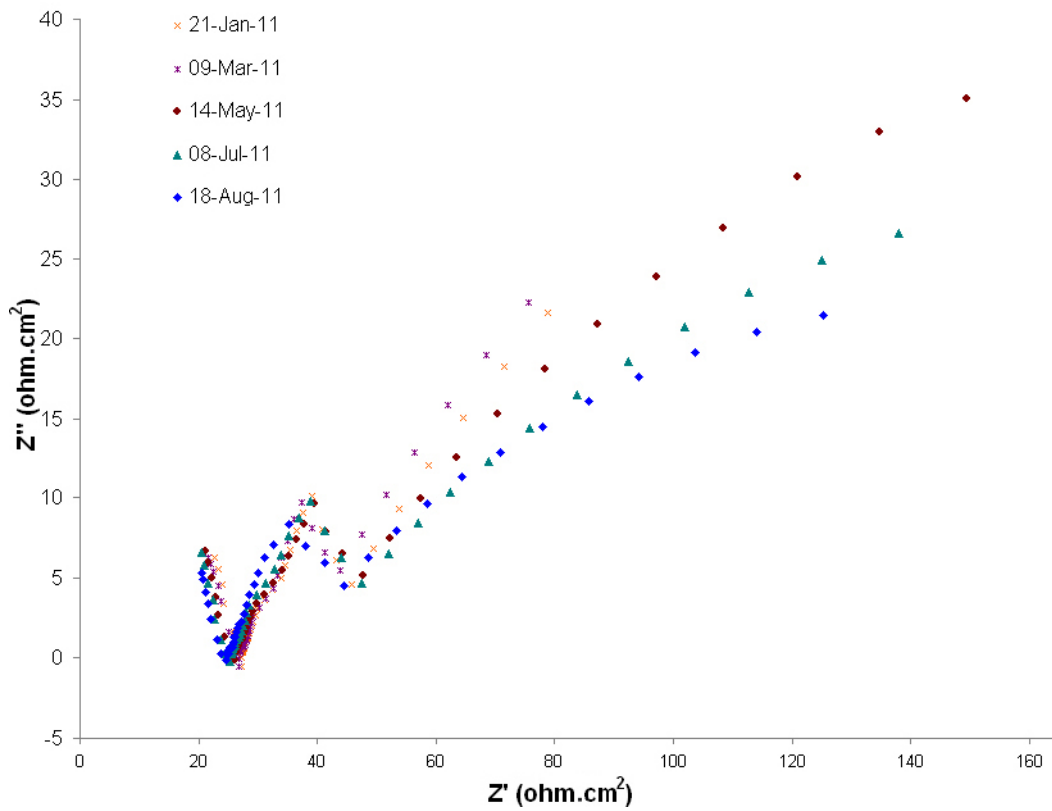


Figure A1-16. ACI plots of copper in Experiment 3 (low density bentonite).



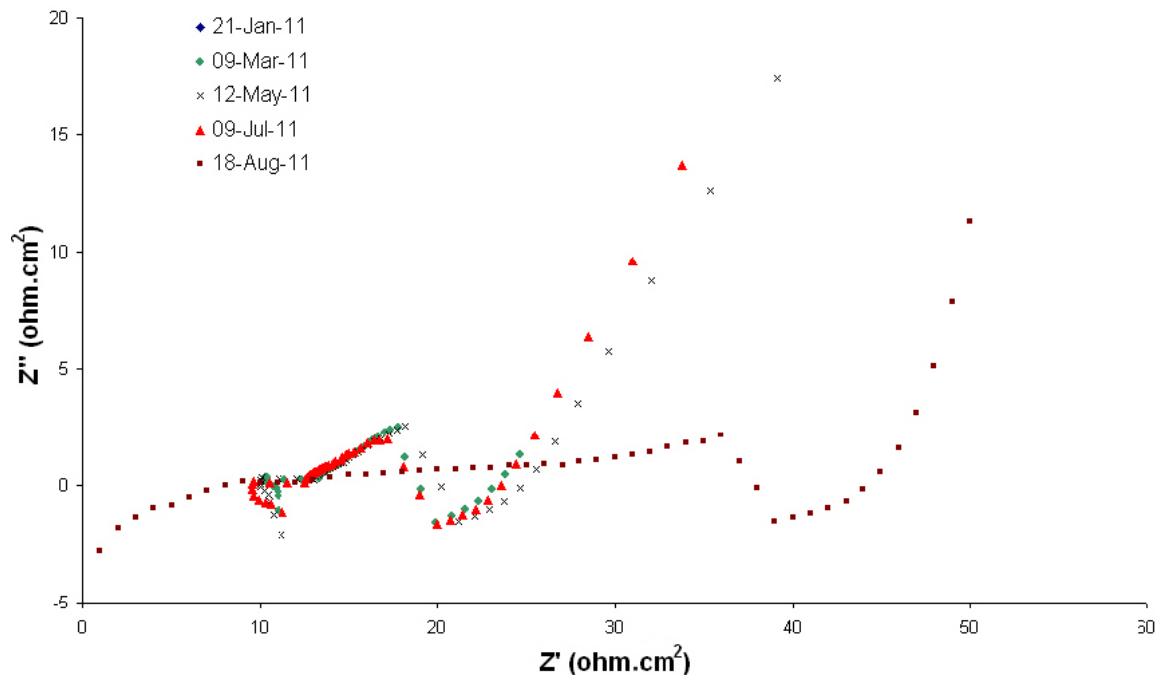


Figure A1-17. ACI plots of cast iron in Experiment 5 (no bentonite).

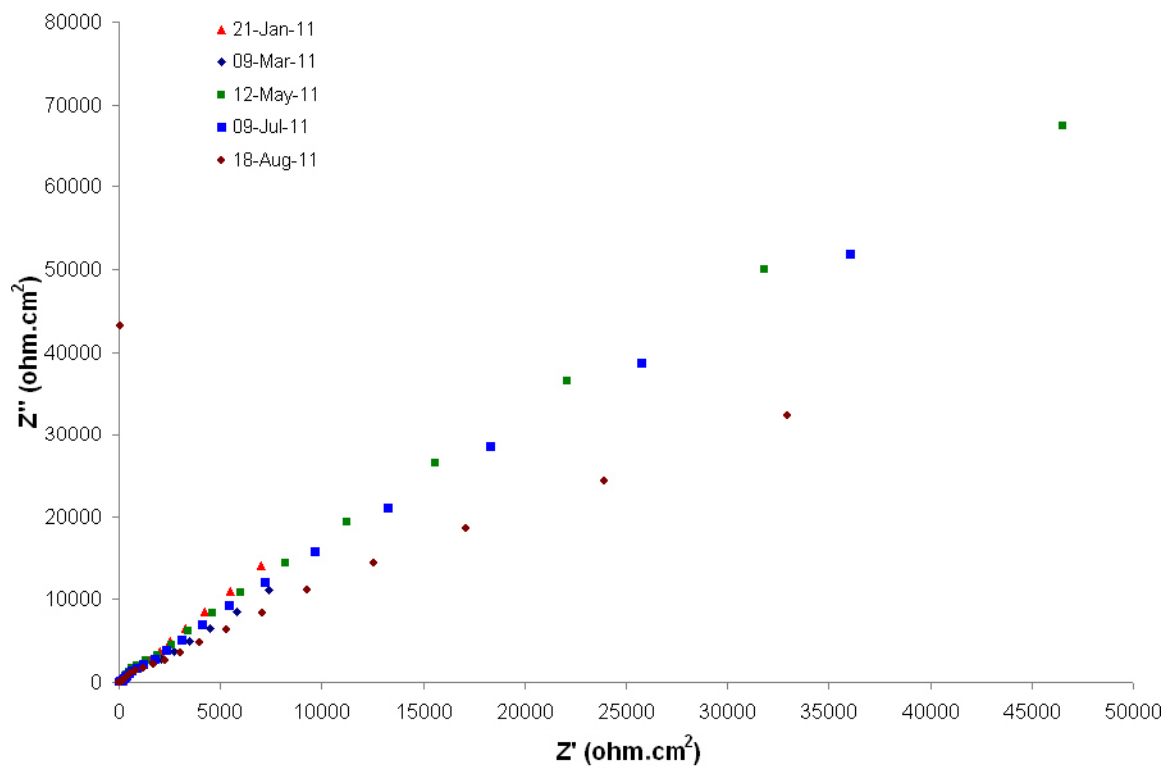


Figure A1-18. ACI plots of copper in Experiment 5 (no bentonite).

