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# **Investigation of Eh, pH and corrosion potential of steel in anoxic groundwater**

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AEA Technology

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# **Investigation of Eh, pH and corrosion potential of steel in anoxic groundwater**

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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 and do not necessarily coincide with those of the client.

# Executive Summary

SKB intend to dispose of the spent nuclear fuel produced by Sweden's eleven nuclear reactors by encapsulating it in corrosion-resistant copper canisters containing a cast iron or carbon steel insert. After encapsulation, the fuel will be transported to a geological repository, where the containers will be deposited at a depth of 500 to 700m in granitic rock and surrounded by a bentonite clay backfill material. If, or when the copper corrosion shield fails, the iron insert will be in contact with oxygen-free water and hydrogen-producing, anaerobic corrosion will start.

SKB have carried out modelling calculations of the oxidising power ( $E_h$ ) of groundwater and wished to confirm the results by carrying out experimental measurements. The objective of the work described in this report was to demonstrate the feasibility of monitoring Eh, pH and corrosion potential in a cell where anaerobic corrosion of steel in artificial groundwater was occurring. To this end, gas cells similar to those used previously for anaerobic corrosion rate measurements were used as the basis for the design of an electrochemical cell. The cell incorporated electrodes to provide an in situ measurement of the redox potential,  $E_h$ , the pH and the corrosion potential of carbon steel. The main stages of the work were:

- Design of the electrochemical cell
- Preparation of silver-silver chloride and calomel reference electrodes
- Calibration of the reference electrodes and commercial glass pH electrodes against a standard hydrogen electrode
- Assembly of the test cell under anoxic conditions
- Monitoring the cell before and after the addition of steel wires to the test solution.

Details of the design of the test cell and the experimental procedures used are described. Two cells were set up. The first employed a silver-silver chloride reference electrode, which was failed after approximately 400 hours, and the second cell therefore used a calomel reference electrode. The results of the electrode calibrations and the results of the electrochemical monitoring are presented. The volume of gas produced by corrosion was also measured. The results showed that the Eh value fell rapidly to approximately  $-400$  mV vs NHE when steel wires were added to the test solution and oxygen was gettered from the artificial groundwater. The pH started at a value of approximately 10.4 but stabilised at a value of 9.7. The reasons for the fall in pH need further investigation. The corrosion potential of steel was approximately  $-620$  mV vs NHE in cell 1, but more positive in cell 2. Anaerobic corrosion of steel wires in both cells produced hydrogen.

The main conclusions from this work are:

- It is possible to make measurements of Eh, pH and corrosion potential in the presence of anaerobically corroding steel in artificial Bentonite equilibrated groundwater at 30°C.
- The presence of corroding steel leads to the rapid local deoxygenation of groundwater and a fall in the redox potential.
- Calomel electrodes appears to be more reliable than silver-silver chloride reference electrodes for long-term electrochemical measurements in artificial groundwaters.

The methods developed during the course of this work could be used to make similar measurements in the presence of dissolved uranium and other actinides. It would then be possible to monitor the environmental conditions while studying the effect of iron corrosion products on the oxidation state and solubility of actinides.

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# 1 Introduction

Sweden has eleven nuclear reactors in operation at four different sites. These reactors produce about 50% of all the electricity used in Sweden. By 2010 the current nuclear programme will have produced approximately 8000 metric tons of spent nuclear fuel. After 30 to 40 years of storage in the intermediate storage facility, CLAB, the fuel will be encapsulated in corrosion resistant disposal containers. After encapsulation, the fuel will be transported to a geological repository, where the containers will be deposited at a depth of 500 to 700m in granitic rock and surrounded by a bentonite clay backfill material. Groundwater in granitic rock in Sweden is oxygen-free and reducing below a depth of 100 to 200 meters. The redox potential below this depth ranges between  $-200$  and  $-300$  mV on the hydrogen scale and the water has a pH ranging from neutral to mildly alkaline [1,2].

Resistance to corrosion can be achieved in several ways. SKB has decided to approach the long-term corrosion problem by choosing a container material, copper, that is as close as possible to being immune to corrosion under the expected repository conditions. However, pure copper does not have sufficient mechanical strength to withstand the external overpressure and so a cast iron or carbon steel insert is used to give the waste package sufficient mechanical strength. If, or when the copper corrosion shield fails, the iron insert will be in contact with oxygen-free water and hydrogen-producing, anaerobic corrosion will start. The anaerobic corrosion rate of the ferrous insert and a number of other corrosion issues associated with this design, including stress corrosion cracking in nitric acid, galvanic corrosion and pitting corrosion, have been addressed by SKB and AEA Technology in previous work [3–14].

SKB have commissioned various chemical modelling programmes to predict the oxidising power ( $E_h$ ) of the aqueous environment in the vicinity of the HLW canisters. They wished to confirm the results of these calculations by carrying out experimental measurements of  $E_h$  in artificial groundwater in which anaerobic corrosion of steel was occurring. If this was successful further measurements would be undertaken to monitor the behaviour in a cell which also contained dissolved actinides. The objective of the current work was to demonstrate the feasibility of monitoring  $E_h$ , pH and corrosion potential in a gas cell where anaerobic corrosion was occurring. This report describes how the experiments were carried out (Section 2), presents the results (Section 3) and discusses them in Section 4.

## 2 Experimental details

The overall aim of the experiments was to set up gas cells similar to those used previously for anaerobic corrosion rate measurements [14], and to incorporate electrodes which would provide an in situ measurement of the redox potential,  $E_h$ , the pH and the corrosion potential of the steel.

The main stages of the work were:

- Design of the electrochemical cell
- Preparation of the electrodes
- Calibration of the electrodes
- Assembly of the test cell under anoxic conditions
- Monitoring the cell before and after the addition of steel wires to the test solution.

### 2.1 Design of electrochemical cell

The cell design was based on the barometric gas cells used previously for measuring the rates of hydrogen generation by anaerobic corrosion [14], but also allowed a number of test electrodes to be inserted into the test solution. The cell design is shown in Figure 1. It was designed to fit into a nitrogen-purged stainless steel glovebox. The principle behind the design of the barometric cell is as follows. When corrosion occurs the hydrogen produced causes the liquid level in the manometer tube to rise. The new volume of hydrogen in the cell can be determined from the height of the manometer liquid and hence the volume of hydrogen ( $\Delta V$ ) produced by corrosion can be calculated.

The cell was equipped with a system to allow the introduction of steel wires into the test solution after the test electrodes had reached equilibrium. The system consisted of a side arm which was designed to hold cut lengths of steel wire. The surface area of the steel wires was the same as used in previous anaerobic corrosion experiments [14].

In addition to monitoring the gas generation rate for the steel wires, measurements of pH,  $E_h$  and corrosion potential,  $E_{\text{corr}}$ , were required. Each of these parameters required a separate indicator electrode, which could be monitored with respect to a reference electrode. The top of the cell was designed to accommodate a glass pH electrode, a reference electrode, a gold electrode, for measuring the redox potential, and a steel wire electrode. The electrodes enter the cell through ground glass joints, which were sealed during the assembly procedure using epoxy resin. The design and manufacture of each of the electrodes and the glassware for preparing and calibrating the electrodes is discussed below.

## 2.2 Preparation of electrodes

### 2.2.1 Silver-silver chloride reference electrodes

There are several published recipes for the preparation of silver-silver chloride (Ag|AgCl) electrodes. The method adopted was a combination of various methods and is described in detail below.

1. Platinum wire (12 cm × 0.025 cm) was boiled in 1:1 nitric acid : water. The wire was sealed into a glass tube incorporating a ground glass joint, leaving 10 cm of exposed wire. The wire was formed into a 2 cm long spiral. Four electrodes were fabricated in this manner.
2. The platinum electrodes were anodised in concentrated nitric acid for thirty minutes at a current density of 1 mA/cm<sup>-2</sup> (total current for four electrodes 3.1mA) and washed thoroughly in distilled water. The cathode was a platinum flag.
3. KAg(CN)<sub>2</sub> salt was recrystallised from triple distilled water. The solubility of this salt is 25g/100g of water at 25°C and 100g/100g of water at 100°C. It was found that the salt was best recrystallised by dissolution in an excess of hot water (40g/100g water) followed by filtration, evaporation and salt recovery by cooling. Attempts to recrystallise using the fourfold change in solubility caused salt precipitation to occur in the filtration vessel, blocking the filter. The salt was dried in an oven at 25°C. The salt was observed to discolour if oven-dried above 55°C.
4. The platinum electrodes were silver plated by cathodising in a stirred solution of KAg(CN)<sub>2</sub> (10g/litre) using a platinum anode and a current density of 0.4 mA cm<sup>-2</sup> for a period of six hours. A drop of AgNO<sub>3</sub> solution was added to the KAg(CN)<sub>2</sub> solution prior to plating to remove excess free cyanide. The turbidity produced by the AgNO<sub>3</sub> addition was allowed to settle and the clear solution was decanted into the plating cell. The plating was carried out in the dark, using an electrolysis cell in which the anode compartment was separated from the main solution across a glass frit. A separate anode compartment is essential to prevent contamination of the silver chloride deposit with adsorbed cyanide. Four platinum electrodes were plated simultaneously. The electrodes were rotated counter clockwise one quarter turn every thirty minutes to ensure an even current distribution across the spiral. The solution was not deoxygenated.
5. The silver plated electrodes were soaked in concentrated ammonium hydroxide for four hours, followed by soaking in distilled water for two days. The water was changed at regular intervals. The electrodes were not allowed to dry out before chloridisation.
6. The silver electrodes were chloridised by anodising in 0.1M HCl at a current density of 0.4 mA cm<sup>-2</sup> for 30 minutes. The cathode was a platinum flag in a separate compartment.



7. The electrodes were soaked in distilled water for a day. The water was changed regularly. They were stored in a solution of 0.01M NaCl with their contacts shorted in a five compartment glass 'candelabra' cell. Two electrodes were used for the calibration of the commercial pH electrode (see section 2.4). The remaining two electrodes were stored for comparison purposes. One of the stored electrodes was used intermittently at frequent intervals to cross-check the stability of a similar electrode permanently being monitored against calomel reference electrode (see section 2.2.2) in simulated groundwater. It was rinsed before and after immersion into the groundwater. The second electrode was unused.

### **2.2.2 Calomel reference electrodes**

Initially, silver-silver chloride reference electrodes were used, but some problems with long-term stability were found (see section 3.2) and a calomel reference electrode was used for one of the corrosion test cells. The design of the calomel electrode is shown in Figure 2. It consisted of a platinum through-glass electrical contact and a ground glass cup to hold the reference solution and the chemical components. Contact was made between the calomel electrode and the test solution via the fine capillary of the ground glass joint. The reference solution was the simulated groundwater, thereby eliminating any errors from liquid junction potentials.

The calomel electrode was prepared in the following way. Sufficient clean dry mercury was placed into the ground glass cup to completely cover the platinum contact wire. Powdered, dry mercurous chloride powder was added on top of the mercury and the cup was inverted several times until the calomel formed a skin around the mercury bead. Artificial groundwater was pipetted into the cup, taking care to remove entrapped gas bubbles, and the electrode was assembled. Fine platinum wire was used to bind the cup onto the holder. The electrode was left several hours in artificial groundwater to equilibrate.

### **2.2.3 Hydrogen electrodes**

A hydrogen reference electrode was required to calibrate the pH electrode. The hydrogen electrode consisted of:

- a palladium black electrode
- a compartment containing a solution of fixed pH that can be pre-saturated with hydrogen at a known partial pressure.
- a system for the removal of oxygen from the hydrogen gas.

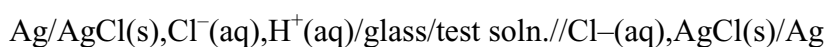
The palladium hydrogen electrodes were fabricated as follows:

1. Platinum wire (12 cm × 0.025 cm) was boiled in 1:1, nitric acid : water. The wire was sealed into a glass containment leaving 10 cm of exposed wire, which was formed into a 2 cm long spiral. Two electrodes were fabricated in this manner. The electrodes were anodised in nitric acid prior to plating. The cathode was a platinum flag.
2. PdCl<sub>2</sub> was purchased in a 1g sealed ampoule. The PdCl<sub>2</sub> was dissolved into a solution of 14 ml of concentrated HCl in 100 ml of triple distilled water (total volume 114 ml). The dissolution of the PdCl<sub>2</sub> was a slow process; it dissolved over 24 hours to give a deep red plating solution. The two platinum spiral electrodes were cathodised simultaneously for three minutes at 0.3A total current. The plating solution was unstirred. The anode was a platinum flag in a separate anode compartment. The platinum was pre-cleaned in aqua regia. The electrodes were rinsed in distilled water after plating.
3. The platinum spiral electrodes coated with palladium black were cathodised in 0.5M H<sub>2</sub>SO<sub>4</sub> solution for 30 minutes at 0.3 mA total current. The anode was a platinum flag in a separate compartment. The electrolysis was carried out immediately prior to the electrode calibration experiment (see section 2.4). It could be repeated at any stage if the hydrogen electrode potentials measured against each other were unstable. The electrodes were washed in distilled water before the calibration experiment to avoid the transfer of protons into the calibration solution.
4. It should be noted that palladium black electrodes should not be allowed to dry out because finely divided palladium is pyrophoric in air. A palladium electrode that had been allowed to dry out spontaneously ignited the hydrogen gas atmosphere in the envelope above the hydrogen electrode compartment when it was lowered into the neck of the vessel. Although this was not unlike the familiar ‘pop’ used in the school experiment to demonstrate hydrogen combustion, the consequences could have been more serious. It is recommended that the electrodes are placed into the solution in the glass envelope before hydrogen gas is bubbled through the solution.
5. Residual oxygen was removed from the hydrogen stream by passing it through a heated column (200°C) containing a catalyst of finely divided copper on a ceramic support (BASF Catalyst R 3-11). In air the finely divided copper is oxidised to cupric oxide and the catalyst was therefore pre-treated by reducing it back to copper in hydrogen at 200°C. This process took several hours and produced a large volume of water as reaction product.
6. The hydrogen was discharged from the electrode compartment through a capillary restriction rather than the classical external bubbler. This avoided pressure fluctuations, which could modify the measured potentials. A tap was included in the cell to divert hydrogen through the envelope above the solution during measurements, rather than disturbing the solution by bubbling the gas. In practice, the tap was not used in the calibration experiments, as fluctuations in the potential due to hydrogen bubbles were not observed when the hydrogen supply was diverted.

