Galvanic Corrosion of Copper-Cast Iron Couples in Relation to the Swedish Radioactive Waste Canister Concept

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Abstract

To ensure the safe encapsulation of spent nuclear fuel rods for geological disposal, SKB are considering using the Copper-Iron Canister, which consists of an outer copper canister and an inner cast iron container. The canister will be placed into boreholes in the bedrock of a geologic repository and surrounded by bentonite clay. In the unlikely event of the outer copper canister being breached, water could enter the annulus between the inner and outer canister and at points of contact between the two metals there would be a possibility of galvanic interactions.

To study this effect, copper-cast iron galvanic couples were set up in a number of different environments representing possible conditions in the SKB repository. The tests investigated two artificial porewaters and a bentonite slurry, under aerated and deaerated conditions, at 30\degree C and 50\degree C. The currents passing between the coupled electrodes and the potential of the couples were monitored for several months. In addition, some bimetallic crevice specimens based on the multi-crevice assembly (MCA) design were used to simulate the situation where the copper canister will be in direct contact with the cast iron inner vessel. The effect of growing an oxide film on the surface of the cast iron prior to coupling it with copper was also investigated.

The electrochemical results are presented graphically in the form of electrode potentials and galvanic corrosion currents as a function of time. The galvanic currents in aerated conditions were much higher than in deaerated conditions. For example, at 30\degree C, galvanic corrosion rates as low as 0.02 \mu m/year were observed for iron in groundwater after deaeration, but of the order of 100 \mu m/year for the cast iron at 50\degree C in the presence of oxygen. The galvanic currents were generally higher at 50\degree C than at 30\degree C. None of the MCA specimens exhibited any signs of crevice corrosion under deaerated conditions.

It will be shown that in deaerated conditions the galvanic corrosion rates of iron coupled to copper are close to the values observed for anaerobic corrosion rates of uncoupled iron. The results from the work presented in the paper will be discussed in relation to understanding the evolution of the environment within the annulus of the SKB canister if premature failure of the outer copper canister were to occur.

Keywords: galvanic, copper, iron, waste, canister
1 Introduction

To ensure the safe encapsulation of spent nuclear fuel rods for geological disposal, SKB are planning to use the Copper- Iron Canister, which consists of an outer copper canister and an inner carbon steel or cast iron container. The canister will be placed into boreholes in the bedrock of a geological repository and surrounded by bentonite clay. In the unlikely event of the outer copper canister being breached, water could enter the annulus between the inner and outer canister and at points of contact between the inner and outer vessels there would be the possibility of galvanic interactions.

In order to investigate the galvanic corrosion interactions between copper and cast iron, electrochemical techniques based on standard methods [1,2] were used to investigate the galvanic corrosion of copper-cast iron couples in conditions relevant to the SKB repository design. This paper presents the results of these measurements and discusses how they may be interpreted in relation to understanding the evolution of the environment within the annulus of the SKB canister if premature failure of the outer copper canister were to occur.

2 Experimental

2.1 Overview of experimental programme

Galvanically coupled copper and cast iron electrodes were set up in artificial groundwaters simulating the environments expected in the SKB repository. The electrochemical potentials of the electrodes, before and after coupling, and the currents passing between them after coupling, were monitored for a period of several months. The relative electrochemical potentials of the uncoupled copper and cast iron electrodes can be used to show whether galvanic corrosion is likely and which electrode will corrode preferentially in the galvanic couple. Generally, the larger the separation in the relative electrochemical potentials of two materials the greater the likelihood of galvanic corrosion. The magnitude of the currents passing between coupled electrodes provides an indication of the galvanic enhancement of the corrosion rate and shows whether the corrosion rate changes with time; for example a decrease in the corrosion rate may occur as an oxide film develops on the surface of one of the electrodes.

For each environment, three pairs of cast iron and copper electrodes were used. One pair was permanently coupled from the start of the experiment and one couple was connected after a period of a few weeks corroding in the uncoupled state. A third pair of electrodes remained uncoupled throughout the test period.

In addition to the electrochemical measurements described above, some multi-crevice assembly (MCA) specimens [3], composed of castellated cast iron nuts bolted tightly in contact with copper sheet, were used to simulate the situation where the outer copper canister will be in direct contact with the inner cast iron vessel. This specimen produced twenty small crevices between the copper and the cast iron.