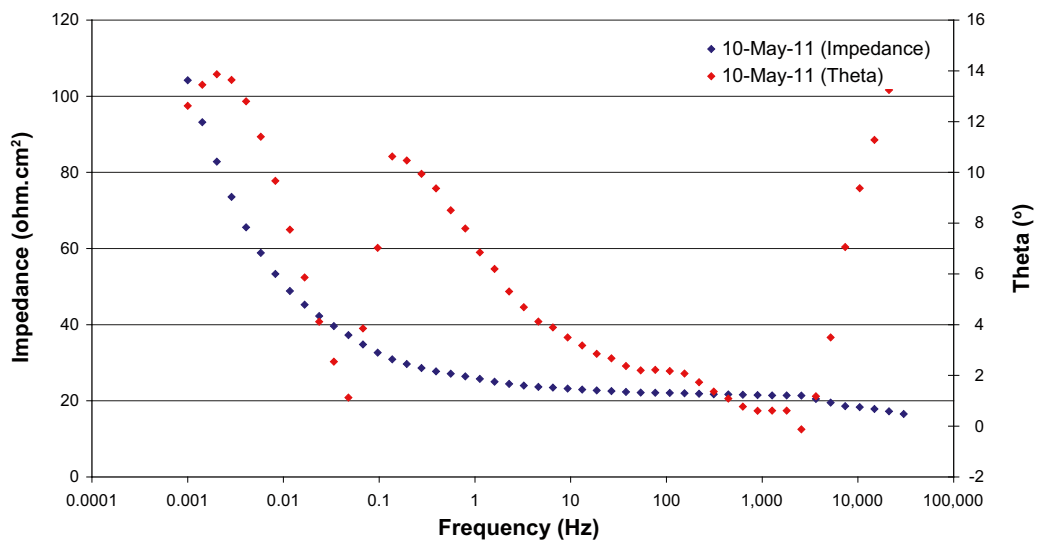
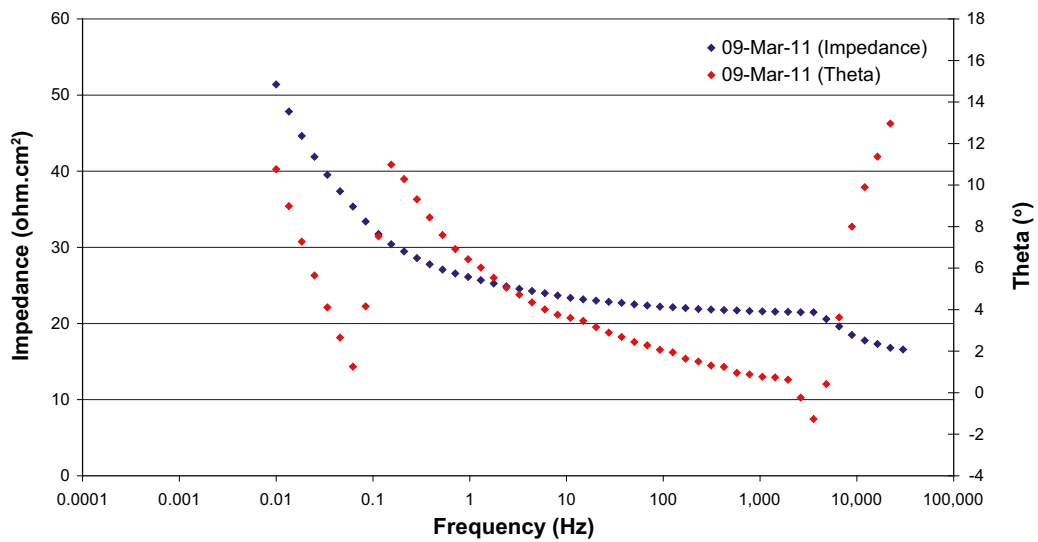
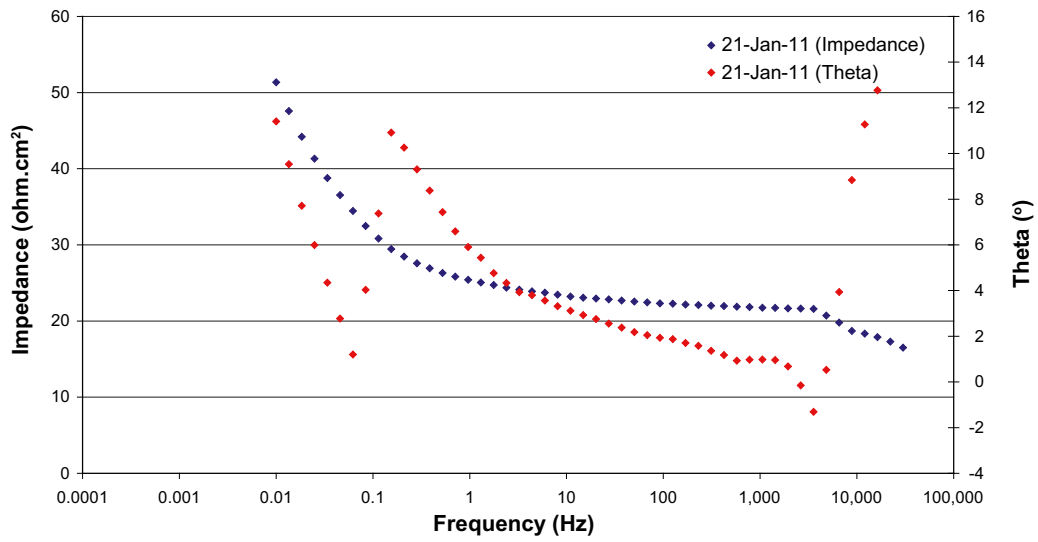


Figure A1-19. Bode plots of cast iron in Experiment 1 (low density bentonite).

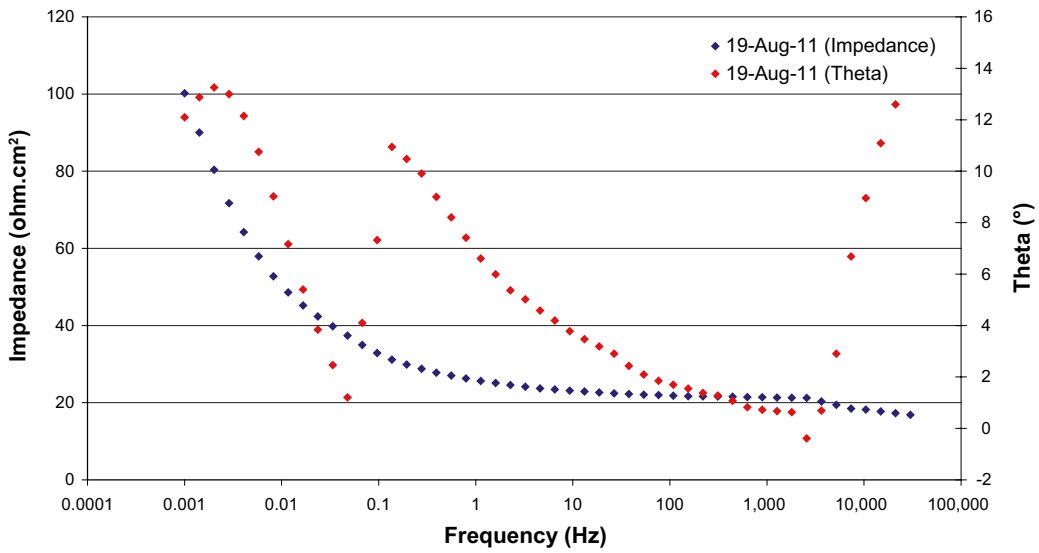
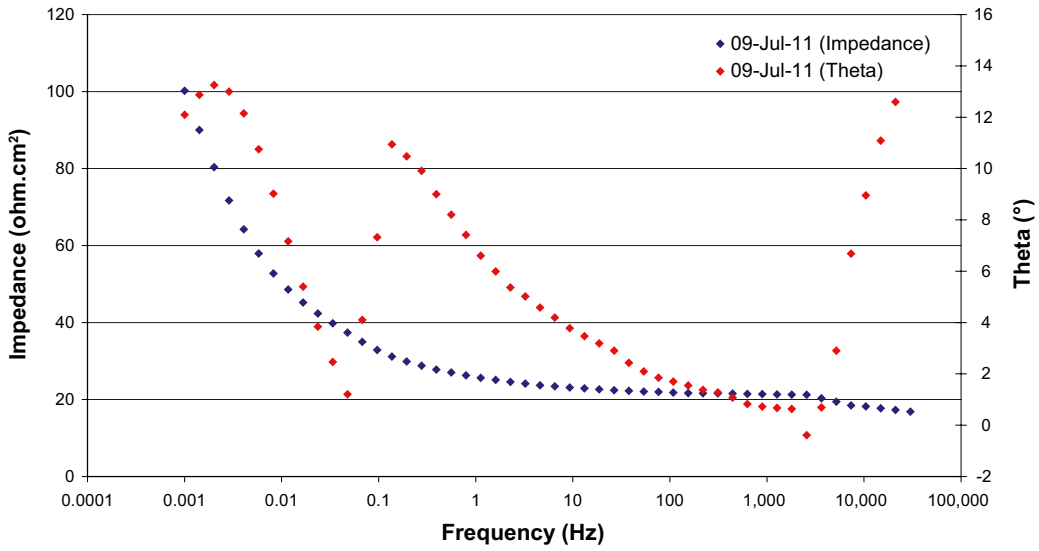


Figure A1-20. Bode plots of cast iron in Experiment 1 (low density bentonite).

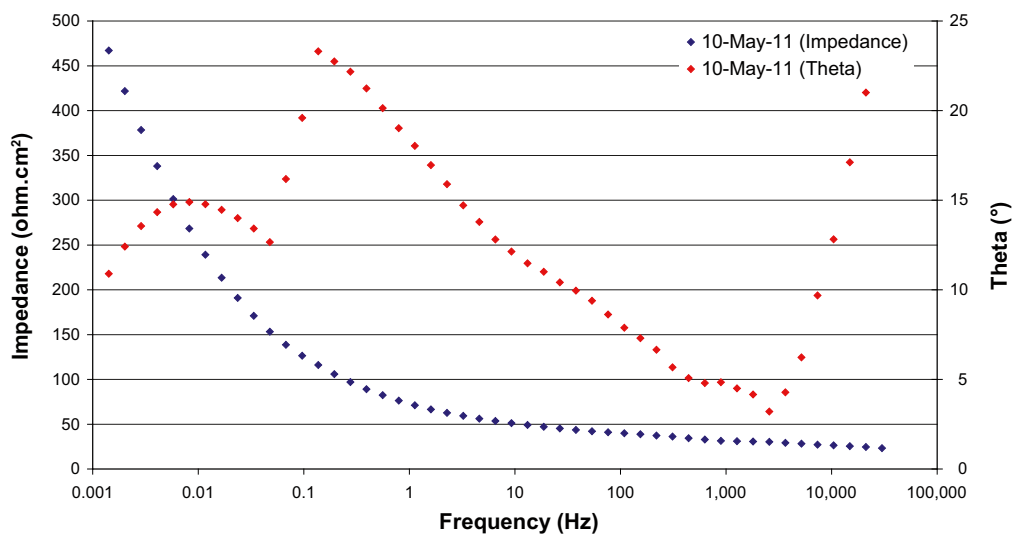
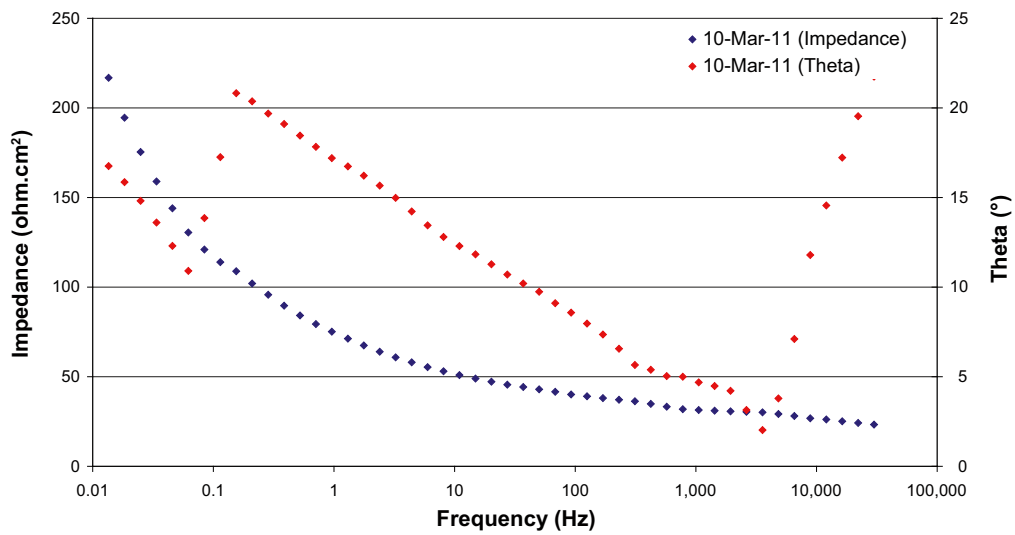
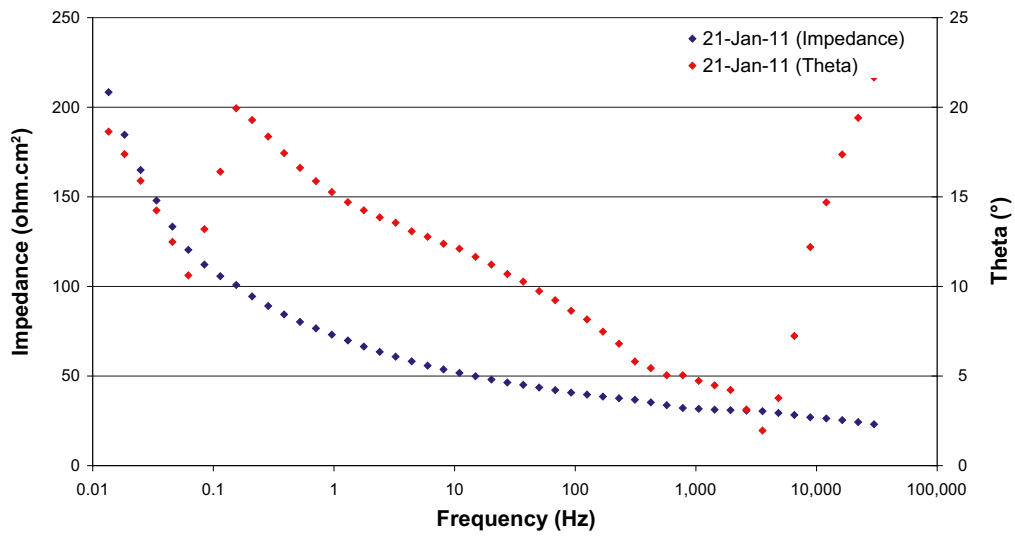