## 2.2.4 pH electrodes

The measurement of pH was made using commercially available glass electrode half-cells which were obtained from Metrohm (Model number 6.0130.100). The electrodes consisted of a glass cylinder, at the tip of which was a glass membrane. Inside the glass cylinder was a silver-silver chloride electrode immersed in a pH 7 buffer solution containing 3M KCl. Metrohm produce two glass types called U-glass and T-glass. T-glass is specifically designed for ion deficient solutions and has a lower resistance. The T-glass variety was chosen for the current work because the T-glass electrodes are supplied with a ground glass joint incorporated into the outer glass sheath and this enabled them to be mounted into the head of the calibration cell and the test cell.

In commercial pH electrodes the sensor is usually a two-electrode cell containing two silver-silver chloride reference electrodes arranged as follows:



The reference electrode and electrolyte on the left are contained within a thin glass electrode membrane and the reference electrode on the right is connected by a salt bridge to the test solution, which contains the unknown concentration of hydrogen ion. In the current experiments, the silver-silver chloride reference electrode on the right hand side of the cell was provided separately and it was mounted directly in the test solution, to avoid the possibility of junction potentials. The potential difference of the cell corresponds to the potential developed across the membrane and is determined by the activity of protons in solution (i.e. the pH). A calomel reference electrode could be used to replace the silver-silver chloride reference electrode in the right hand side of the cell shown above.

## 2.2.5 E<sub>h</sub> electrode

The E<sub>h</sub> redox electrode was a gold wire coil. The gold was attached to platinum wire, which was sealed through the glass tip of an electrode feedthrough to an external wire connector. Only the gold electrode was in the solution. To avoid possible galvanic potential errors, the connection between the platinum wire and the gold wire was isolated from condensate using a blob of epoxy resin. Before insertion into the corrosion cell the gold was flamed and then electrochemically treated by potential cycling in a solution of HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (1:1:1 by volume) against a platinum counter electrode. The gold was cycled between +1.2V to -1.8V at a sweep rate of 10mV/s. The gold was held at -1.8V for 5 minutes, washed in distilled water and transferred to the cell.

## 2.2.6 Steel electrode

A 1 mm diameter BS4360 grade 43A carbon steel wire was used as the electrode for measuring the corrosion potential. It was attached to a platinum wire that was sealed through a glass envelope to an external wire connection. The platinum wire was not in contact with the test solution. To prevent a possible galvanic potential developing at the

platinum electrode junction through condensation the contact was protected with an epoxy resin coating.

Steel wires of the same composition as the steel electrode were used in the side arm. The wires were approximately one centimetre long, which gave a total surface area of  $\sim 0.094\text{m}^2$ . The total weight of wires was 177g and 173g in cell 1 and cell 2 respectively.

### **2.3 Measuring equipment and datalogging**

Potential measurements were made using a high precision, high input impedance ( $10^9\text{ohm}$ ), calibrated digital voltmeter (Schlumberger 7081). The electrodes were connected permanently to individual voltage followers to further increase the input impedance to  $10^{12}\text{ohm}$ . A Solartron Minate 7010 multiplexer unit was used to interface between the voltmeter and the voltage followers. This enabled eight input voltages to be scanned at periodic intervals under the control of a personal computer equipped with an IEEE interface card. The datalogging control programme was written in Visual Basic. The voltmeter performed a running average to obtain a six figure reading (i.e. the resolution of the instrument was  $1\ \mu\text{V}$ ). Six consecutive readings were displayed for each measurement. The variation between these readings was of the order of  $\pm 5\ \mu\text{V}$ . Only the last reading in each set was permanently recorded.

### **2.4 Calibration of reference electrodes**

The purpose of the calibration procedure was to determine the following:

- The potential of the silver-silver chloride electrodes with respect to the standard hydrogen electrode;
- The reproducibility of the silver-silver chloride electrodes;
- The relationship between the potentials of the glass electrodes and pH.

The calibration cell consisted of a reaction vessel with a separate, removable inner compartment containing the hydrogen electrode assembly. The inner compartment consisted of two hydrogen electrodes and a bubbler to presaturate the solution with hydrogen. The electrolyte in the inner compartment was separated from the electrolyte in the reaction vessel by a large bore capillary restriction. This arrangement allowed rapid chemical component mixing throughout the electrolyte while maintaining a stable hydrogen partial pressure in the inner compartment. The hydrogen could be passed through the solution during presaturation or above the solution during measurement by the use of a two-way tap. The reaction vessel contained feedthroughs for two pH electrodes, two silver-silver chloride electrodes and a burette. A photograph of the apparatus is shown in Figure 3.

A 0.01M sodium chloride solution was prepared using triple distilled water. The sodium chloride had been recrystallised three times from triple distilled water followed by pyrolysis in a platinum crucible. A 0.01M hydrochloric acid solution was prepared from a standard 0.1N concentrated volumetric solution (Convol, BDH Ltd) which was further diluted by a factor of 10. The Convol HCl product was  $0.1N \pm 0.2\%$ . A 400 ml aliquot of 0.01M NaCl was added into the cell, which was then placed in a water bath controlled to  $30.0 \pm 0.1^\circ\text{C}$ . Two pH electrodes and two silver chloride electrodes were fitted to the cell and allowed to equilibrate. Oxygen-free hydrogen was bubbled over the palladium electrodes at a flow rate of  $50 \text{ ml min}^{-1}$ , using a Tylan mass flow controller. The hydrogen was saturated with water vapour before it entered the test cell by passing it through a Dreschel bottle containing 0.01M NaCl solution at  $30^\circ\text{C}$ .

The potentials of two pH glass electrodes and two palladium black hydrogen electrodes were measured simultaneously against a silver-silver chloride electrode in an aqueous solution of 0.01M NaCl. The potential of the silver-silver chloride electrode was measured against a separate silver-silver chloride electrode in the same solution to monitor the reproducibility and stability of the reference electrode. It was observed that it could take up to thirty minutes to saturate the solution enclosed within the hydrogen electrode compartment with hydrogen and for stable potentials to be reached.

The pH of the solution was adjusted, while maintaining constant chloride ion concentration, by the addition to the reaction vessel of aliquots of 0.01M HCl, according to the method of Gran [15]. Initially, two acid additions were made to the 0.01M NaCl solution using a burette. However, the accuracy of the burette was suspect due to the retention of titrant in a bulb in the delivery capillary that had formed in the glass during the modifications that were made to fit the burette into the cell. All further acid additions were made with a pipette. The potentials of the two glass electrodes and the two hydrogen electrodes were recorded at equilibrium against a silver-silver chloride electrode for acid concentrations in the range 2.7 to 4 units of pH. Equilibrium could take up to an hour to be established for each acid addition. This was because chemical mixing between compartments was restricted and the cell was unstirred to prevent the distribution of residual oxygen into the hydrogen electrode compartment. The pressure was monitored at each potential measurement to allow the hydrogen electrode potential to be corrected for standard temperature and pressure if necessary. This correction also required the vapour pressure of the solution at the temperature of the experiment to be known. The value for water vapour pressure at  $30^\circ\text{C}$  was taken as 31.82 mm Hg. The reduction of vapour pressure due to salt addition in 0.01M solution at  $30^\circ\text{C}$  is negligible.

It was found that the potentials of the commercial pH electrodes were noisy. The noise was of two types: general pickup from the laboratory, and a downward drift in measured potential caused by attaching the precision voltmeter (Schlumberger 7081) between the reference electrode and the pH electrode during multiplexed sampling. The input impedance of the voltmeter was  $10^9 \Omega$ . To overcome this problem a voltage follower was constructed using a 3140 operational amplifier mounted directly on the top of the pH electrode where it left the cell. This improved the input impedance to  $10^{12} \Omega$  and reduced the noise pickup from the laboratory to an acceptable level.

The voltmeter performed a running average to obtain a six-figure reading. Three such iterations were required to establish a consistent reading to  $\pm 0.00005\text{V}$  after connection between the reference and the pH electrode. A drift of  $0.1\text{mV}$  or less was observed. The reason for this behaviour is not fully understood, but it may have been due to removal of charge from the highly resistive glass electrode, even though it was continuously connected to the operational amplifier input and such a drift would not be expected. The performance of the operational amplifier and the calibration of the voltmeter were checked at intervals against a Weston standard cell. No offset voltage drift of the operational amplifier was observed throughout the seven-day period of the calibration experiments.

## **2.5 Experimental procedure**

### **2.5.1 Assembly of test cell**

Before assembly, to ensure that no contamination occurred, all the glassware was soaked in a solution of potassium permanganate and concentrated sulphuric acid in the ratio of  $1\text{g KMnO}_4 / 11\text{H}_2\text{SO}_4$ . This solution oxidises any organic contamination on the surface of the glassware. The acid was rinsed out with demineralised water, then steam cleaned until no condensation was visible, indicating that the glassware was clean. The glassware was allowed to dry naturally in air.

The test solution, artificial Bentonite-equilibrated groundwater, was prepared using triple distilled water to which  $31.56\text{ g/litre}$  sodium chloride and  $1.06\text{ g/litre}$  sodium carbonate were added. The pH of freshly prepared solution was  $\sim 10.2$ .

The carbon steel test electrode and the wires to be used in the side arm were pickled to remove the air-formed oxide film by immersion in  $10\%$  HCl for five minutes, followed by washing in distilled water and ethanol. The pickled wires were loaded into the sidearm using a custom-built glass loading funnel.

The calibrated electrodes were assembled into the two test cells and the ground glass joints were sealed by applying epoxy resin to the surface of the joints. The Dreschel bottle reservoir was filled with di-n-butyl phthalate (DBP, a low vapour pressure liquid). The cell was then filled with artificial groundwater to a level  $1\text{ cm}$  below the point of attachment of the wire electrodes to the platinum feed-through wires. The cell was transferred to the nitrogen-purged glovebox where it was allowed to deaerate for two days. The valves were then closed, the assembly was removed from the glovebox and the precision bore tube was sealed in place with epoxy resin.

Finally, the cell was evacuated through the central gas tap and backfilled with hydrogen three times. A hydrogen atmosphere was retained in the cell. The test cell temperature was controlled by immersion in a thermostatically controlled water bath at  $30\pm 2^\circ\text{C}$ .

### **2.5.2 Monitoring the test cell**

After assembly, the test cells were monitored for a few days using the PC-controlled datalogging system, until stable values were reached, and then the steel wires were transferred from the side arm to the main body of the cell using a permanent magnet. The potentials of the various electrodes against the reference electrodes were monitored every twenty minutes for over five thousand hours using the PC based datalogging system.

The volume of hydrogen produced through anaerobic corrosion was determined by measuring the height of the liquid column in the manometer.

## 3 Results

### 3.1 Electrode calibration

#### 3.1.1 Calibration of silver chloride electrode

The results of the Gran titration for the silver-silver chloride electrode against the two hydrogen electrodes are shown in Figure 4. The figure shows the change in the potential of the hydrogen electrode in 0.01M sodium chloride against a silver-silver chloride electrode as the pH was changed by titration with 0.01M hydrochloric acid. The potential changes were due to the relationship between pH and the potential of the hydrogen electrode. The potential of a hydrogen electrode is determined by the reduction of protons on the surface of the palladium black electrodes, according to the equation:



The electrochemical potential for this reaction,  $E$ , is given by the Nernst equation:

$$E = E_0 - 2.303 \frac{RT}{nF} \log \frac{[\text{H}_2]}{[\text{H}^+]^2} \quad (2)$$

Where  $R$  is the gas constant,  $T$  is the temperature in Kelvin,  $n$  is the number of electrons transferred in reaction 1,  $F$  is Faraday's constant, and  $[\text{H}_2]$  and  $[\text{H}^+]$  are the activities of hydrogen and protons respectively.  $E_0$  is the standard equilibrium potential of the hydrogen electrode at unit activity of protons and hydrogen, which by definition is zero volts. Equation (2) can be written as:

$$E = E_0 + 2.303 \frac{2RT}{nF} \log [\text{H}^+] - 2.303 \frac{RT}{nF} \log [\text{H}_2] \quad (3)$$

and substituting  $\text{pH} = -\log [\text{H}^+]$  gives:

$$E = E_0 - 2.303 \frac{2RT}{nF} \text{pH} - 2.303 \frac{RT}{nF} \log [\text{H}_2] \quad (4)$$

Since the activity of hydrogen is equivalent to its pressure in atmospheres, at 298K, and taking  $R$  as  $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $n$  as 2, and  $F$  as  $96,484.6 \text{ C equiv}^{-1}$ , this equation reduces to:

$$E = E_0 - 0.059 \text{ pH} - 0.0295 \log [\text{p}_{\text{H}_2}] \quad (5)$$

where  $\text{p}_{\text{H}_2}$  is the partial pressure of hydrogen. Therefore, a plot of potential against pH should produce a plot with a slope of 59 mV and an intercept of zero, for a pressure of 1 atmosphere and temperature of 25°C. At 30°C the slope should be 60.1 mV; the actual



slope of the plot in Figure 4 is 59 mV. Since the potentials were measured against the silver-silver chloride electrode the intercept of the line at pH 0, which corresponds to the standard conditions for the hydrogen electrode, is equivalent to the equilibrium potential for the silver-silver chloride electrode in 0.01M chloride against a normal hydrogen electrode (NHE). The values for the silver-silver chloride electrode with respect to the two standard hydrogen electrodes were 344.6 mV and 345.4 mV. These values were not corrected for variations in atmospheric pressure, but a change of 20 mm Hg gives a variation in the hydrogen potential of only ~0.4 mV, based on equation (5), which was within the experimental variation between the hydrogen electrodes. Formally, the correction to the measured EMF due to the deviation of the partial pressure of hydrogen,  $p_{H_2}$ , from unity is given by:

$$p_{H_2} = p_{\text{barometric}} - p_{H_2O} + 0.03h \quad (6)$$

where  $p_{\text{barometric}}$  is the barometric pressure and  $p_{H_2O}$  is the vapour pressure of water in mm Hg respectively. The last term allows for the hydrostatic pressure change created because the bubbler was below the surface of the solution and also for a correction due to supersaturation with hydrogen in the vicinity of the electrodes, caused by the excess pressure within the bubble. The term 0.03h is empirically derived [16], where h is the depth of immersion of the bubbler below the solution in mm. The corrections to the potentials are of the order of 6–10  $\mu\text{V}$ , and are therefore insignificant for the purposes of the measurements.