2.2 Electrochemical cells

The experiments were carried out in standard glass electrochemical cells which used an inner polyethylene container to avoid contamination of the test solutions by silicates which would be released by alkaline attack of glass. A gas tight seal was maintained by using greased ground glass joints. Low dissolved oxygen concentrations were achieved by passing nitrogen over the test solutions. The nitrogen was passed through an oxygen trap (Oxy-trap, Alltech Associates Inc) to remove trace quantities of oxygen before entry into the cells.
2.3 Materials and electrode design

2.3.1 Working electrodes

Oxygen-free copper (UNS C10100, Cu-OF1) was used for the galvanic corrosion experiments. It was obtained as 12.7 mm diameter rod. The cast iron was procured according to EN 1563 (which replaces BS 2789 grade 420/12 and is equivalent to the old Swedish standard 0717). It was obtained as 51 mm diameter round bar. The material supplier’s data for the compositions of the materials are as follows (wt%), cast iron: C 3.69; Si 2.72; Mn 0.112; S 0.013; P 0.032; Mg 0.071; Fe bal and copper: 99.99% min, P 2 ppm, Pb 4 ppm.

The specimens were machined as round-nosed bullets to avoid edge effects and to allow any gas bubbles generated on the electrodes to rise to the surface. The surface area ratio for the copper to cast iron was approximately 1:1 and the exposed surface area of each specimen was approximately 10.1 cm$^2$. Electrical connection to the specimens was made using threaded stainless steel rod, which was protected from exposure to the test solution using sheathing and masking agent at the interface between the sheathing and the specimen. Prior to testing, the specimens were abraded with 600 grit abrasive paper then degreased in acetone. The cast iron specimens were acid pickled and washed in demineralised water before use to remove surface oxide.

2.3.2 Reference electrodes, redox electrodes and counter electrodes

Proprietary sintered silver-silver chloride reference electrodes immersed directly in the test solution were used. They were calibrated against commercial mercury sulphate electrodes. Gold wire redox electrodes were used. Before insertion into the corrosion cell they were cleaned by flaming and then electrochemically treating in a solution of HNO$_3$:H$_2$O$_2$:H$_2$O (1:1:1 by volume). Copper gauze was used for the counter electrodes for corrosion rate measurements on uncoupled copper and cast iron electrodes.

2.4 Test solutions and test temperatures

Tests were carried out in two artificial groundwaters, denoted Allard groundwater and ‘bentonite-equilibrated’ groundwater. The tests were carried out in stagnant conditions. The composition of the artificial groundwaters is shown in Table 1; pH was adjusted by addition of NaOH.

Tests were also carried out in bentonite slurry. The slurry was prepared using MX-80 bentonite clay, a sodium montmorillonite, which was wetted using bentonite-equilibrated groundwater to give a composition of 30% bentonite in water. Freshly prepared bentonite slurry had a pH of 8.1. Tests were performed at 30ºC and 50ºC, by mounting the test cells in ovens.

2.5 Oxygen concentration

To achieve deaerated conditions, the test cells were assembled in a nitrogen-purged glove box and transferred to the oven. A slow stream of nitrogen was passed over the surface of the test solutions rather than being bubbled through it. The oxygen concentration in the inlet gas was measured as 1-2 ppm. The oxygen concentration in the outlet gas was measured using an oxygen meter as <20 ppm. Occasionally spikes in the oxygen concentration occurred when a gas cylinder had to be changed. For a cover gas composition of nitrogen containing 2-20 ppm oxygen the oxygen concentration in solution can be calculated from Henry’s law to have been in the range 0.085 to 0.85 ppb. Although this is higher than is present in groundwater at the repository level it was sufficiently low to demonstrate the effect of deaeration on the galvanic corrosion of copper-cast iron couples. In some experiments, the solution was initially aerated.
and subsequently deaerated. This procedure aimed to simulate the occurrence of residual oxygen in the repository.

<table>
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*Table 1. Composition of artificial groundwaters used for galvanic corrosion experiments.*

2.6 Electrochemical measurements

The electrochemical potentials of the coupled electrodes and the currents passing between them were measured using an ACM Instruments Galvo Gill 12 Auto ranging ZRA. The potential of the uncoupled electrodes was logged using a separate datalogging system consisting of a high precision, high input impedance (10⁹ohm) digital voltmeter (Schlumberger 7081). A Solartron Minate 7010 multiplexer unit was used to interface between the voltmeter and the electrochemical cells. Some potential data were also recorded using a Grant Squirrel 1200 datalogger. The corrosion rate of uncoupled electrodes was estimated from linear polarisation resistance measurements or AC impedance measurements, obtained using standard electrochemical software (Corware) and a Solartron 1286 potentiostat.