Figure A1-21. Bode plots of copper in Experiment 1 (low density bentonite).

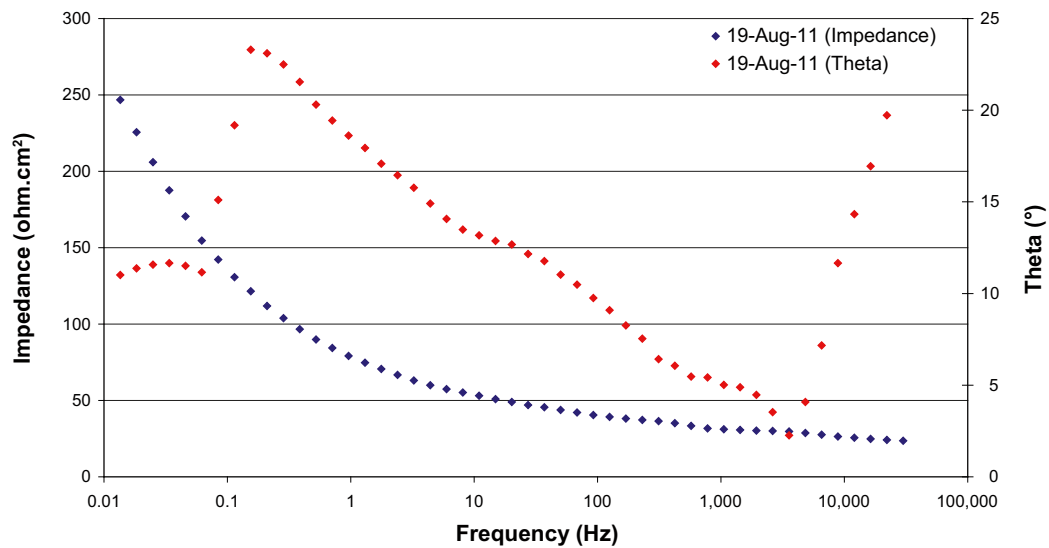
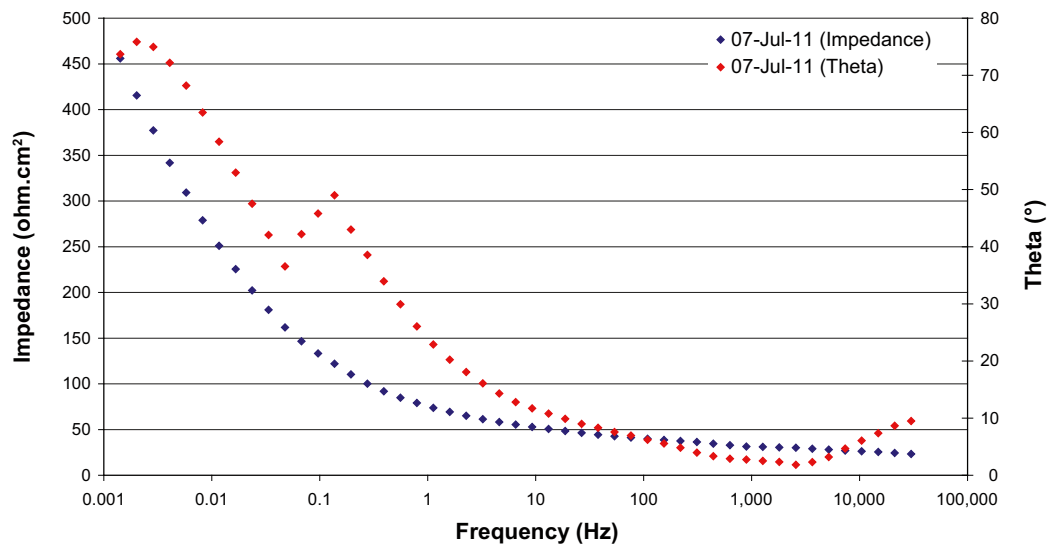


Figure A1-22. Bode plots of copper in Experiment 1 (low density bentonite).

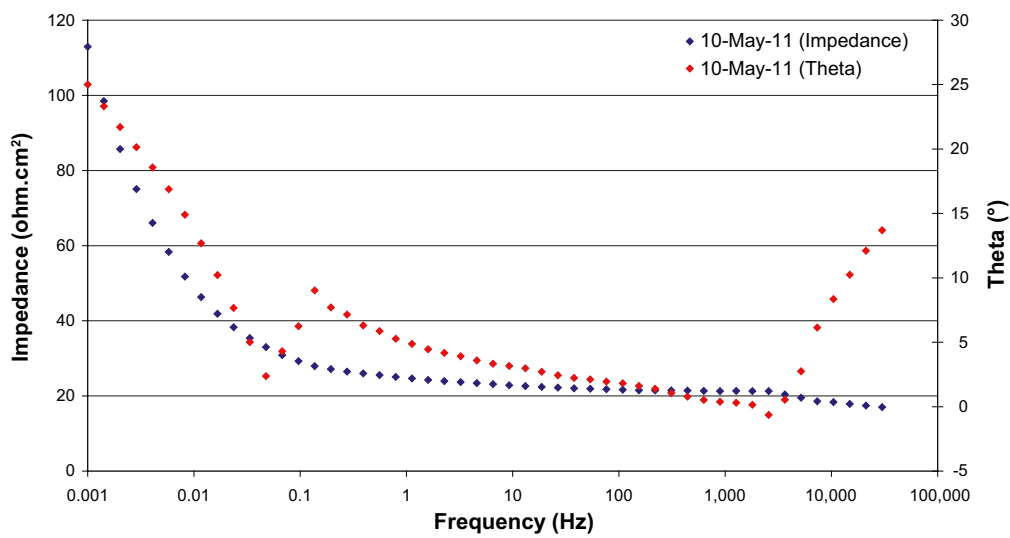
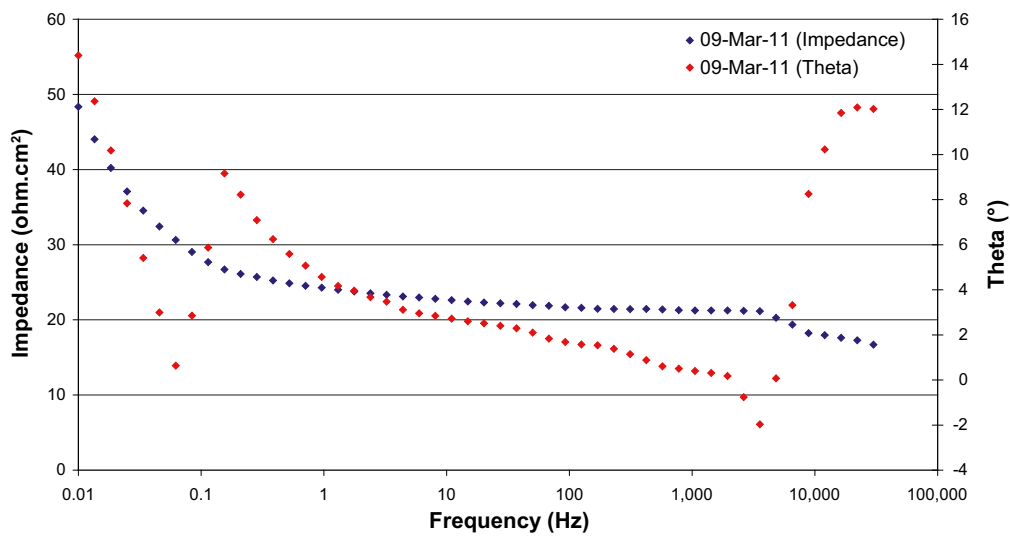
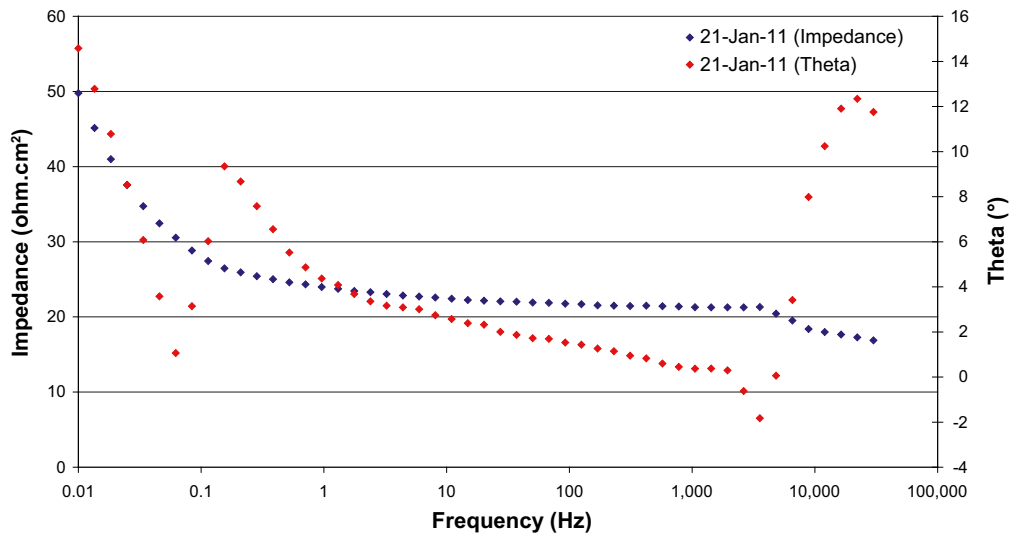