The potential of the silver-silver chloride electrode depends on the activity of chloride and is given by:

$$E = E_{0,Ag/AgCl} - 2.303 \frac{RT}{nF} \log [a_{Cl}] \quad (7)$$

where  $a_{Cl}$  is the activity of chloride ion. The activity can be calculated by taking the product of the concentration in molality,  $m$ , and the activity coefficient,  $\gamma$ . At 0.01M the molality is virtually identical with the molarity. The mean activity coefficient for sodium chloride at 0.01m is 0.902 [17]. Using these values in equation 6, the values of  $E_{0,Ag/AgCl}$ , the standard equilibrium potential for silver-silver chloride in unit activity chloride, based on the two hydrogen electrodes and taking the temperature, T, as 303K, were 222.4 and 221.6 mV vs NHE. For comparison, the reported values for  $E_{0,Ag/AgCl}$  at 303K are 219.0–219.2 mV vs NHE [18].

Using equation 6 the absolute value of the silver-silver chloride potential in the test groundwater can be calculated, assuming a molality of 0.54m and an activity coefficient of 0.682 (based on the value for 0.5m NaCl [17]). This calculation assumes that the activity coefficient for sodium chloride is unaffected by the presence of sodium carbonate in the groundwater. The calculated values for the silver chloride reference electrode in groundwater were 247.7 mV or 248.5 mV vs NHE, based on the two hydrogen electrode measurements. For the purposes of the monitoring experiments a potential of 248 mV vs NHE was used.

### 3.1.2 Calibration of glass electrodes

The results of the Gran titration for the glass electrodes against the two hydrogen electrodes are shown in Figure 5. The potential of the glass electrode is given by:

$$E_{glass} = E_{0,glass} - \frac{2.303 RT}{nF} [pH] \quad (8)$$

Thus a plot of potential,  $E_{glass}$ , against  $\log[H^+]$  should be linear, with a slope of  $-60$  mV for a temperature of  $30^\circ\text{C}$ . Figure 5 shows that the slope of the calibration plot was  $-58.6$  mV. At pHs greater than  $\sim 3.3$  the graph is non-linear. This non-linearity is due to an artefact of the titration method. The pH of the  $0.01\text{M}$  NaCl at the start of the titration had a value of  $\sim 6.0$  but it decreased with time due to dissolution of carbon dioxide into the reaction vessel. Also the titrant was relatively concentrated, causing a large pH change for a very small volume of added titrant. The errors in the proton concentration were therefore large at the beginning of the experiment. However, as the pH in the reaction vessel approached within two units of the titrant the accumulative errors became very much reduced and below pH 3.3 the plots were linear. The value of the intercept,  $E_{0,glass}$ , was  $+276$  mV vs silver-silver chloride ( $0.01\text{M}$  Cl), which, by applying equation 6, is equivalent to  $+373$  mV vs silver-silver chloride in artificial groundwater. The potential of a glass electrode is independent of the chloride concentration, but the presence of sodium ions can introduce an error of a few mV. The Metrohm pH electrode 6.0130.100 uses a T-glass membrane which has no cross sensitivity to sodium ions at  $\text{pH} < 12$ . Therefore the equation describing the response of the glass electrode in artificial groundwater is:

$$E = 0.373 - 0.586 [pH] \quad (9)$$

so that for a given potential measurement for the glass electrode in artificial groundwater against silver-silver chloride, the pH is given by:

$$pH = \frac{0.373 - E}{0.0586} \quad (10)$$

This relationship was used in monitoring and calculating the pH in the test cells.

## 3.2 Results of monitoring

### 3.2.1 Corrosion cell 1

The results of monitoring the pH,  $E_h$  and corrosion potential of steel in cell 1 during the first seventeen days are shown Figure 6 to Figure 9. The steel wires were transferred to the test solution after 239 hours. A decrease in pH of about 0.3 pH units was observed, prior to addition of the wires. The pH response was noticeably more noisy after addition of the wires.

The potential of the gold electrode,  $E_h$ , was stable for approximately 180 hours, with a noise amplitude of less than 5 mV and a mean value of approximately +200 mV vs NHE (Figure 7). This noise may have been due to spurious electrical interference or localised fluctuations in redox potential. After approximately 180 hours the  $E_h$  value became more negative and when the steel wires were transferred from the sidearm the  $E_h$  value became more negative by 4–500 mV, Figure 8.

The corrosion potential of the steel electrode remained at approximately –600 mV vs NHE during the first part of the experiment. This negative value is consistent with anaerobic corrosion occurring by the reduction of water to hydrogen.

The response of the pH,  $E_h$  and steel electrodes over the entire monitoring period of almost 7,500 hours are shown in Figure 10. These plots show that there was a sudden change in the potential of all the electrodes after ~470 hours. The fact that the electrodes shifted potential simultaneously indicates that there had been a failure of the silver-silver chloride reference electrode and consequently the use of an alternative reference electrode system, the calomel reference electrode, was considered and implemented in cell 2.

### 3.2.2 Calibration of calomel electrode system

In order to address the unexpected failure of the silver-silver chloride electrode in cell 1, some trials were carried out with a calomel reference electrode of the design shown in Figure 2. The stability of a calomel reference electrode was assessed by monitoring its potential difference against a pair of silver-silver chloride electrodes. One silver-silver chloride electrode had been prepared according to the instructions in section 2.2.1. The other electrode was a commercially available silver-silver chloride electrode supplied by Clarke Electromedical Instruments (model number E207). The solution for this stability test was a naturally aerated artificial Bentonite-equilibrated groundwater. The results are shown in Figure 11.

No degradation of either of the silver-silver chloride electrodes was observed during 5000 hours of testing. The Ag/AgCl potential was  $-46 \pm 4$  mV and  $-50 \pm 5$  mV vs calomel for the AEA and Clarke Electromedical electrodes respectively over the first 2200 hours. Between 2000 and 2500 hours there was a spurious unexplained decrease in the measured potential and after this point the potential of the two electrodes deviated. The AEA electrode returned to a potential of  $-45 \pm 2$  mV. The Clarke electrode became noisy and decreased to a minimum potential of –70mV. It is clear that water was being lost from the container by evaporation and this altered the chloride concentration of the groundwater. The evaporation loss was sufficient to break the contact of the Clarke Instruments electrode with the test solution. The Clarke electrode is a porous pressed AgCl pellet composition around a silver wire. The electrode was mounted vertically with the sensor tip below the surface of the solution. As the tip of the electrode approached loss of contact with the solution the chemical composition within the pores could have been very different to that in the bulk solution and the signal became noisy. When contact with the solution was lost the voltage follower output was driven towards the negative voltage rail (–14V). Four such transitions were observed at 2700, 4100, 4500 and 4900 hours respectively. Spikes can be observed in the potential of the AEA

silver chloride electrode where water has been added to the container to restore the contact. The AEA electrode performed well showing an expected positive potential shift with the chloride ion dilution followed by a decrease in potential over time as evaporation proceeded. The Clarke Medical electrode deviated from the theoretical value and its chemistry was modified with age in the groundwater. The AEA construction was more reliable and more reproducible.

The stability of the calomel reference was also checked by measuring the potential of a freshly prepared calomel electrode against the ageing calomel reference. Fresh calomel electrodes were introduced after 4 days, 112 days and 188 days. The difference between the two calomel electrodes after these periods was +1.2 mV, -3.0 mV and +1.0 mV respectively. The measurement was achieved by replacing the Clark electrode with the freshly prepared calomel electrode. Two spikes corresponding to the 122 day and 188 day test are labelled in Figure 11. The freshly prepared calomel electrode was removed from the solution after the measurement.

The potential of an Ag|AgCl electrode prepared as described in section 2.2.1 was also measured against the ageing calomel reference. This electrode had been prepared at the same time and under the same conditions as the Ag|AgCl electrode introduced into Cell 1 but had been stored permanently in aqueous 0.01M NaCl. The electrode was introduced into the solution and removed immediately after a potential measurement had been made. The potential of Ag|AgCl measured against ageing calomel was -47mV and -52mV after 25 and 188 days respectively.

These results demonstrate that both Ag|AgCl and calomel electrodes can be used to provide reliable potentials in naturally aerated artificial Bentonite-equilibrated groundwater over a 5000 hour period. The AEA silver chloride electrode maintained a potential of  $-46 \pm 6$  mV over this period despite some changes in chloride concentration introduced by solvent evaporation. This stability implies an equal performance of the calomel reference electrode. This was confirmed by the potential measurements against freshly prepared calomel.

The potential difference between the calomel reference and each of the other indicator electrodes was measured through individual voltage followers to ensure that equilibrium was maintained during the measurement. An error in potential can be introduced into the measurements caused by a drift in the voltage offset between the inverting and non-inverting inputs of each voltage follower. To investigate this drift further the two inputs of a voltage follower were shorted together and the output potential, which in this configuration is equivalent to the voltage offset drift, was monitored for 2000 hours. The voltage offset was not zeroed out for this experiment. The result is shown in Figure 12. With the exception of a period between 1200 and 1500 hours the voltage offset drift was of the order of 100  $\mu$ V about the 300  $\mu$ V mean value. The drift was most probably thermally induced. The short period oscillations superimposed on this drift correspond to a day cycle and are also thermal effects. This would introduce a potential error drift of 0.1 mV into the measured potentials, which over a 2000 hour experiment is negligible. During the period 1200–1500 hours the Clarke Electromedical electrode had lost contact with the solution and this had driven the output of its voltage follower to the potential of the negative power supply rail. The increase in current output required to satisfy this condition would have dragged down the power supply voltage. As the voltage offset drift is corrected using a potential divider circuit to the negative rail of the power supply the loss in contact of Clarke electrode (or any other electrode in the set)

could have affected all voltage followers driven from the same power supply. The effect is small,  $\pm 0.5\text{mV}$ , and could be removed with a better design of power supply. The voltage offset drift could be removed by periodic calibration of the voltage followers.

### 3.2.3 Corrosion cell 2

The results of monitoring the pH,  $E_h$  and corrosion potential of the steel in cell 2 are shown in Figure 13 and Figure 14. The potentials were normalised with respect to NHE by assuming that the potential of silver-silver chloride electrode with respect to calomel was  $-46.0\text{ mV}$  in the groundwater (i.e. calomel in groundwater was  $+294\text{ mV}$  vs NHE).

### 3.2.4 Gas Monitoring

The rate of anaerobic corrosion of carbon steel can be evaluated by monitoring the rate of hydrogen evolution. The apparatus to measure the hydrogen generation is called a gas evolution displacement cell and has been described previously [11]. In this cell the hydrogen gas evolved displaces a low vapour pressure fluid (di-n-butylphthalate (DBP)). The quantity of fluid displaced is monitored and hence the corrosion rate can be calculated. The anaerobic corrosion cells are fitted with gas evolution displacement cells and some measurements of hydrogen evolution rate have been taken. The results are presented in Figure 17. The gas evolution rate in Cell 1 and Cell 2 decreased to a value of  $0.5\text{ dm}^3\text{ m}^{-2}\text{ yr}^{-1}$  which is equivalent to a corrosion rate of  $0.15 \pm 0.05\text{ }\mu\text{m yr}^{-1}$ .

The displacement cells were included as a means of monitoring the corrosion rate while the electrochemical measurements were being made. During the filling process a small amount of DBP was sucked back into the corrosion vessel. This condition was irreversible because at that stage all of the ‘through-cell connections’ had been sealed with adhesive resin. A small amount of DBP contamination was present in both of the corrosion cells tested. The effect of DBP contamination on the measurement of  $E_h$  and pH is not known. It is recommended that in future the procedure for filling liquid displacement cells is modified to prevent the possibility of DBP being sucked back into the corrosion cell. Alternatively the planned follow-on experiments with actinide additives could be performed in vessels without liquid displacement cells.

## 4 Discussion

### 4.1 Performance of reference electrodes

In cell 1 a large shift in the potential of all the electrodes occurred after ~470 hours. The change in potential was 800–850 mV. Since the potentials of all three electrodes changed simultaneously it was concluded that it was the potential of the reference electrode that had changed. The solubility of silver chloride is known to increase in solutions containing high concentrations of chloride ion due to the formation of complexes of the type  $\text{AgCl}_2^-$ . One possible reason for failure could be dissolution of the silver chloride coating on the silver-silver chloride electrode, leaving the underlying platinum wire exposed to the test solution. Alternatively, the silver chloride coating could have cracked and spalled, exposing the potential-determining platinum beneath. In either case the electrode would have assumed the potential of a hydrogen electrode. The effect on the observed potentials in cell 1 is best explained by referring to the construction shown in Figure 15, assuming 1 atmosphere hydrogen pressure and an activity coefficient of 1. The glass electrode was calibrated against an Ag|AgCl electrode in 0.01M NaCl (potential 0.345V vs NHE). Extrapolation of this calibration to high pH values can be used to obtain the pH of the groundwater. Cell 1 electrodes were measured against Ag|AgCl electrodes in artificial groundwater, a combination which has a potential of +0.248V vs NHE. Immediately before the reference electrode failure, the glass, Au and carbon steel electrodes had potential values shown by the red dots, Figure 15. Using the calibration for the glass electrode the pH of the solution was approximately 9.8 units immediately before failure. If at this point the reference electrode reverted back to a platinum wire it would have adopted a potential close to +0.580V vs NHE at pH 9.8 and all the potentials of the electrodes would have moved relative to the new reference potential. Based on this assumption the potential of the electrodes was corrected to the NHE scale, as shown in Figure 15. A consequence of this construction is that the potential of the glass electrode should have become a constant value, as the platinum reference and glass electrodes would have had the same response to changes in pH. This was not observed over the longer time scale. If the platinum wire electrode and/or the glass electrode deviated from ideality then fluctuations in potential could be a qualitative indication of changes in pH. The potential of the gold and carbon steel wires could also be affected slightly. For example, a change in pH would slightly affect the measured potential of the platinum – gold couple but it would be impossible to distinguish a potential change due to a redox potential shift on the gold from a pH change.

When a calomel electrode was monitored against the silver chloride electrodes for a period of 2,500 hours the potential was reasonably stable, but it was punctuated by periods of high noise activity. This may have been due to electrical interference in the laboratory power supplies. The theoretical difference between the two types of electrode is 45.3 mV. The variation seen in the monitoring experiments was 42 to 60 mV. Some of the observed variation may have been due to drift in the voltage follower, but this is not expected to be more than 0.1 mV. The silver chloride electrode did not display the failure observed with the silver chloride electrode used in corrosion cell 1. The calomel

electrode was shown to be within 3mV of a freshly prepared electrode even after 4500 hours, indicating a high stability for the calomel electrode.

It should be noted that the degradation of the reference electrode in cell 1 occurred after the addition of steel wires to the test solution and some effect of dissolved ferrous ions on the silver chloride electrode cannot be ruled out.

The glass electrode exhibited a linear response during the calibration process, within a limited pH range, but it should be recognised that the electrodes were actually used in a different pH range to that in which they were calibrated. In principle they should exhibit a linear response in the alkaline pH range, which can be extrapolated from the calibration in acidic conditions, but this has not been demonstrated experimentally.

## 4.2 Monitoring pH, $E_h$ and steel corrosion potential

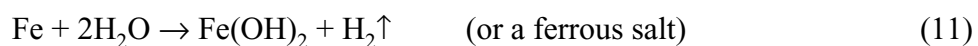
### 4.2.1 Monitoring pH

In both cells a decrease in pH was observed, which in cell 1 accelerated after addition of the steel wires. In both cells the longer-term pH stabilised at approximately 9.7, having started at a value of approximately 10.4. The reason for the decline in the pH is not clear. One possible reason is dissolution of the glass vessel to form hydrosilicic acid. The corrosion reaction would be expected to cause an increase in the pH due to formation of hydroxyl ions by water reduction.

### 4.2.2 Monitoring Eh

The potential of the gold electrode will be a mixed potential determined by the various electrochemical couples which could arise in the solution. Possible couples include the ferrous/ferric couple ( $Fe^{3+}/Fe^{2+}$ ), oxygen reduction, and hydrogen reduction. In addition, for cell 1, there would have been a small concentration of silver dissolved in the test solution, from the dissolution of the silver-silver chloride electrode.

As the steel corrodes anaerobically by the reaction



the concentration of  $Fe^{2+}$  ions would be expected to increase in the test solution. The concentration will be determined by the solubility product of  $Fe(OH)_2$ . The standard equilibrium potential for the couple



is 0.771 V vs SHE [19]. From the Nernst equation, the equilibrium potential of the  $Fe^{3+}/Fe^{2+}$  couple is given by:

$$E = E_0 + 2.303 \frac{2RT}{nF} \log[Fe^{3+}] - 2.303 \frac{RT}{nF} \log[Fe^{2+}] \quad (13)$$

For  $Fe^{2+}$  and  $Fe^{3+}$  activities of 0.01 and 0.00001 respectively, the value of E is 1.426 V.

The rapid decrease in the value of Eh when the steel wires were placed in the test solution indicates the onset of more reducing conditions. This can be attributed to the removal of residual dissolved oxygen from the test solution by reaction with the surface of the steel wires. For oxygen the standard equilibrium potential for the couple



is 1.229 V vs SHE [19]. From the Nernst equation, the equilibrium potential of the  $O_2 / OH^-$  couple is given by:

$$E = E_0 + 2.303 \frac{2RT}{nF} \log[pO_2] - 2.303 \frac{RT}{nF} \log[H^+] \quad (14)$$

or

$$E = E_0 + 0.015 \log[pO_2] - 0.059 \log[H^+] \quad (14)$$

It can be seen that as the partial pressure of oxygen falls the potential of the couple falls to more negative potentials. As an illustration, at pH 10.4 and a partial pressure of  $10^{-9}$  atmospheres of oxygen the equilibrium potential for oxygen reduction is  $-734$  mV.

#### 4.2.3 Monitoring $E_{corr}$

The negative value observed for the corrosion potential of the steel ( $-620$  mV vs NHE, cell 1,  $-480$  to  $-420$  mV vs NHE, cell 2) are consistent with anaerobic corrosion occurring by the reduction of water to hydrogen. Similar values of corrosion potential have been observed previously [14] in electrochemical measurements carried out for SKB in artificial KBS TR36 groundwater. The equilibrium hydrogen evolution potential at pH 10.4 is  $-610$  mV and  $-570$  mV at pH 9.7.

### 4.3 Further work

This work has demonstrated the feasibility of measuring electrochemical parameters in the presence of anaerobically corroding steel wires. The methods used in this work could be applied to making similar measurements in the presence of dissolved uranium. It would then be possible to monitor the environmental conditions while studying the effect of iron corrosion products on the oxidation state and solubility of actinides.

It is proposed that the electrochemical cells should be dismantled and solution analysis carried out. This would aid in the interpretation of the changes in pH and Eh that were observed during the course of this work.



## 5 Conclusions

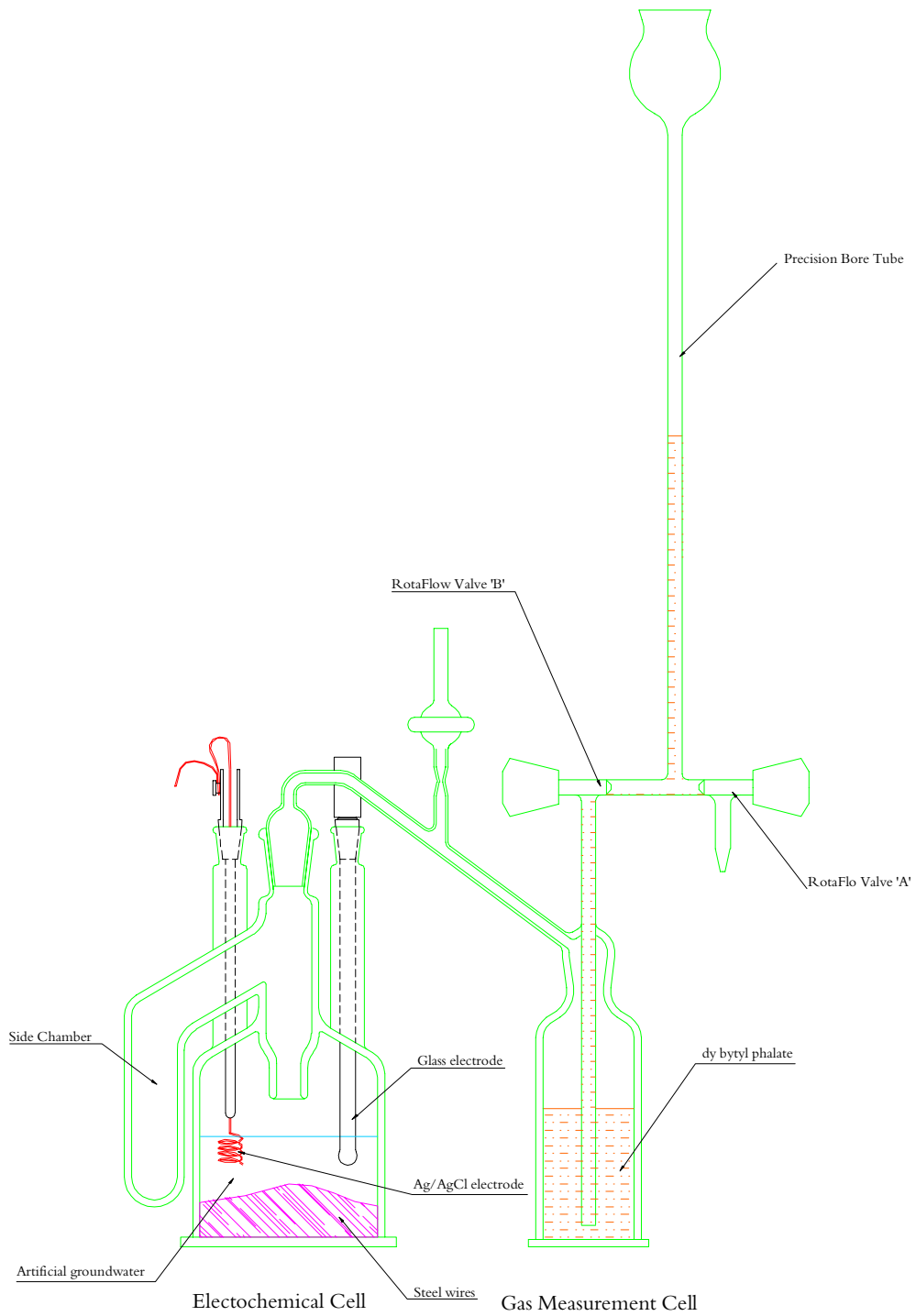
The main conclusions from this work are:

- It is possible to make measurements of Eh, pH and corrosion potential in the presence of anaerobically corroding steel in artificial Bentonite equilibrated groundwater at 30°C.
- The presence of corroding steel leads to the rapid local deoxygenation of groundwater and a fall in the redox potential.
- Calomel electrodes appear to be more reliable than silver-silver chloride reference electrodes for long-term electrochemical measurements in artificial groundwaters.

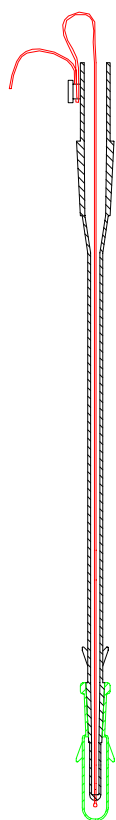
## 6 References

- 1 J.A.T. Smellie, P. Wikberg, *J. Hydrol.* **126**, 129, 1991.
- 2 J.A.T. Smellie, M. Laaksoharju, P. Wikberg, *J. Hydrol.* **172**, 147, 1995.
- 3 G.P. Marsh, *A Preliminary Assessment of the Advanced Cold Process Canister*, AEA Technology Report, AEA-InTec-0011, 1990.
- 4 J. Henshaw, A. Hoch and S.M. Sharland, *Further Assessment Studies of the Advanced Cold Process Canister*, AEA Technology Report, AEA-D&R-0060, 1990.
- 5 G.P. Marsh, K.J. Taylor and A.H. Harker, *The Kinetics of Pitting Corrosion of Carbon Steel Applied to Evaluating Containers for Nuclear Waste Disposal*, AEA Technology Report, AEA-InTec-0565, 1991.
- 6 N. Platts, D.J. Blackwood and C.C. Naish, *The Anaerobic Oxidation of Carbon Steel in Granitic Groundwaters: A Review*, AEA Technology Report, AEA-InTec-1413, 1993.
- 7 D.J. Blackwood, A.R. Hoch, C.C. Naish, A. Rance and S.M. Sharland, *Research on Corrosion Aspects of the Advanced Cold Process Canister*, AEA Technology Report, AEA-D&W-0684, 1994.
- 8 D.J. Blackwood, C.C. Naish, A. Rance and S.M. Sharland, *Further Research on Corrosion Aspects of the Advanced Cold Process Canister*, AEA Technology Report, AEA-ESD-0052, 1994.
- 9 J. Henshaw, *Modelling of Nitric Acid Production in the Advanced Cold Process Canister due to Irradiation of Moist Air*, AEA Technology Report, AEA-D&W 0706, 1994.
- 10 D.J. Blackwood and C.C. Naish, *The Influence of Galvanic Coupling Between the Outer Copper Canister and the Inner Carbon Steel Container on the Corrosion Performance of the Advanced Cold Process Canister Under Aerobic Conditions*, AEA Technology Report, AEA-ESD-0053, 1994.
- 11 D.J. Blackwood, C.C. Naish, N. Platts, K.J. Taylor & M.I. Thomas, *The Anaerobic Corrosion of Carbon Steel in Granitic Groundwaters*, AEA Technology Report, AEA-InTec-1414, 1995.
- 12 D.J. Blackwood, J. Henshaw, N. Platts and J.P. Hilditch, *Stress Corrosion Cracking of the Advanced Cold Process Canister: Carbon Steel in Nitric Acid Vapour*, AEA Technology Report, AEA-ESD-0288, 1995.