Figure A1-23. Bode plots of cast iron in Experiment 2 (low density bentonite).

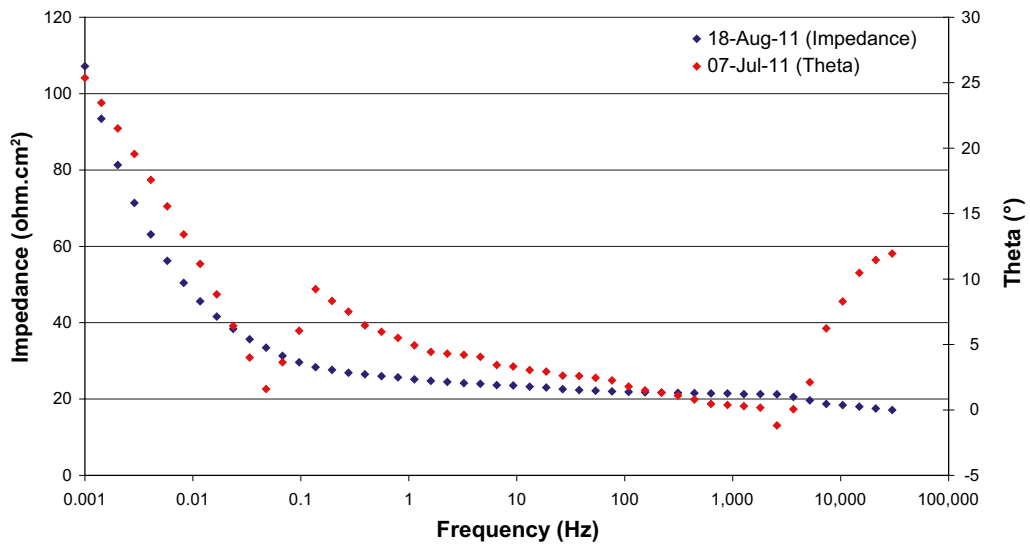
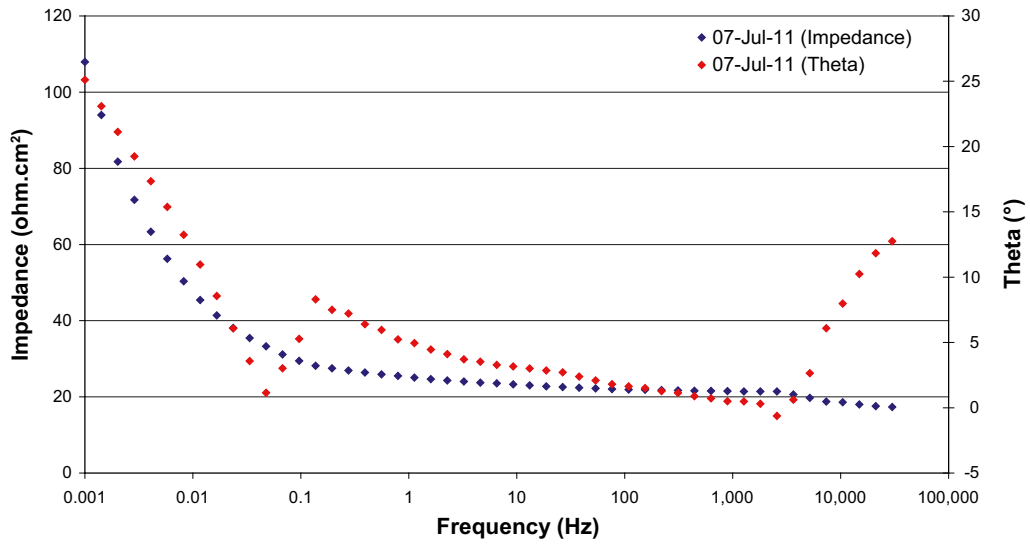


Figure A1-24. Bode plots of cast iron in Experiment 2 (low density bentonite).

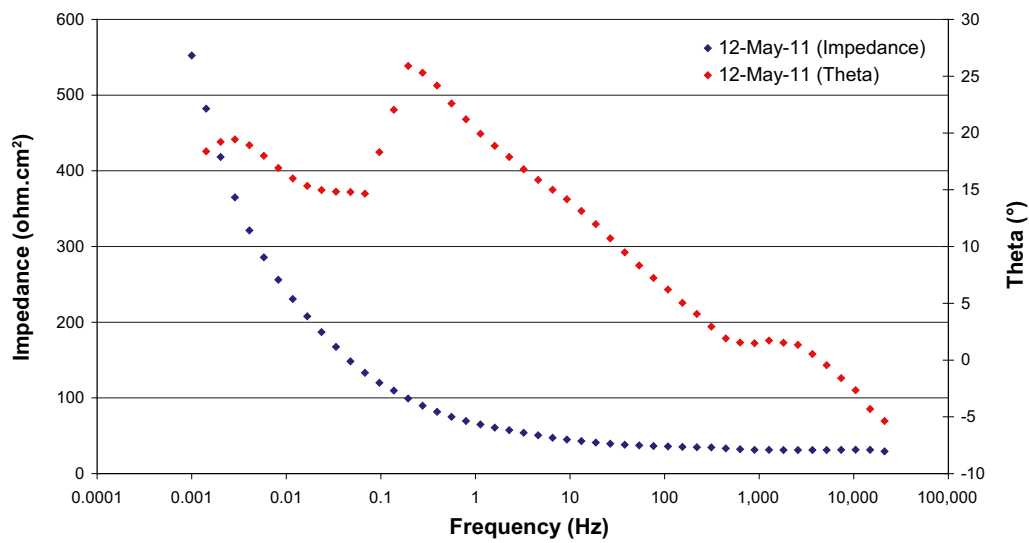
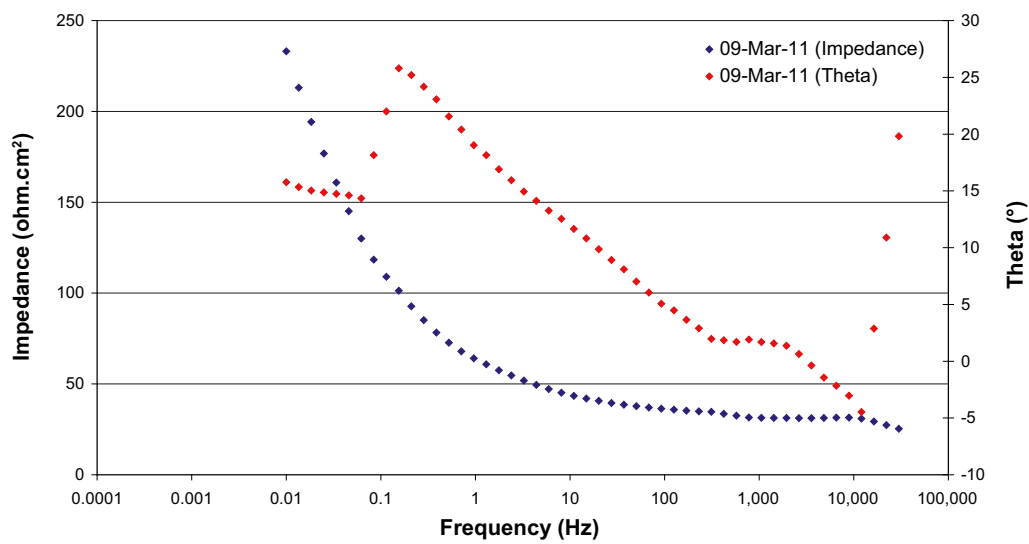
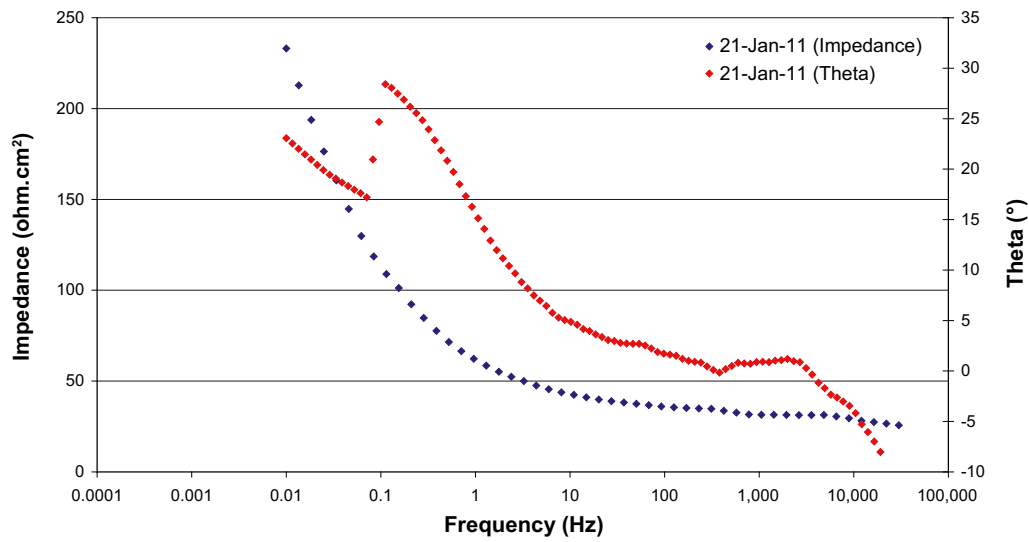


Figure A1-25. Bode plots of copper in Experiment 2 (low density bentonite).