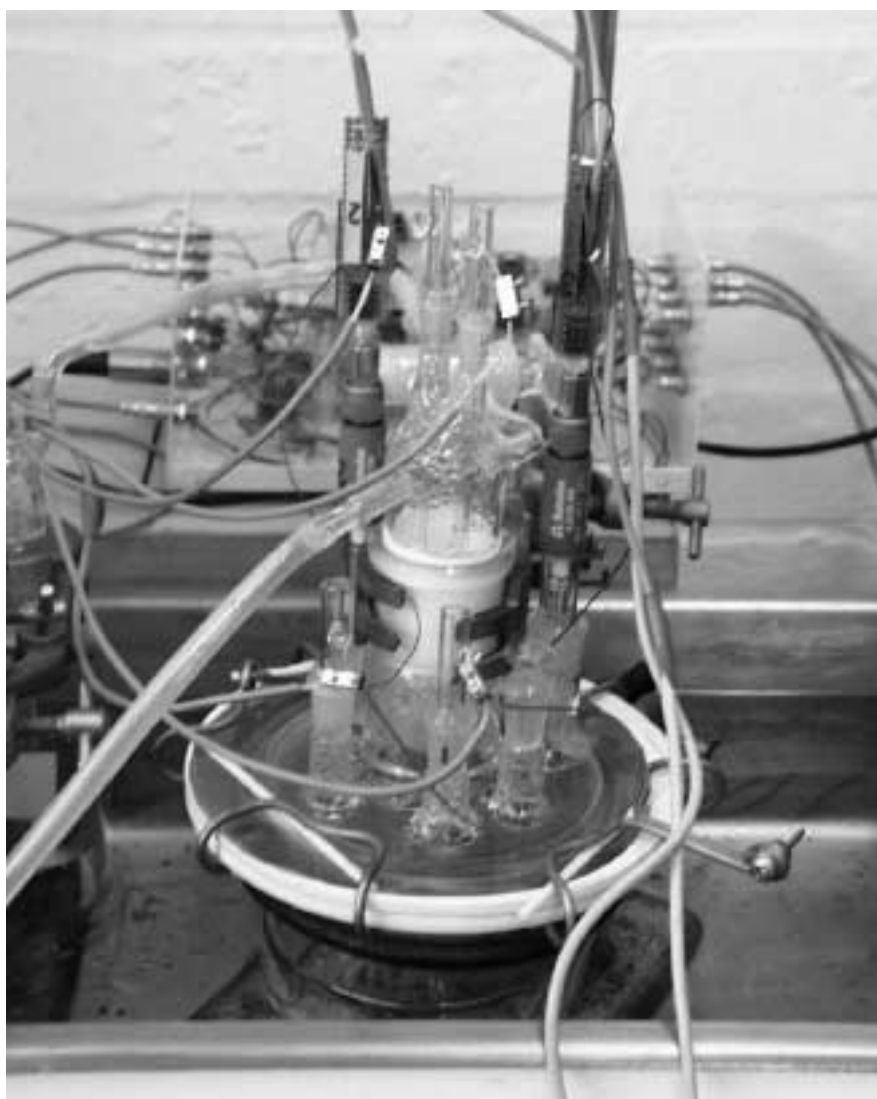
- 13 N.R Smart, A.P. Rance and D.J. Blackwood, *Corrosion Aspects of the Copper-steel/iron Process Canister: Consequences of Changing the Material for the Inner Container from Carbon Steel to Cast Iron*, SKB 97-04, 1997.
- 14 N.R. Smart, D.J. Blackwood and L. Werme, *The Anaerobic Corrosion of Carbon Steel and Cast Iron in Artificial Groundwaters*, submitted to *Corrosion*, 2000.
- 15 G. Gran, *Determination of the Equivalence Point in Potentiometric Titrations. Part II.*, International Congress on Analytical Chemistry **77**, 661, 1952.
- 16 Hills G.J. and Ives D. J.G, *Nature*, 163, 997, 1949.
- 17 D. Dobos, *Electrochemical Data*, Elsevier, 1975.
- 18 D.J.G. Ives and G. J. Janz (eds), *Reference Electrodes. Theory and Practice*, Academic Press, 1961
- 19 A.J. Bard, R. Parsons and J. Jordan, *Standard Potentials in Aqueous Solutions*, Dekker, 1985.



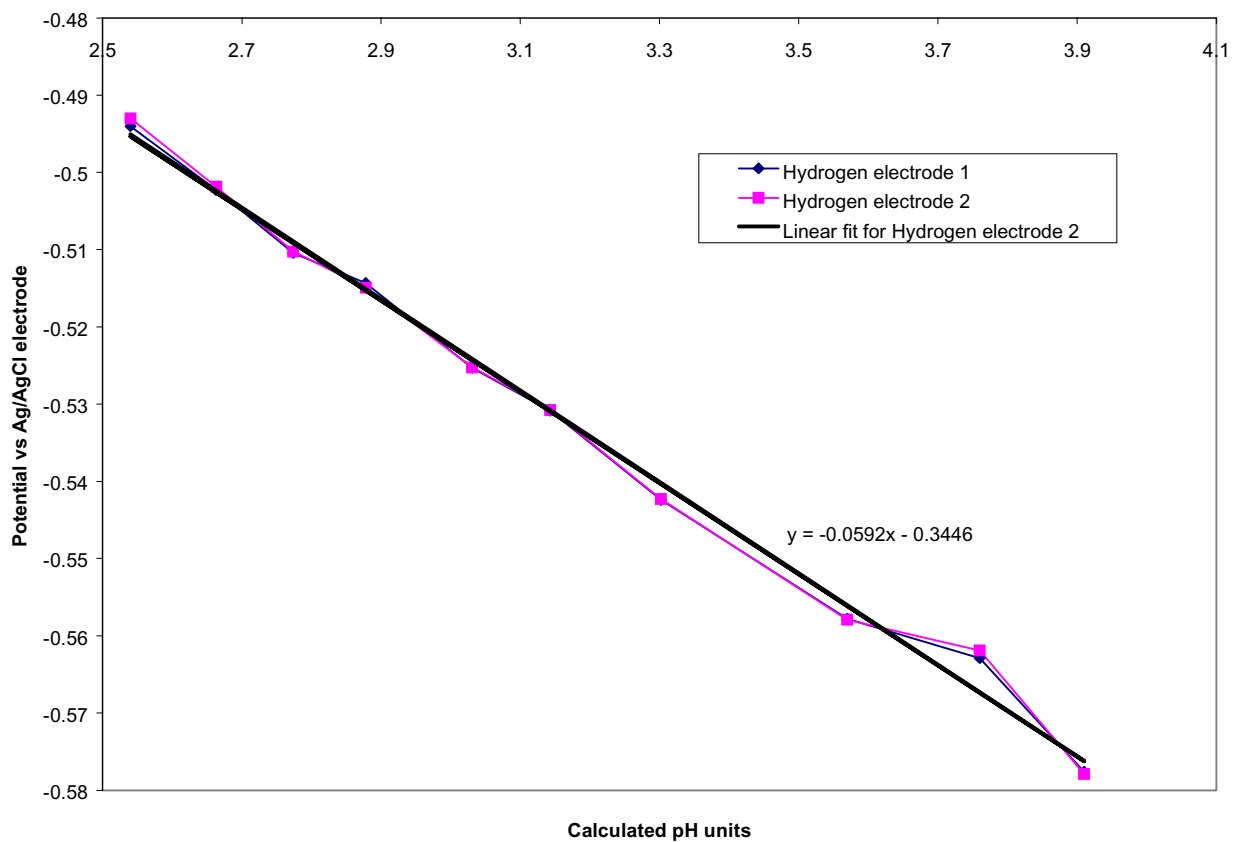
**Figure 1.** Schematic diagram of test cell.



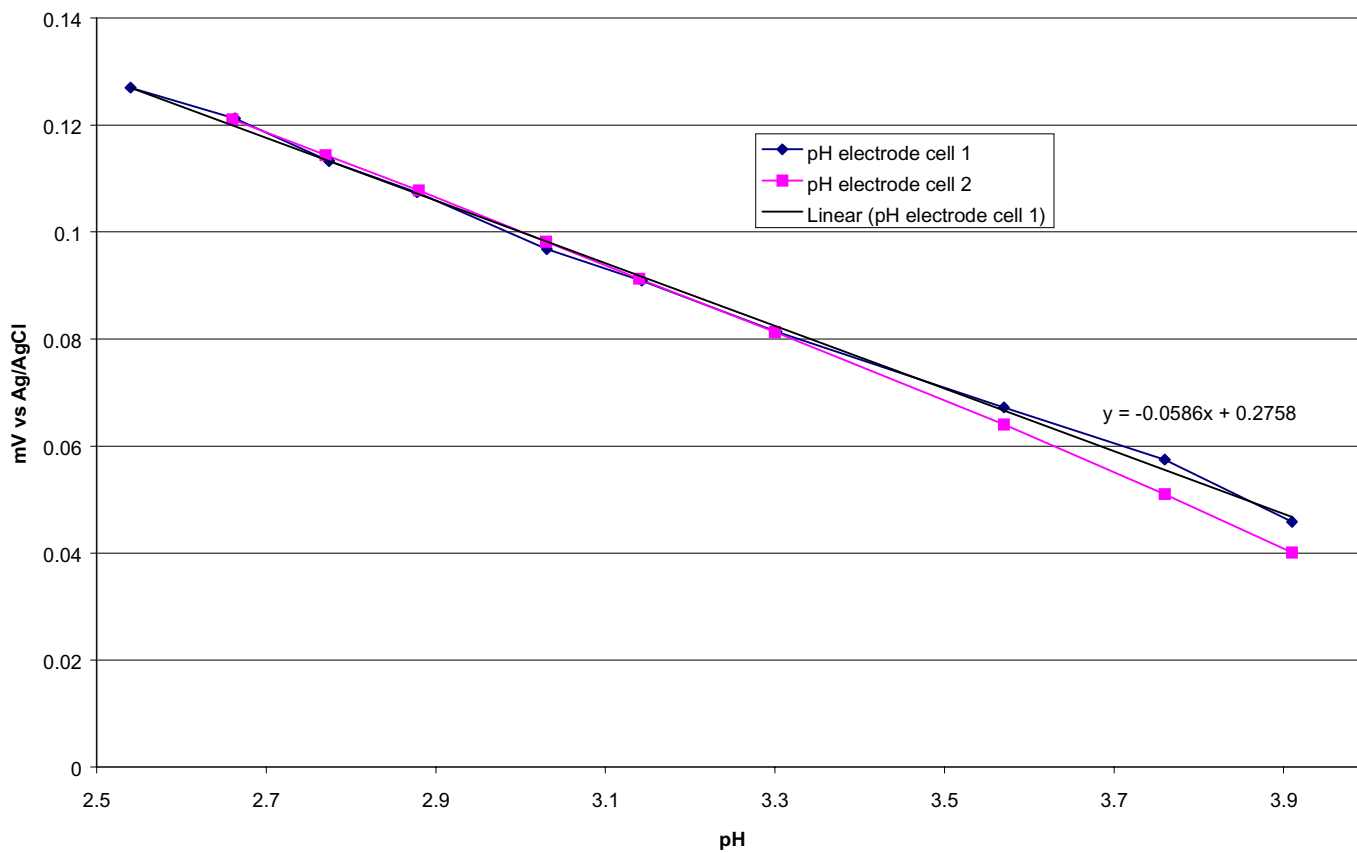
**Figure 2.** Schematic diagram of calomel electrode construction.



**Figure 3.** Photograph of calibration cell in oil bath, showing central hydrogen electrode assembly, two glass electrodes and two silver chloride electrodes.

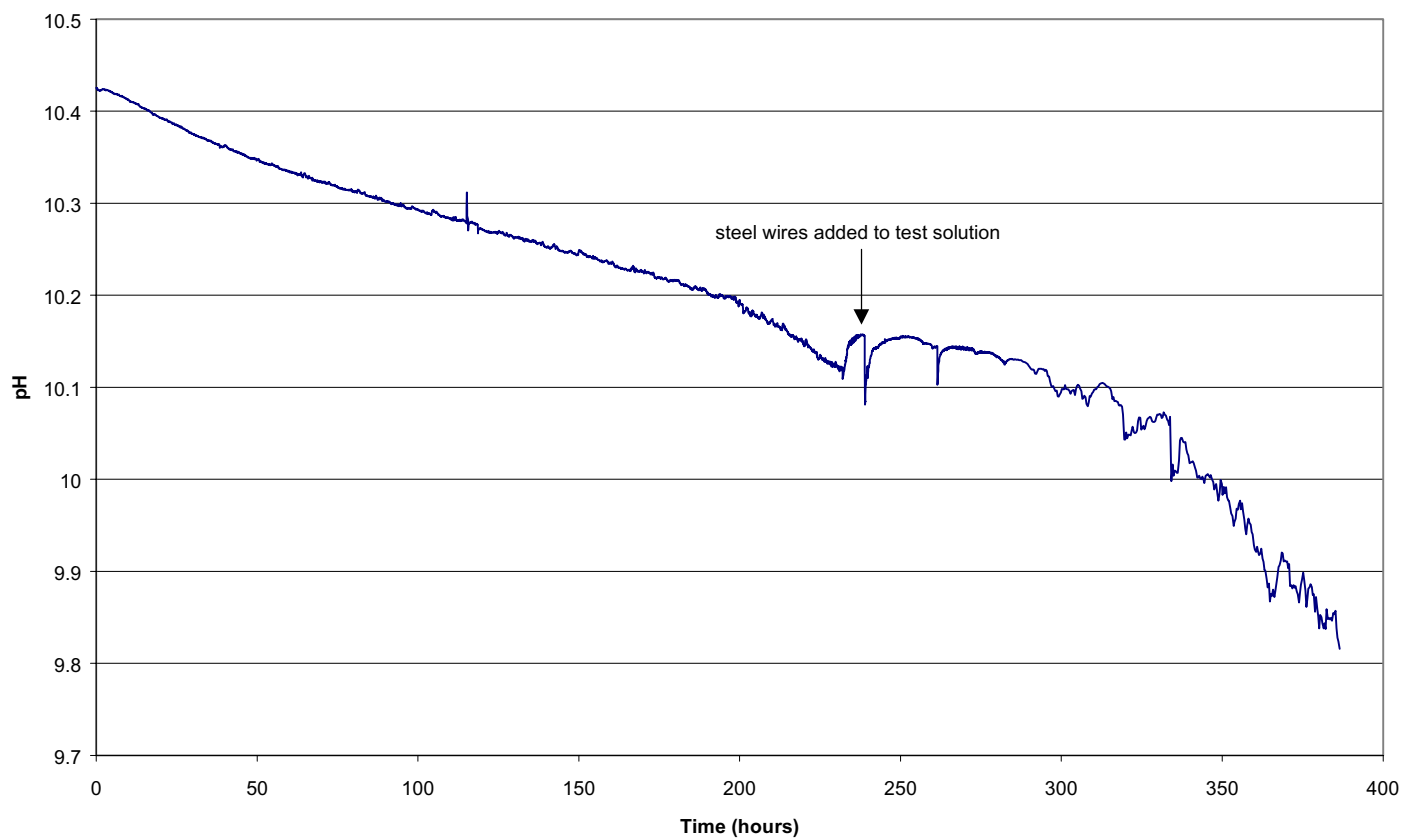


**Figure 4.** Calibration of silver-silver chloride electrode against standard hydrogen electrodes in 0.01M sodium chloride, by titration with 0.01M hydrochloric acid.