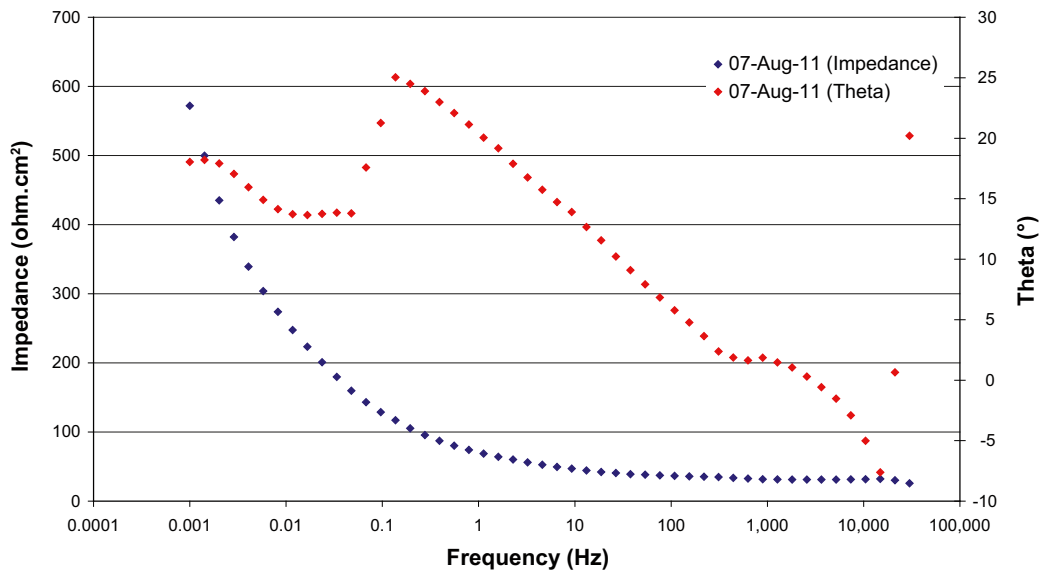
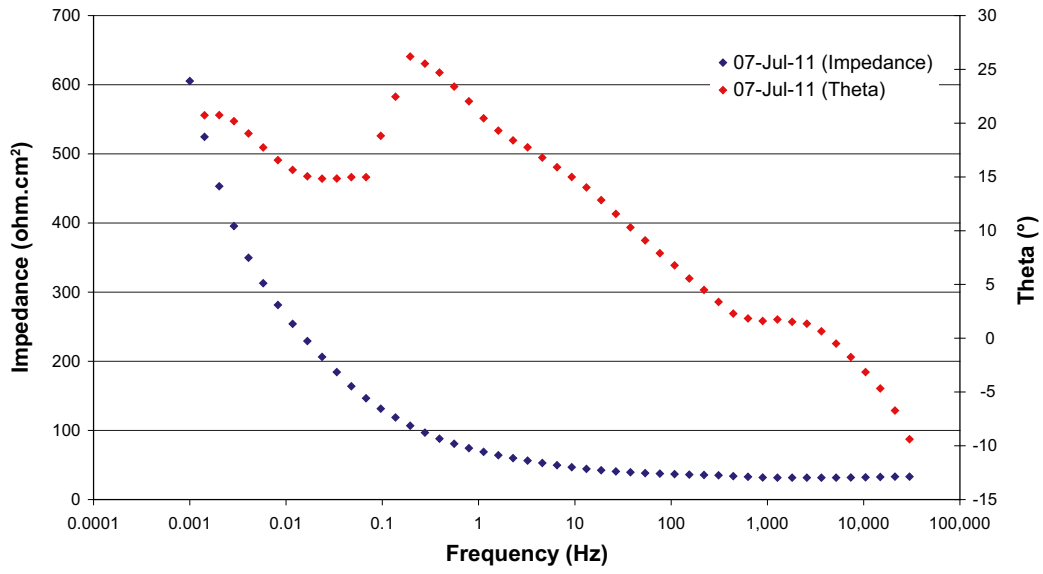


Figure A1-26. Bode plots of copper in Experiment 2 (low density bentonite).

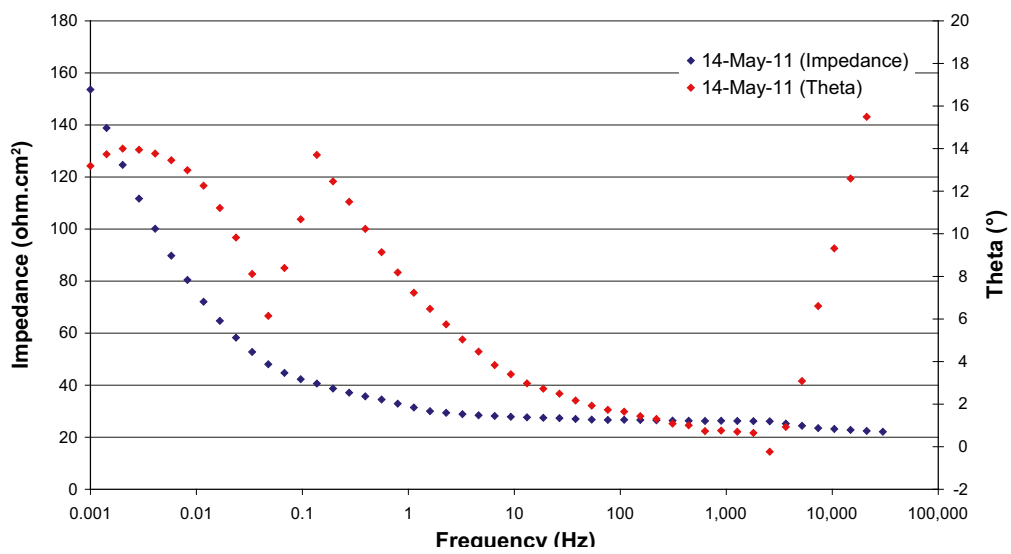
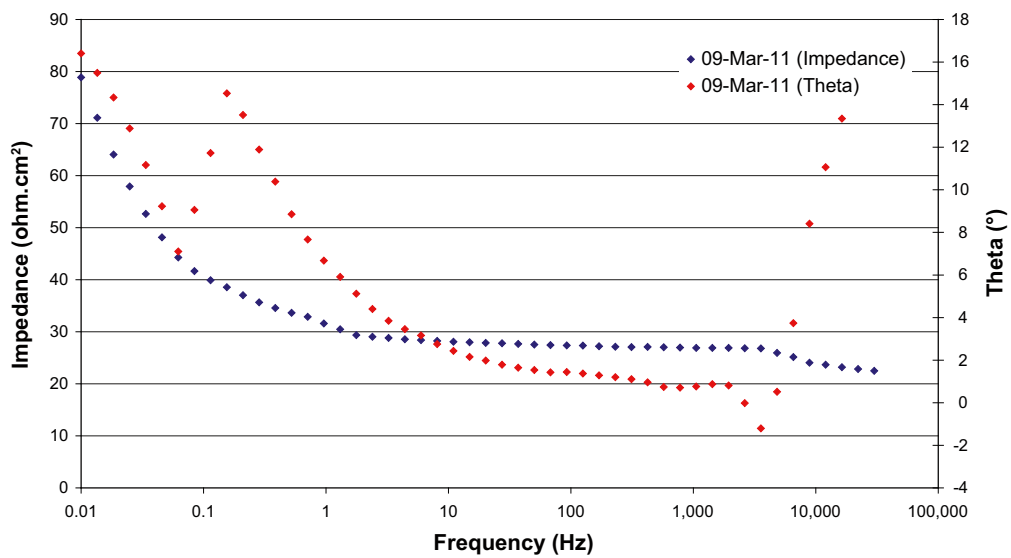
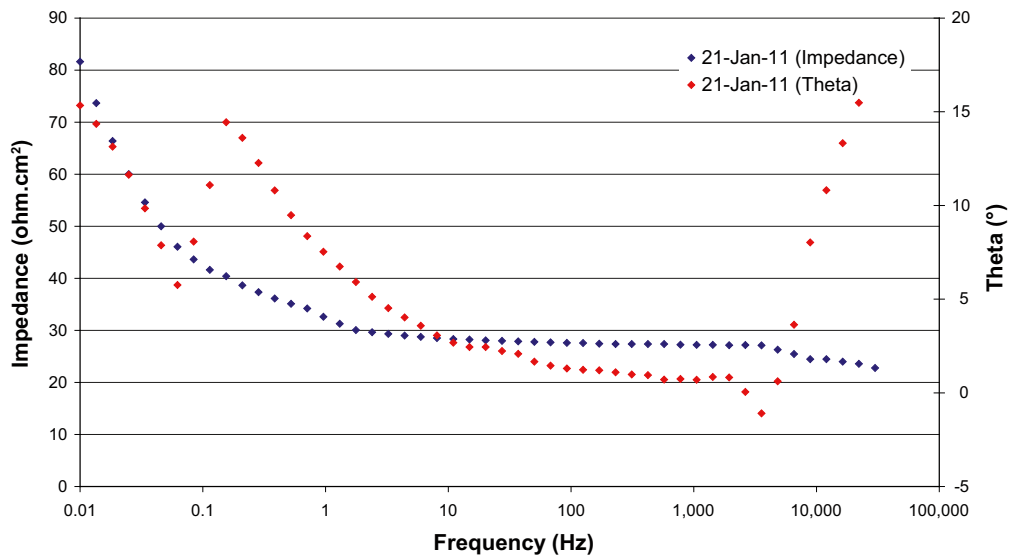


Figure A1-27. Bode plots of cast iron in Experiment 3 (low density bentonite).

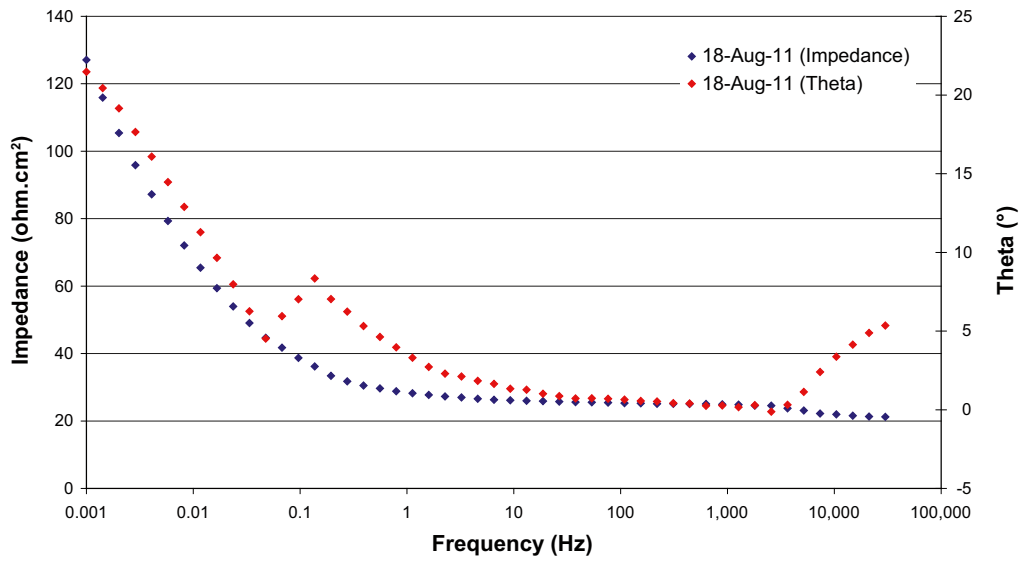
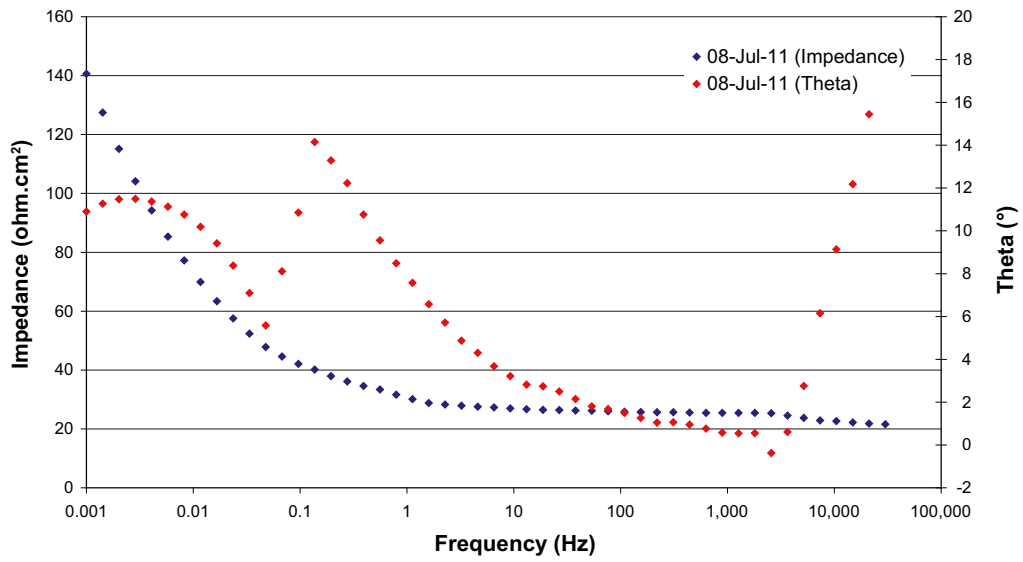


Figure A1-28. Bode plots of cast iron in Experiment 3 (low density bentonite).

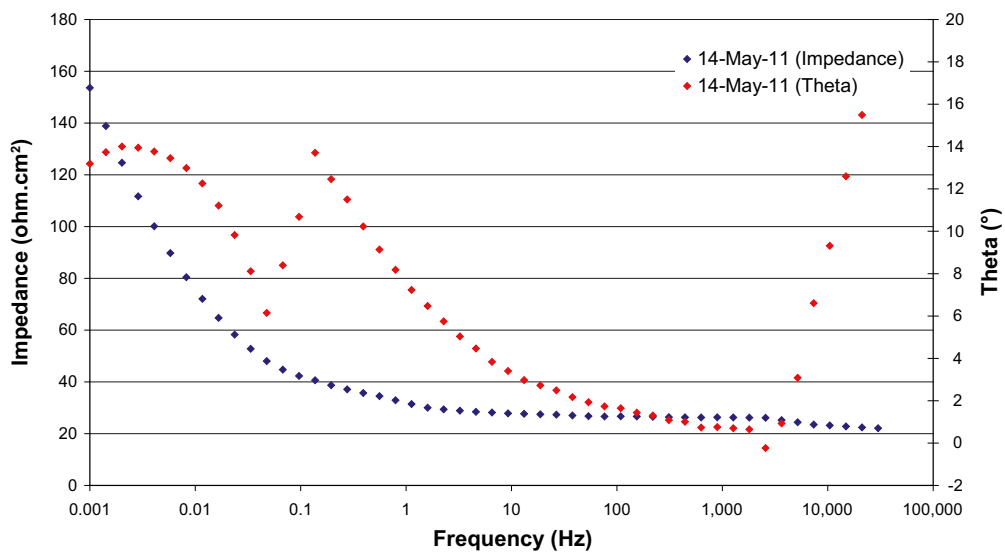
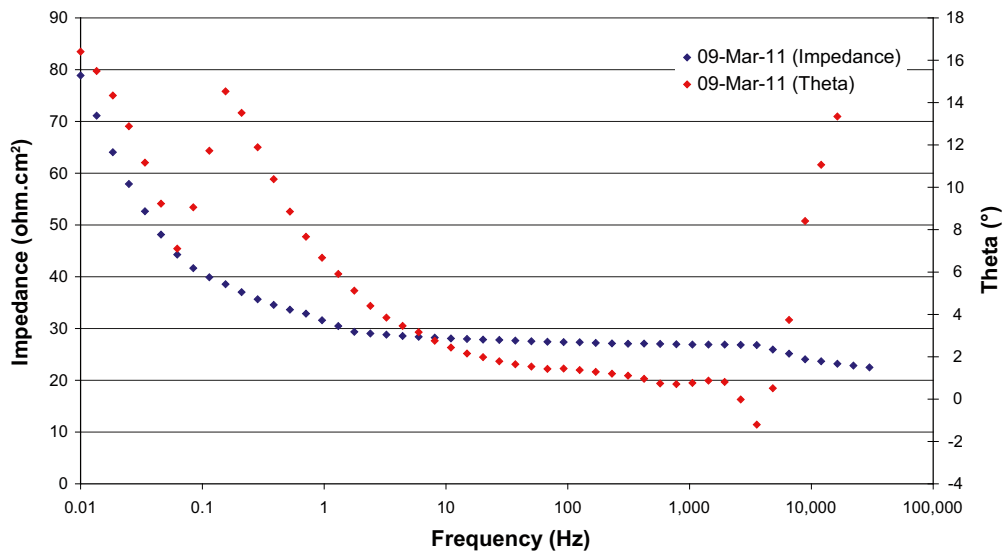
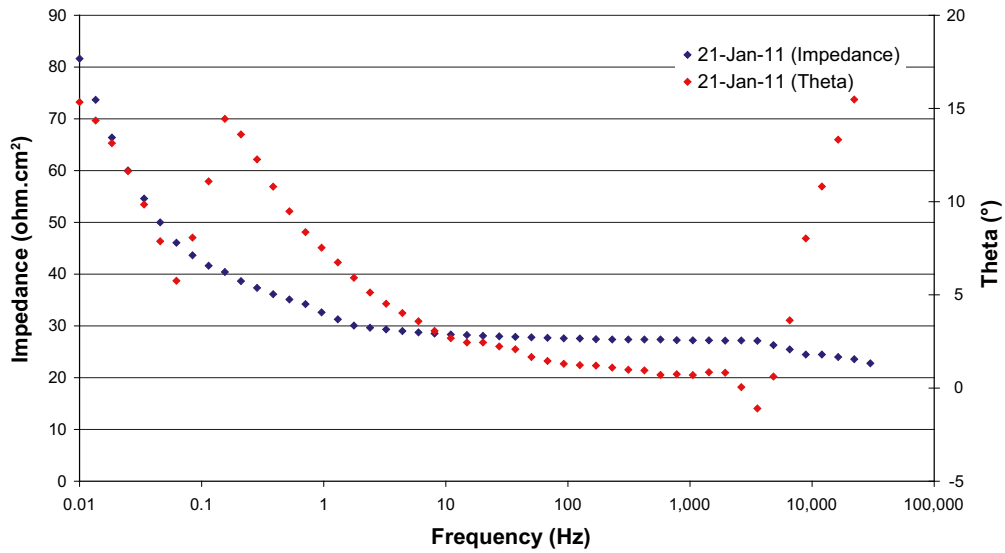


Figure A1-29. Bode plots of copper in Experiment 3 (low density bentonite).