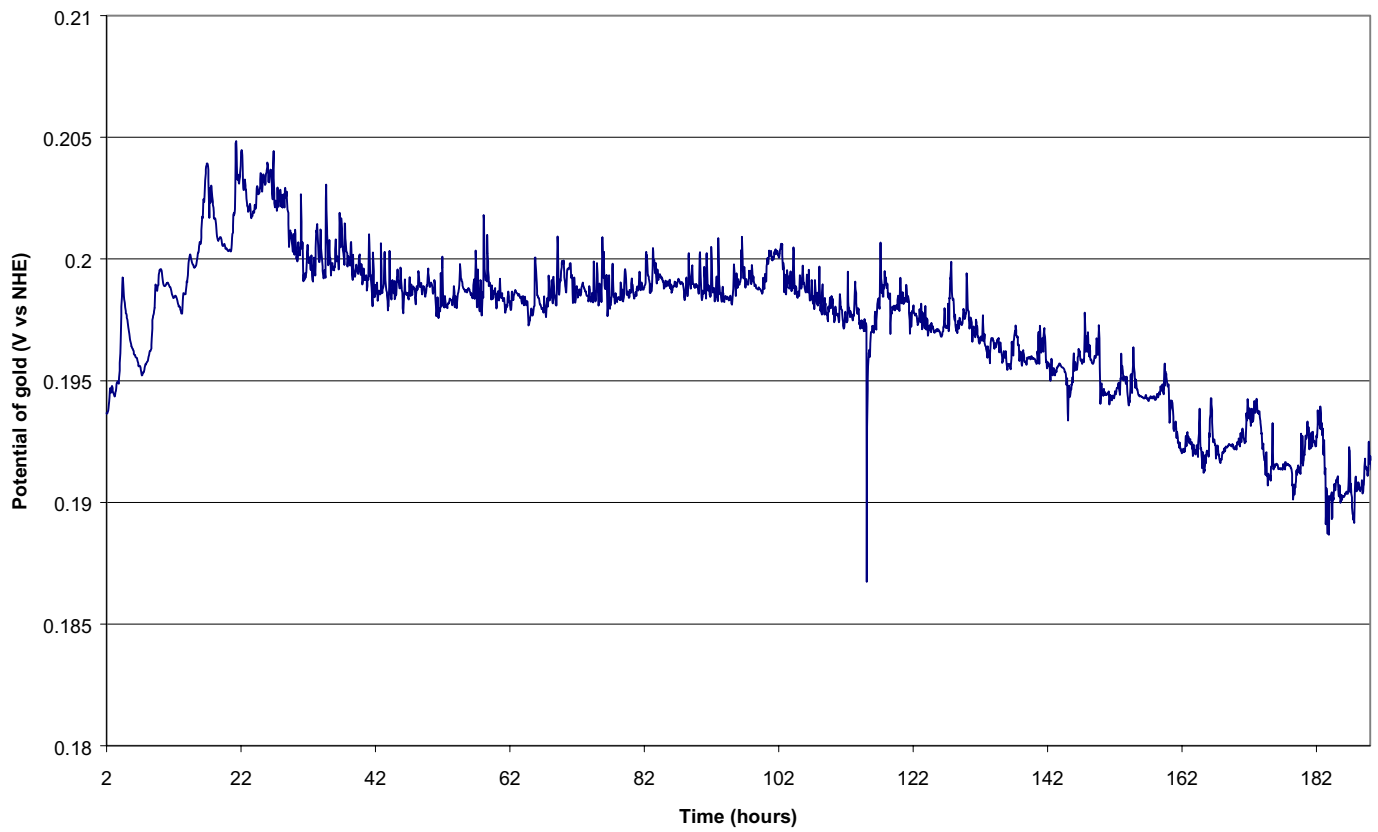


**Figure 5.** Calibration of glass pH electrodes against two hydrogen electrodes in 0.01M sodium chloride, by titration with 0.01M hydrochloric acid.

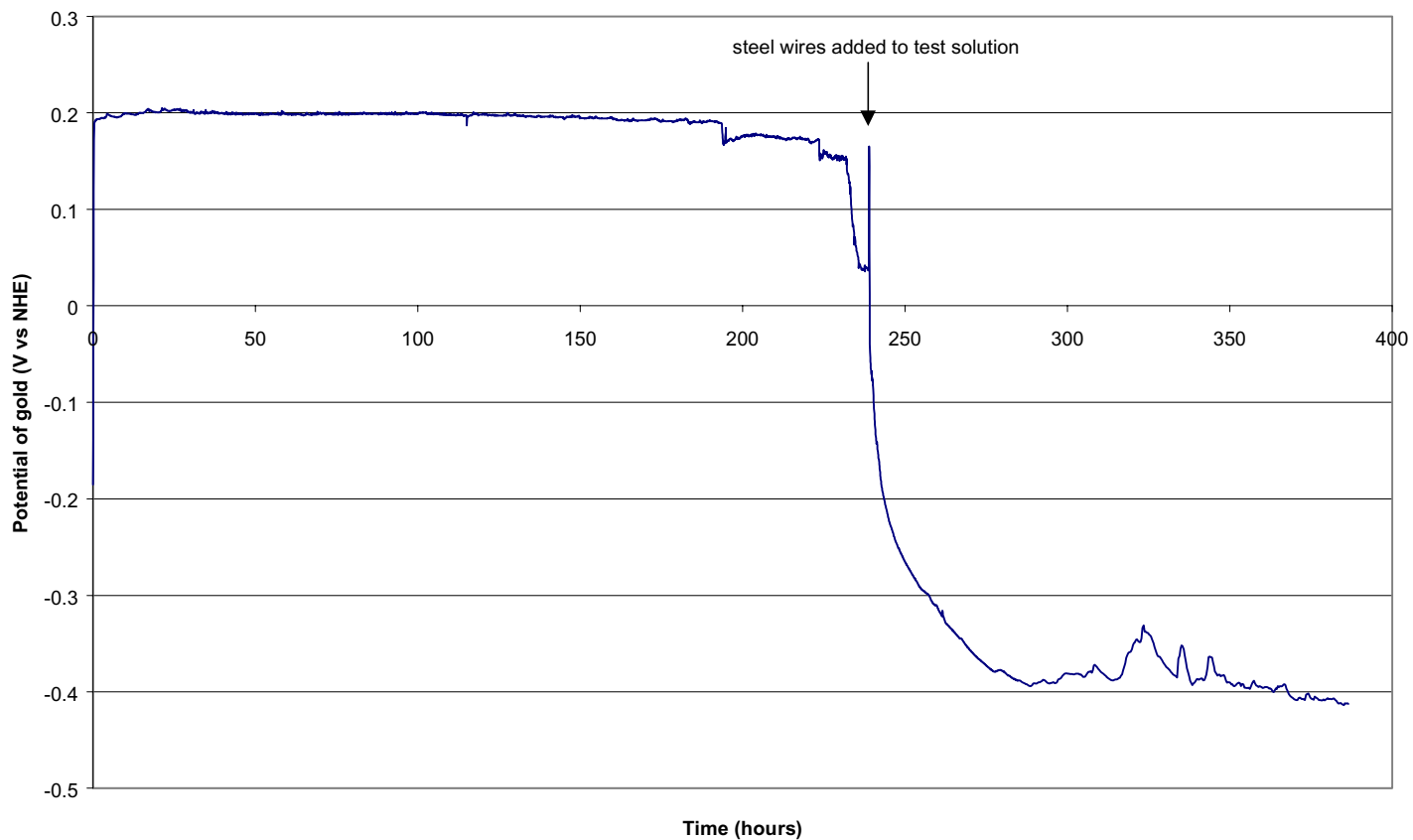




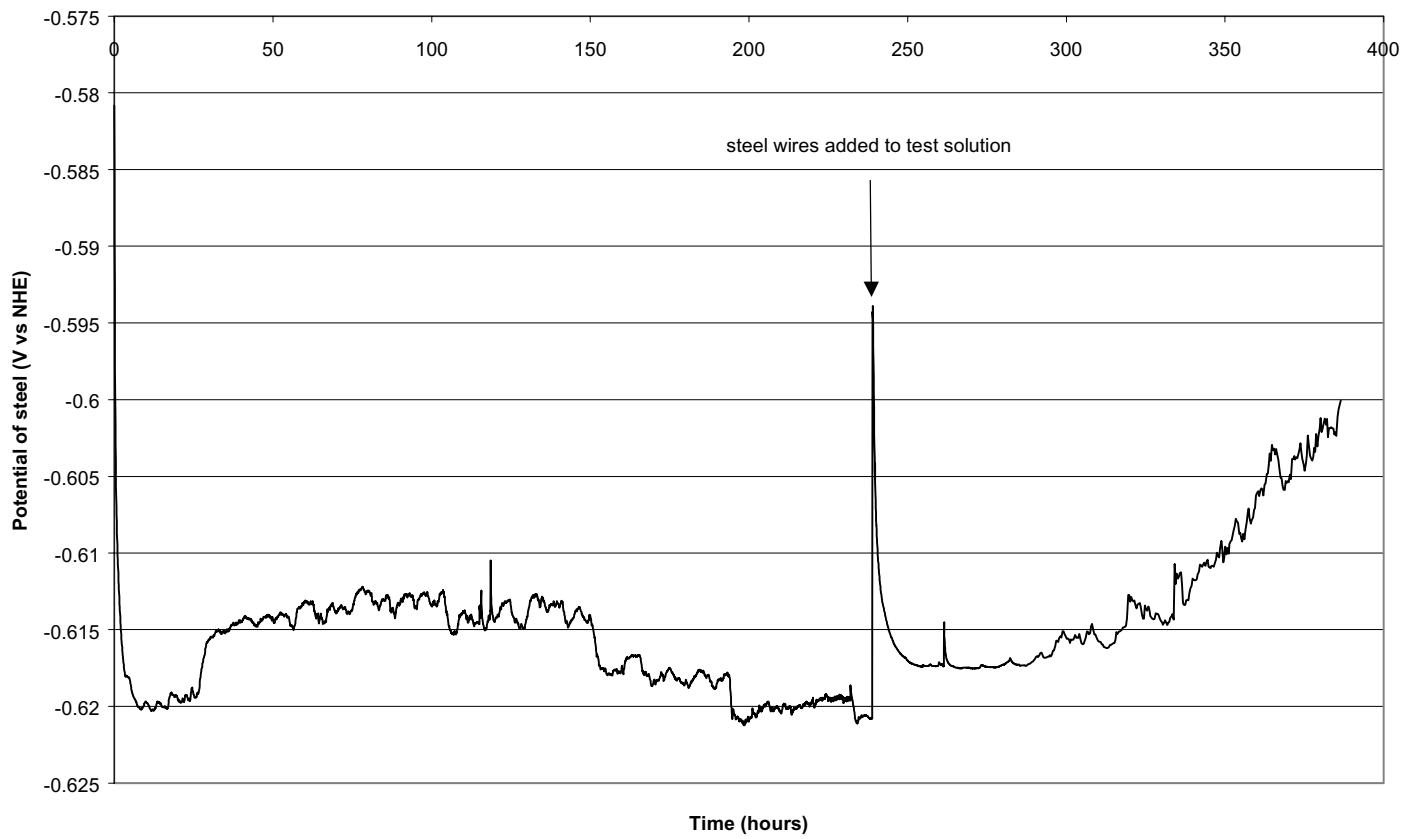
**Figure 6.** pH in cell 1, containing artificial Bentonite-equilibrated groundwater at 30°C, during first seventeen days.



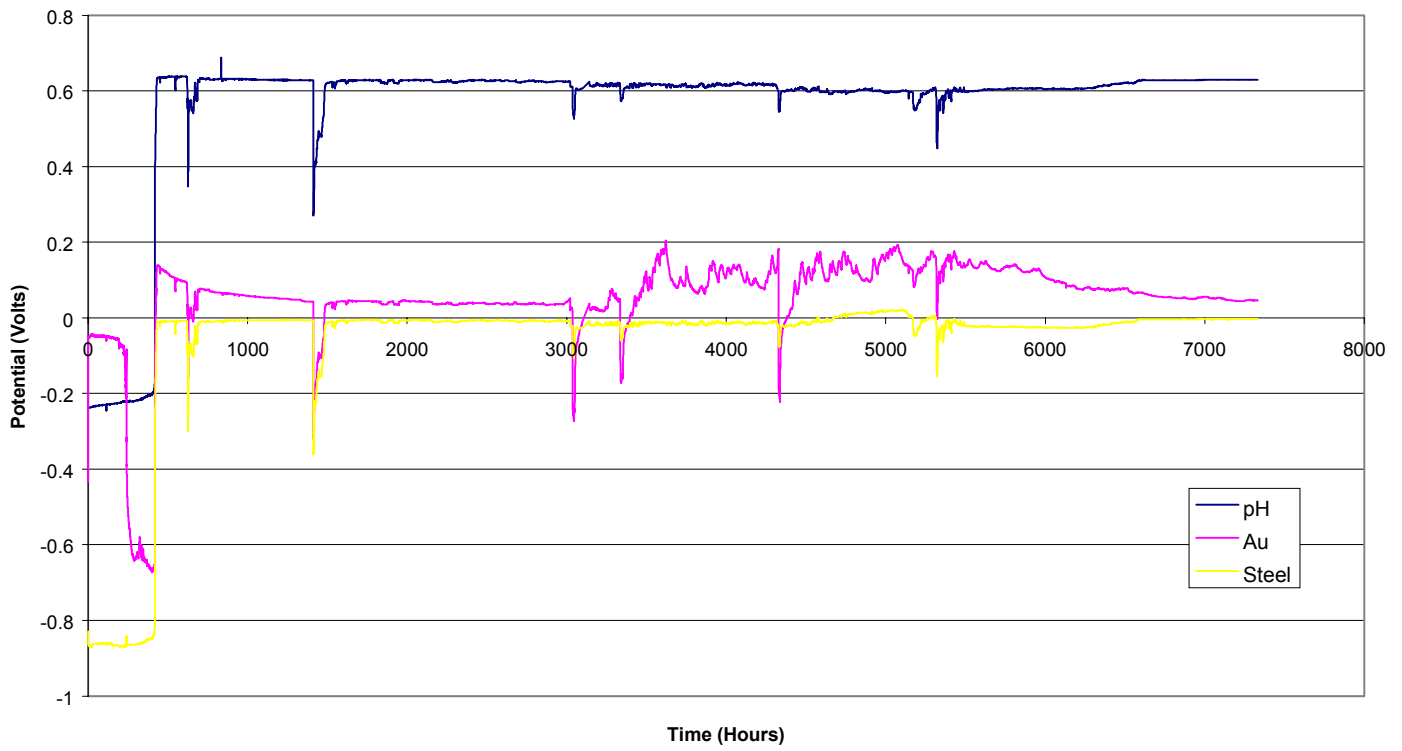
**Figure 7.** Potential of gold electrode,  $E_h$ , in cell 1, containing artificial Bentonite-equilibrated groundwater at 30°C, during initial equilibration period.



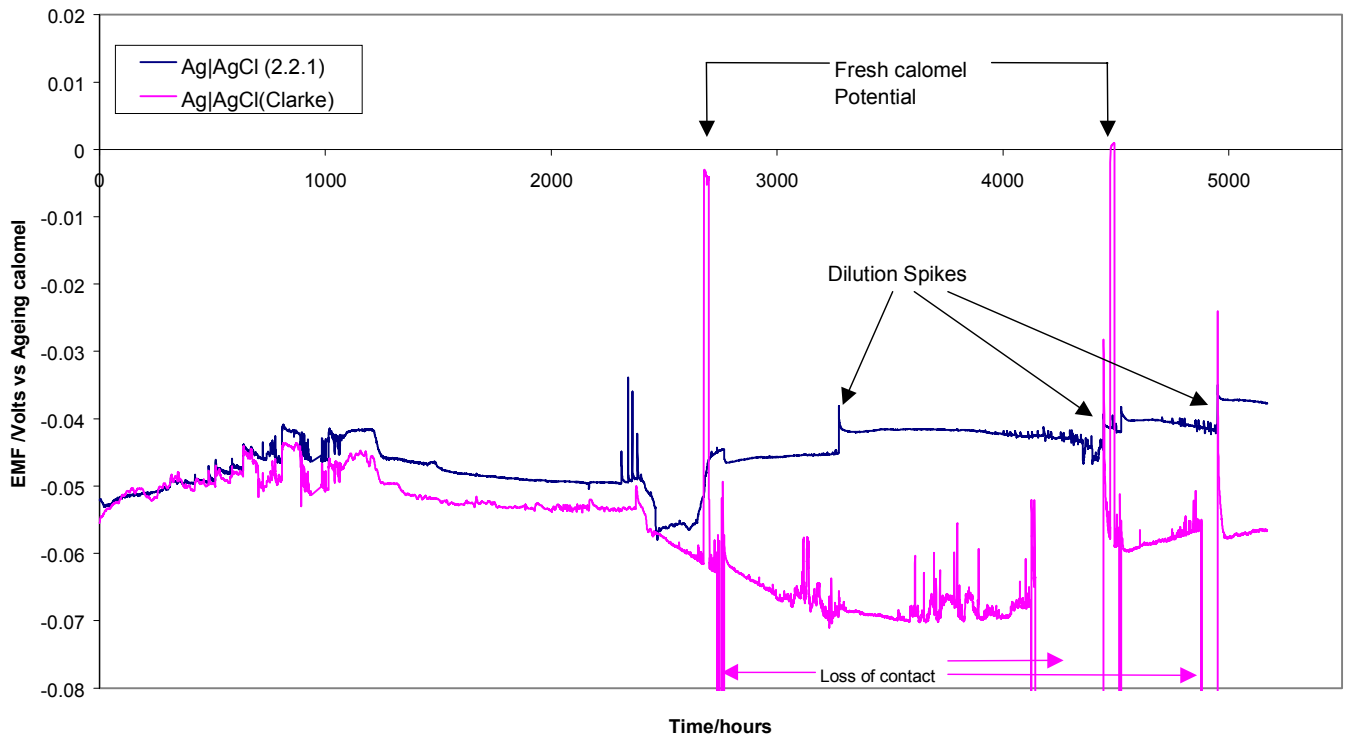
**Figure 8.** Potential of gold electrode,  $E_h$ , in cell 1, containing artificial Bentonite-equilibrated groundwater at 30°C, during first seventeen days.



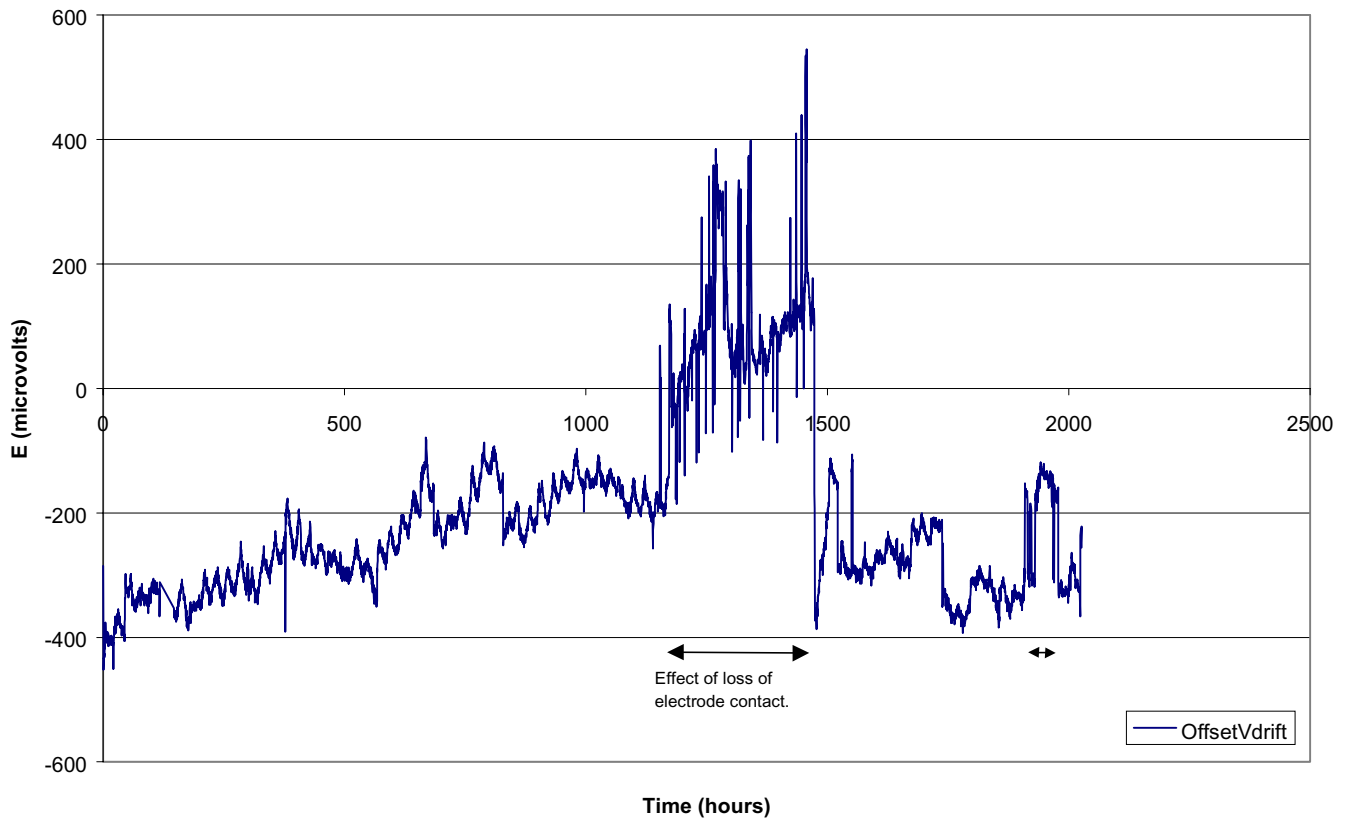
**Figure 9.** Potential of steel in cell 1, containing artificial Bentonite-equilibrated groundwater at 30°C, during first seventeen days.



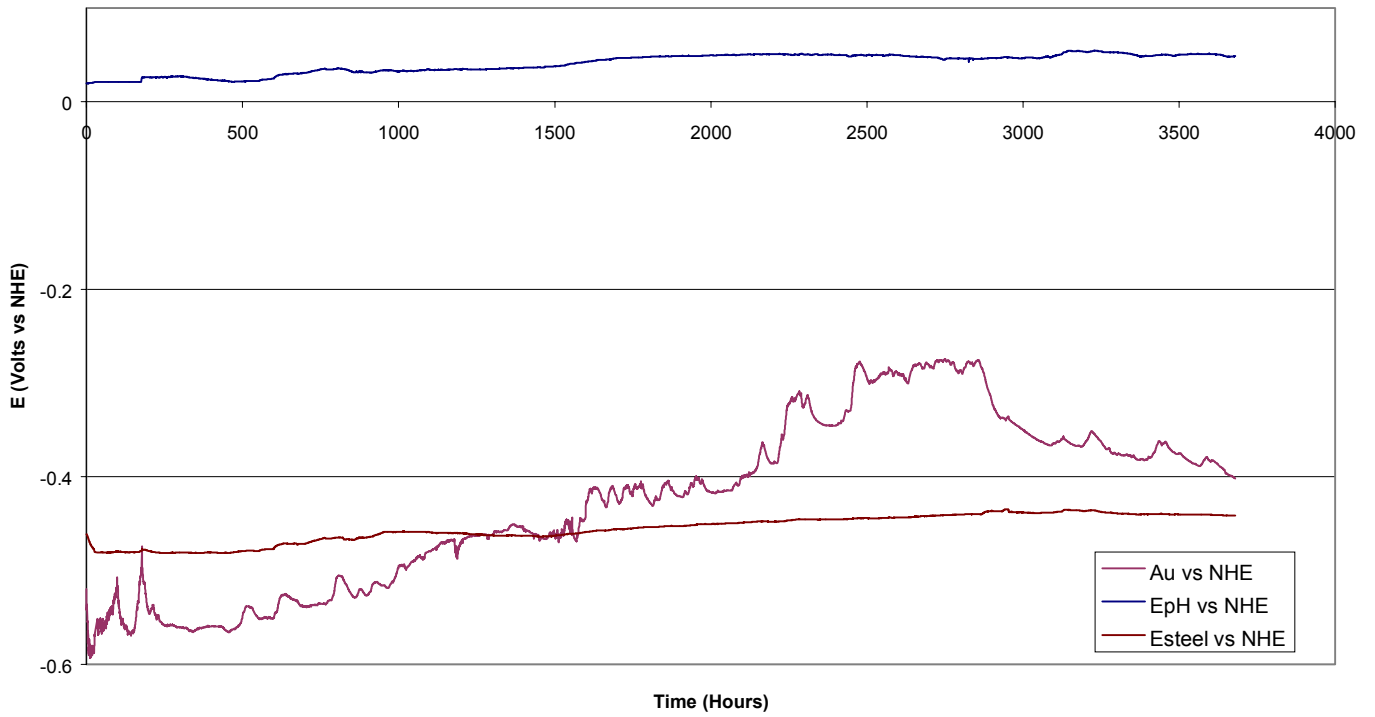
**Figure 10.** The potential of pH, gold, and carbon steel electrodes in artificial Bentonite equilibrated groundwater at 30°C for cell 1.



**Figure 11.** The potential of Ag|AgCl electrodes against a calomel electrode in artificial Bentonite equilibrated groundwater at 30°C.