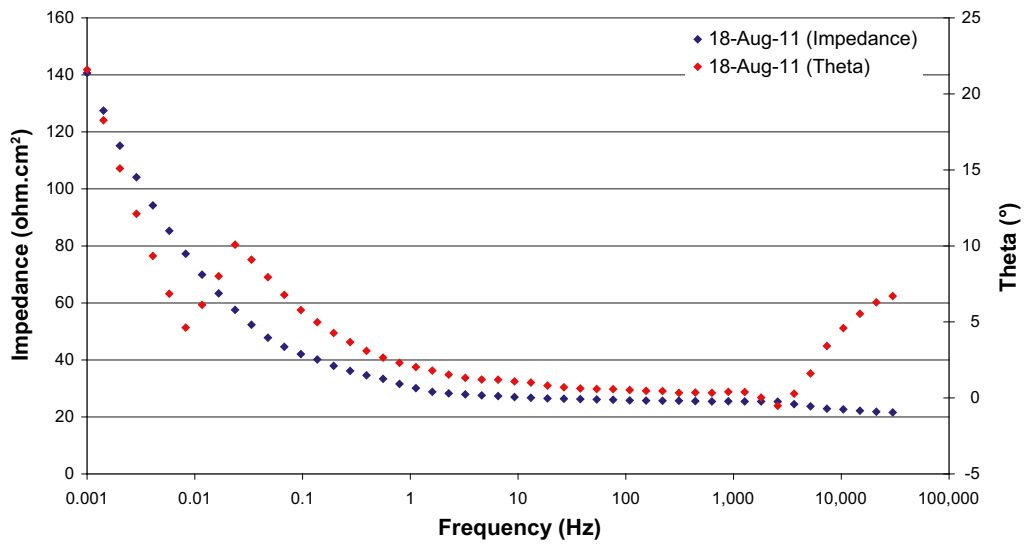
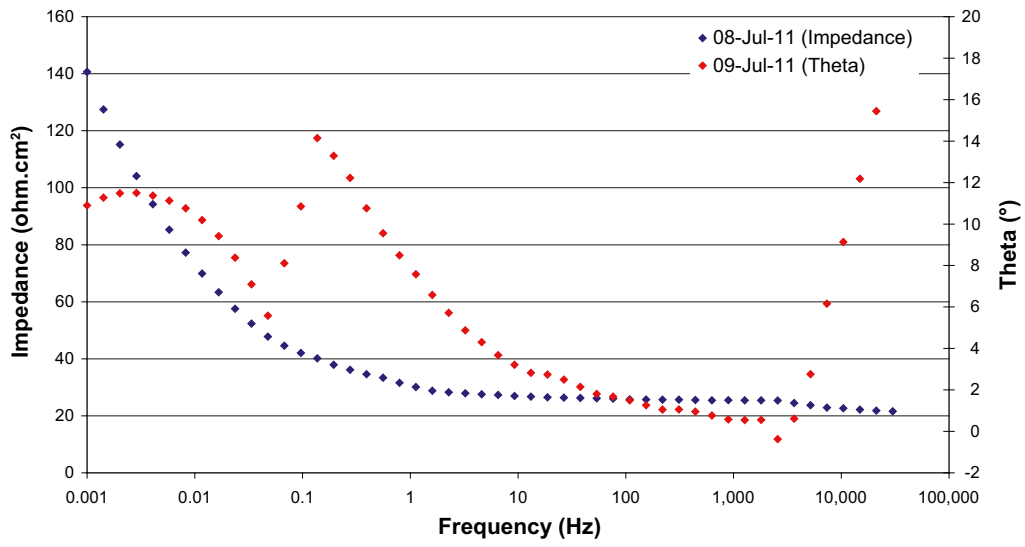


Figure A1-30. Bode plots of copper in Experiment 3 (low density bentonite).

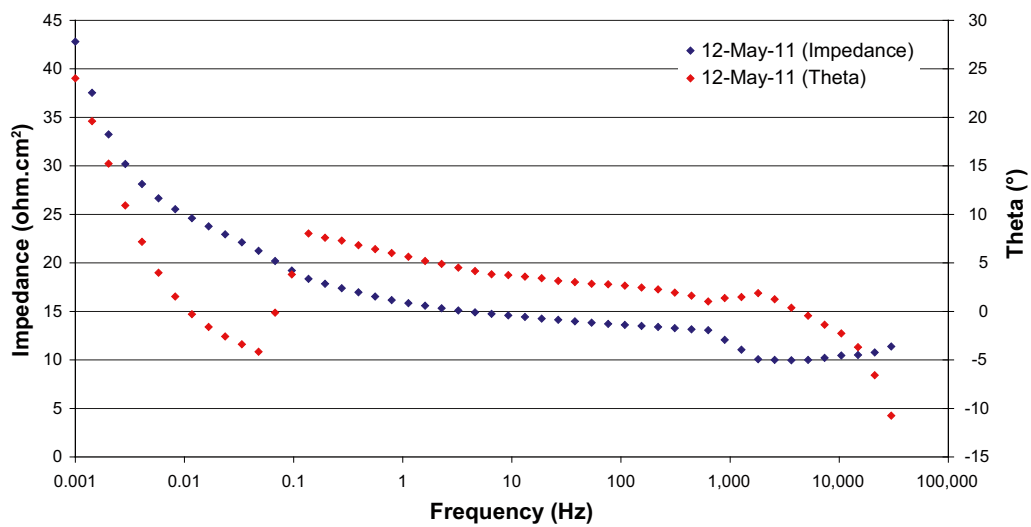
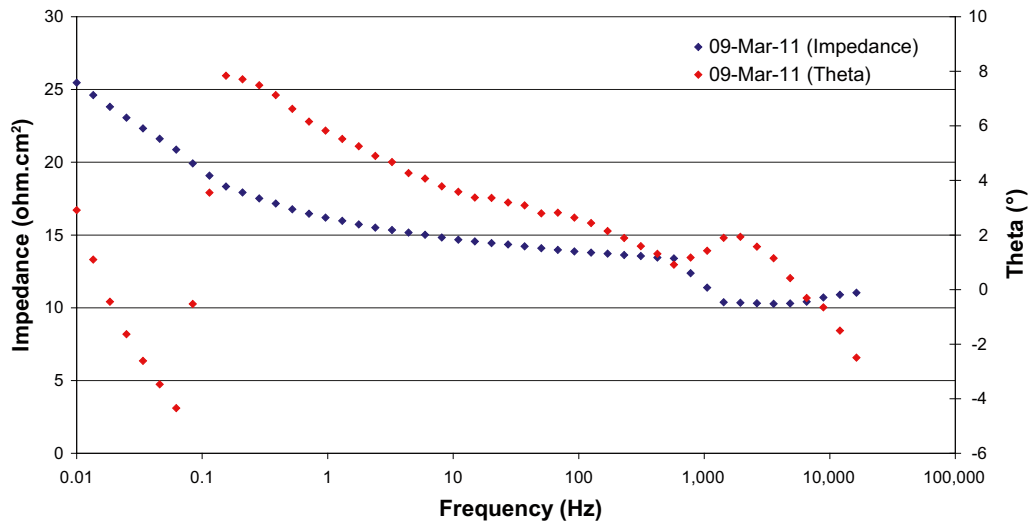
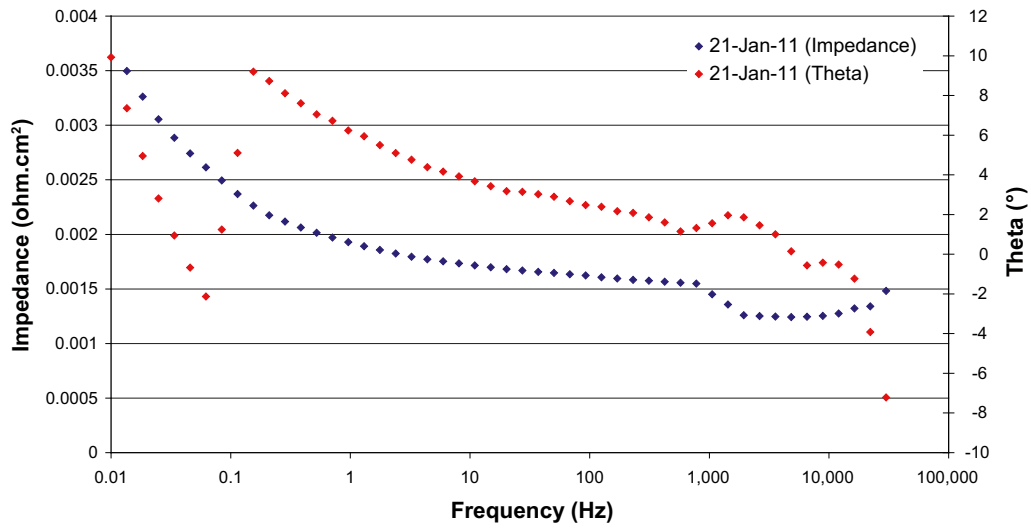


Figure A1-31. Bode plots of cast iron in Experiment 5 (no bentonite).

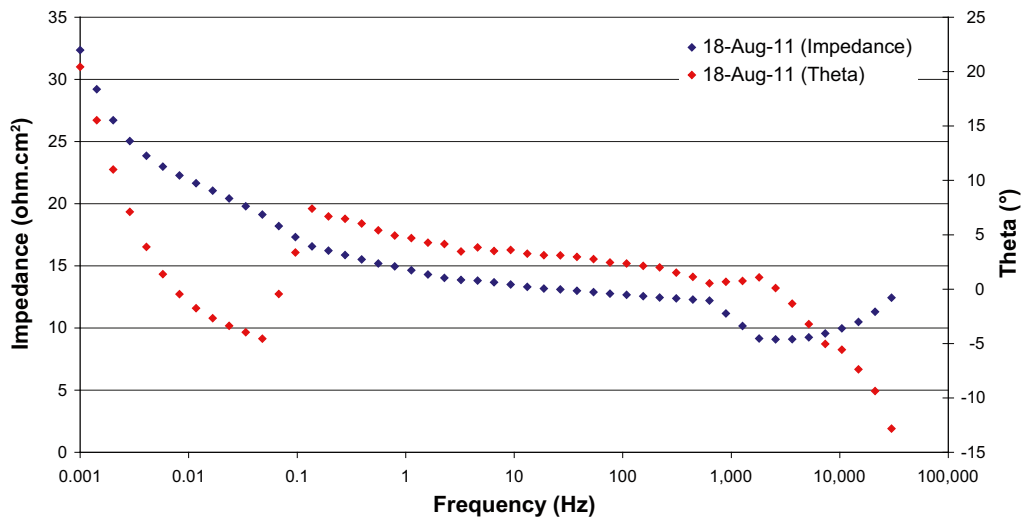
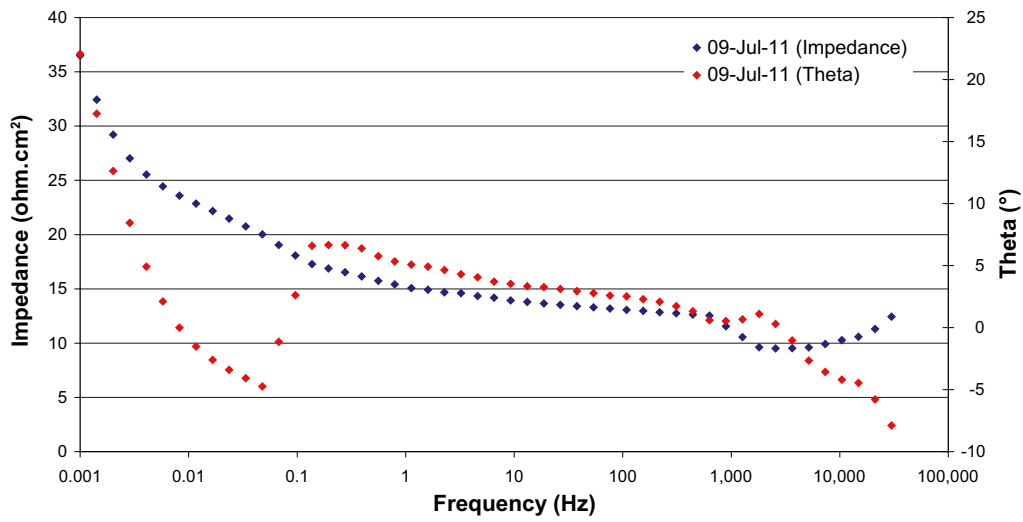


Figure A1-32. Bode plots of cast iron in Experiment 5 (no bentonite).