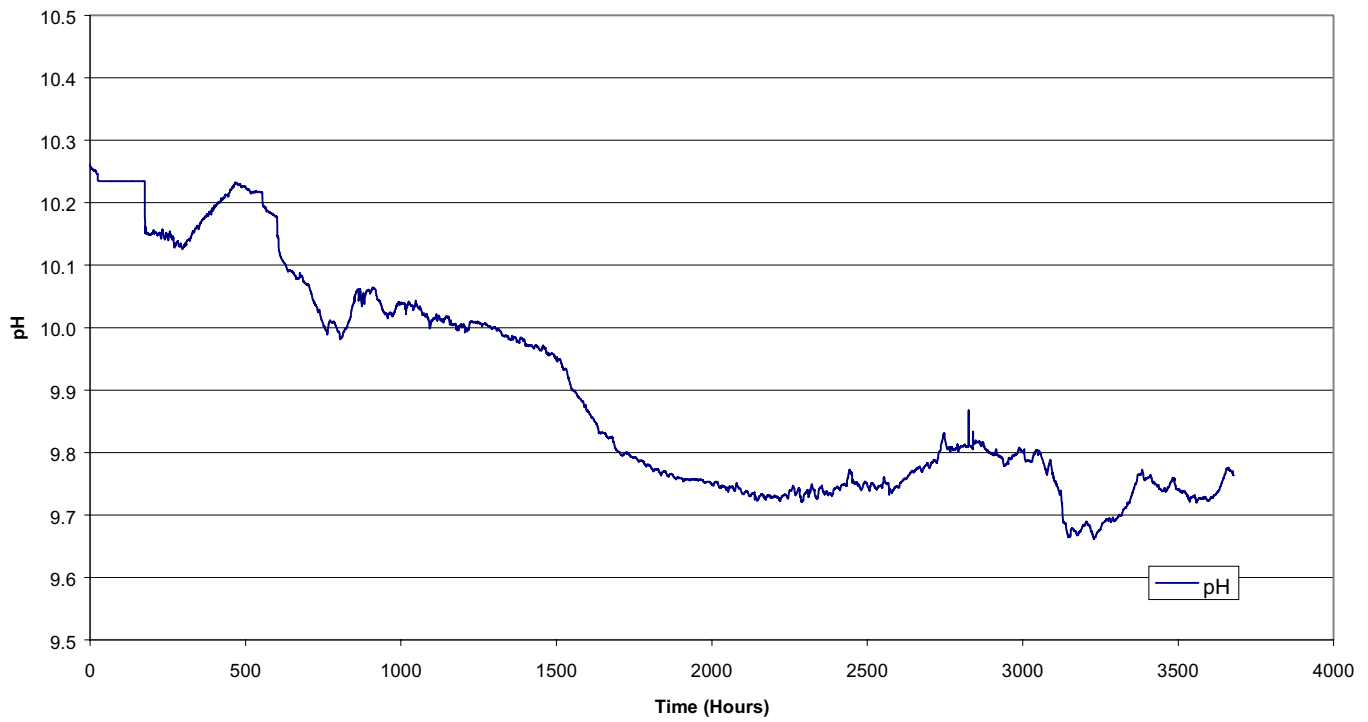


**Figure 12.** Offset voltage drift for a 3140 operational amplifier with shorted inputs.

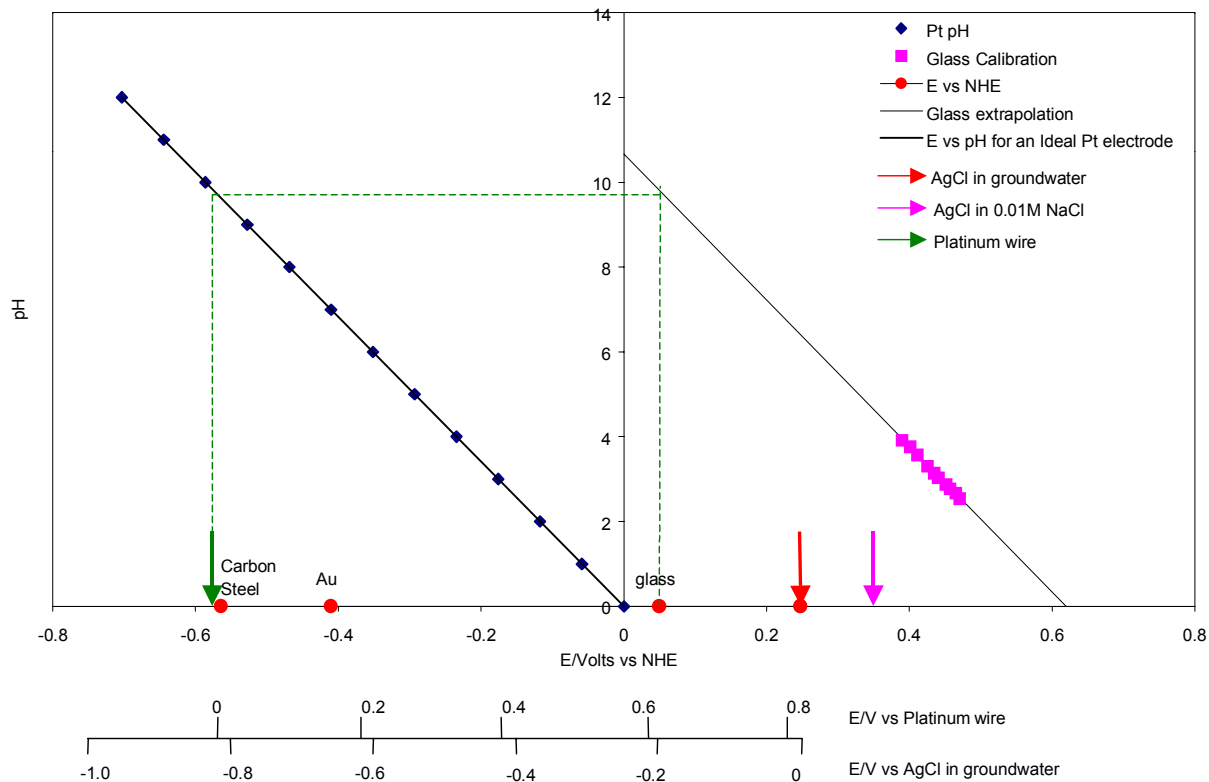


**Figure 13.** Potential of pH, gold and carbon steel electrodes corrected to NHE in artificial Bentonite equilibrated groundwater at 30°C for cell 2.

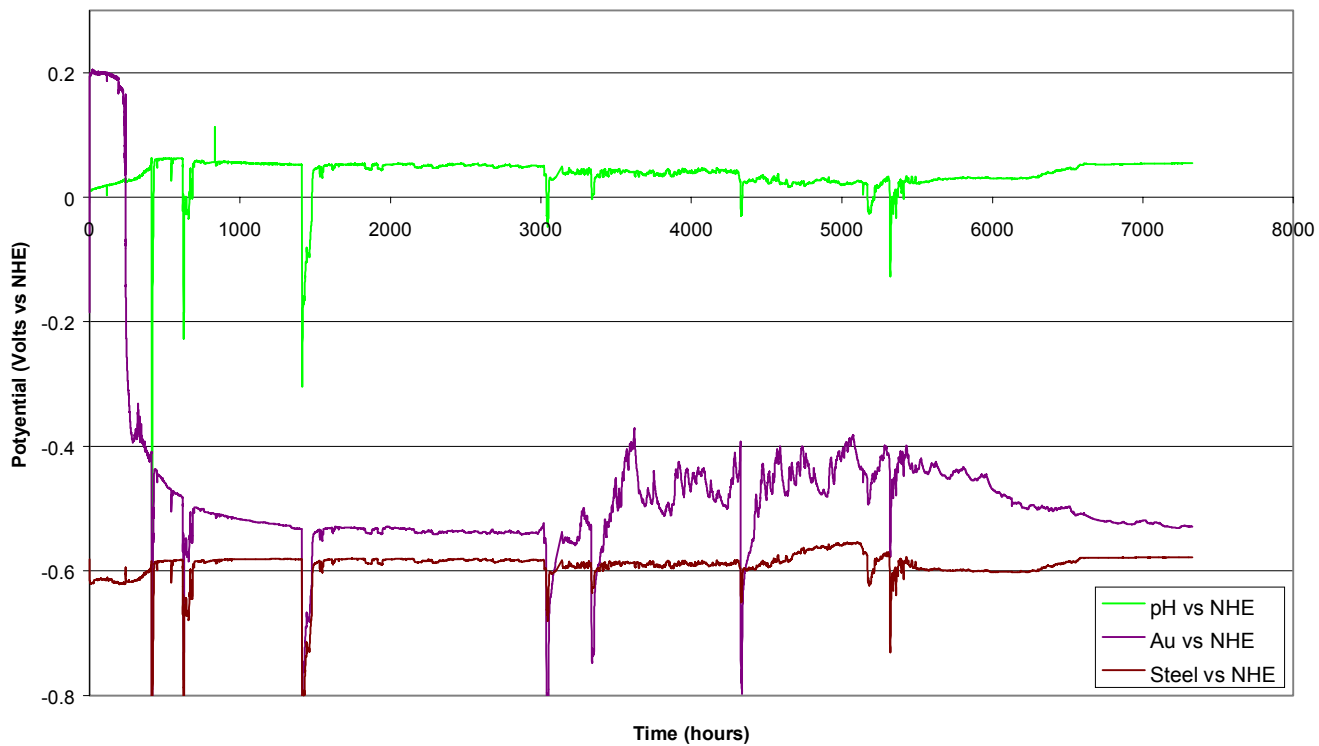




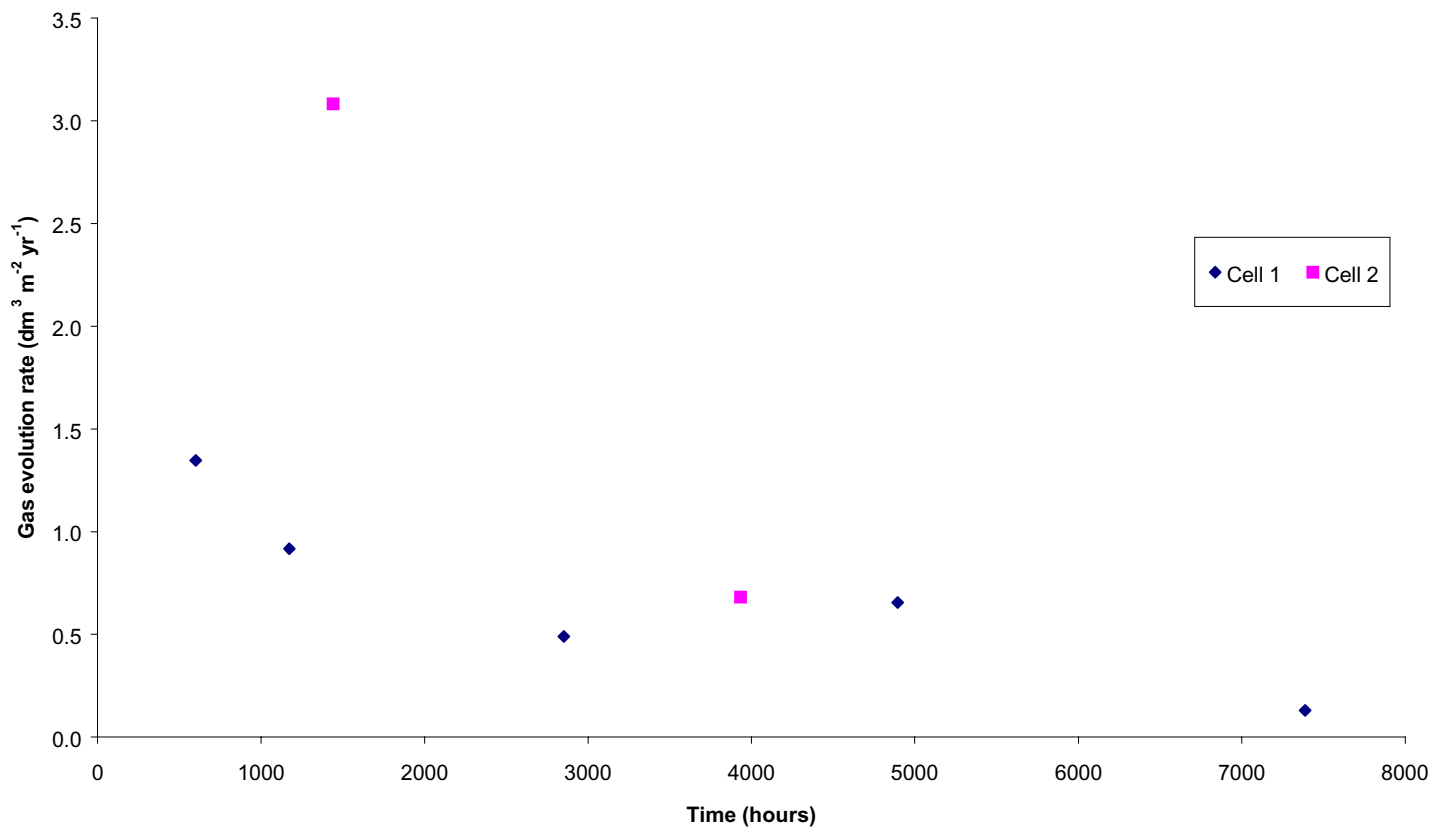
**Figure 14.** *The pH in cell 2 containing artificial Bentonite equilibrated groundwater at 30°C.*



**Figure 15.** Reference electrode scales; see text in section 4.1 for details.



**Figure 16.** Potential of pH, gold, and carbon steel electrodes against Ag|AgCl for cell 1 after correction for a failure of the reference electrode.



**Figure 17.** The rate of hydrogen evolution during the anaerobic corrosion of carbon steel at 30°C.

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