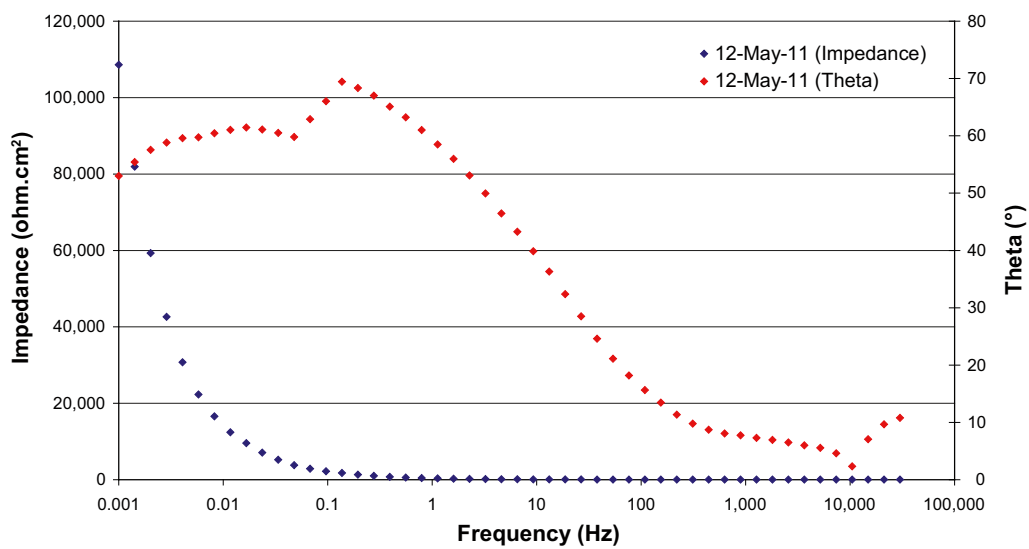
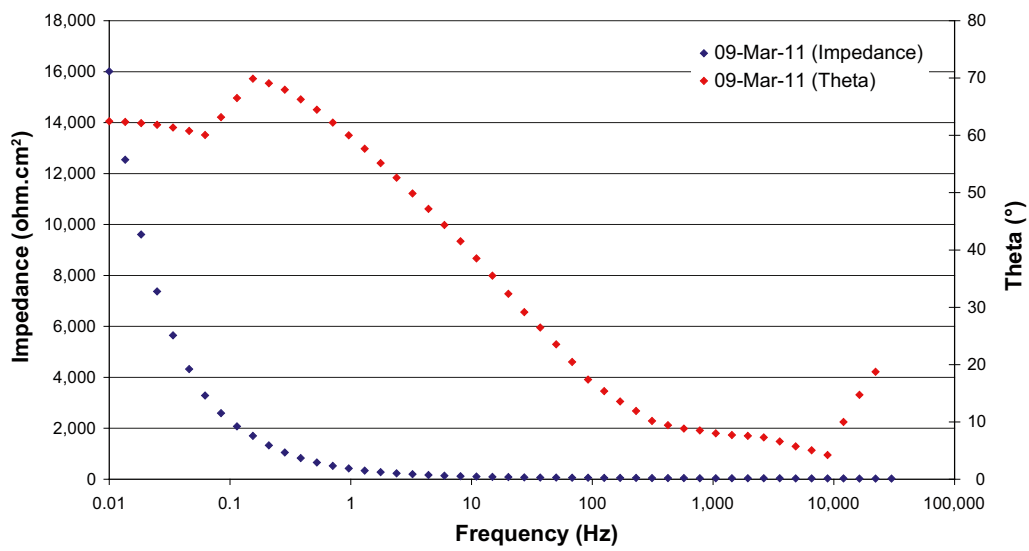
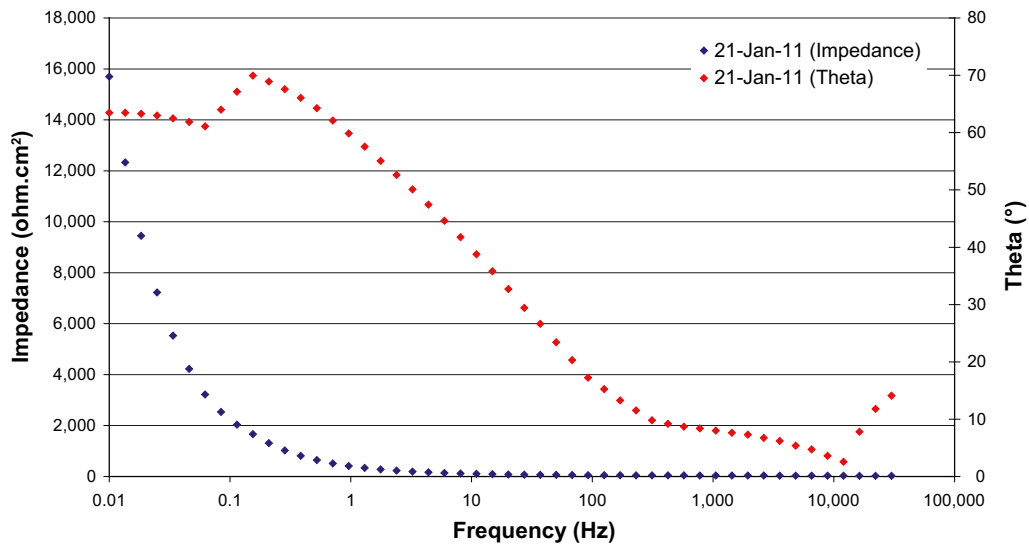


Figure A1-33. Bode plots of copper in Experiment 5 (no bentonite).



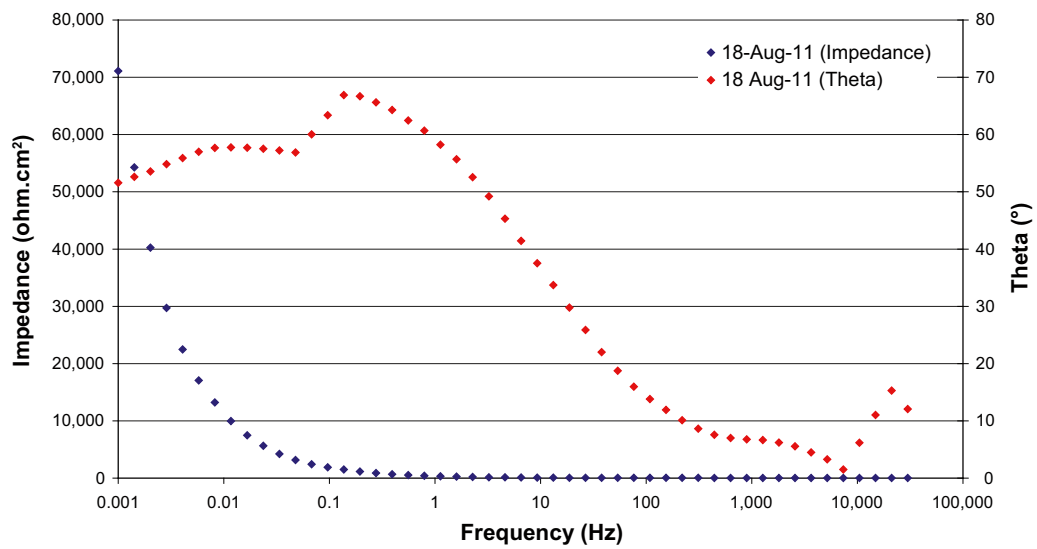
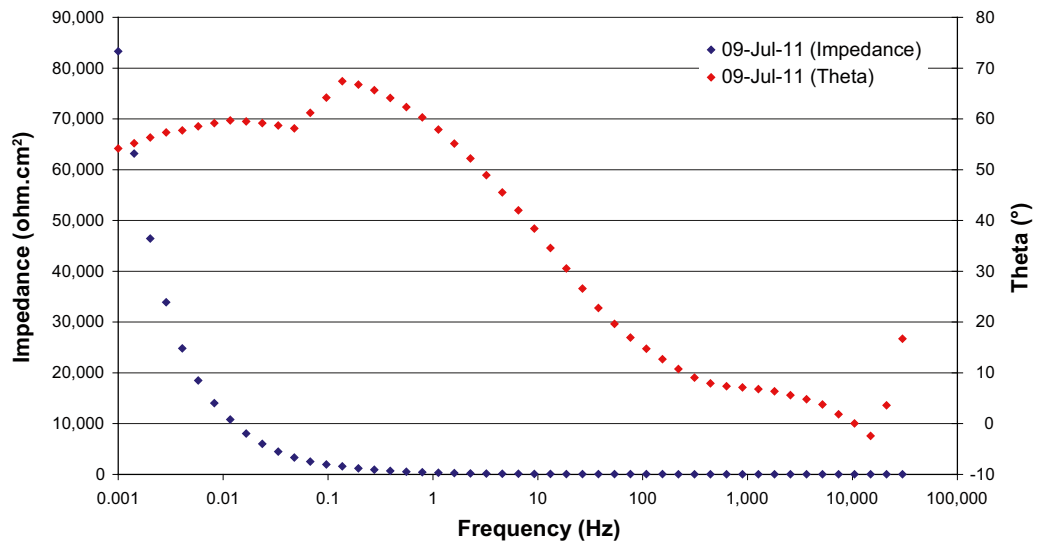


Figure A1-34. Bode plots of copper in Experiment 5 (no bentonite).