3 Results

Unless stated otherwise the corrosion potential data are quoted with reference to the normal hydrogen electrode (NHE). Current data are reported in units of µA. A current of 1 µA corresponds to a current density of ~0.09 µA/cm², which for iron corresponds to a corrosion rate of ~1.02 µm/year, assuming the corrosion reaction is Fe → Fe²⁺ + 2e⁻. For ease of interpretation it can be assumed that a current of 1 µA is approximately equivalent to a corrosion rate of 1 µm/year. A selection of the electrochemical data obtained from a large number of measurements are presented in Figure 1 to Figure 6; more detailed information is available in reference [4].

The potentials of cast iron, copper and gold electrodes in deaerated Allard water at 30 °C are shown in Figure 1 and the current passing between permanently coupled cast iron and copper electrodes in the same environment are shown in Figure 2. The potential of iron in deaerated Allard water (Figure 1) stabilised at ~-640 mV and the potential of the permanently coupled electrodes (Figure 2) was also ~-640 mV, showing that the potential of the couple was governed by the cast iron rather than the copper. The current passing between the permanently coupled electrodes fell to very low values (<0.1 µA). On occasions the polarity of the current switched, indicating that the copper had become the anode (i.e. the current became negative in Figure 2), but after some time the polarity reverted to iron being the anode.
The current passing between the electrodes that were initially corroded separately (i.e. uncoupled), then coupled in Allard water at 30°C, is shown in Figure 3. The galvanic currents in this experiment were of the order of 0.01 µA. This figure also shows potential and current transients which were caused by the temporary ingress of oxygen when the nitrogen purge gas cylinders had to be replaced. These peaks show that oxygen was rapidly consumed by reaction with the test electrodes and the potentials fell to their previous values in deaerated conditions (typically 0.01 µA).

A further experiment was carried out on the same couple in which the temperature was increased to 50 °C to determine whether there was any direct effect of temperature on the galvanic current. The results of this experiment are shown in Figure 4. This experiment showed that the increase in temperature caused an increase in the galvanic current by a factor of ~×4.

The marked effect of deaeration is illustrated in Figure 5, which shows the results from an experiment in which bentonite-equilibrated water at 50°C was initially naturally aerated and then deaerated by passing a nitrogen cover gas over it. The currents passing between permanently coupled cast iron and copper electrodes fell rapidly from a galvanic current equivalent to ~60 µm/year under aerated conditions to a value of ~0.3 µm/year approximately 200 hours after deaeration commenced. There was a temporary loss of potential data in this experiment between 615 and 767 hours. The temperature of the test solution was subsequently increased to 50 °C and again there was a step increase in the current as a result.

The results of measurements in the bentonite slurry before and after deaeration are shown in Figure 6. These data show that deaeration did not lead to such a rapid decrease in the current in bentonite slurry as in aqueous conditions (compare Figure 5 and Figure 6). Nevertheless the current decreased from around 30 µA under aerated conditions to about 4 µA within 100 hours after deaeration.
Figure 2. Currents passing between permanently coupled cast iron and copper electrodes in deaerated Allard water at 30° C, and potential of coupled electrodes (Test 5, Cell B).

Figure 3. Currents passing between cast iron and copper electrodes in deaerated Allard water at 30° C, and potential of coupled electrodes (Test 5, Cell A) – electrodes coupled after 3410 hours of uncoupled corrosion.
Figure 4. Currents passing between coupled cast iron and copper electrodes in deaerated Allard water at 30º C, and potential of coupled electrodes (Test 5, Cell A) - electrodes coupled after 3410 hours of uncoupled corrosion, showing effect of temperature increase.

Figure 5. Currents passing between permanently coupled cast iron and copper electrodes in bentonite-equilibrated groundwater and potential of coupled electrodes (Test 9, Cell A). The solution was initially aerated then deaerated after 647 hours and the temperature was increased from 30 ºC to 50 ºC after 1172 hours.
The lowest current achieved in this experiment under deaerated conditions, after a period of 2700 hours, was 1.8 µA. The reason that the current was higher in the bentonite slurry could be that oxygen was less mobile than in aqueous conditions (i.e. the oxygen was not extracted from the test environment as rapidly by the purge gas as in aqueous conditions), or that the presence of bentonite led to an increase in the corrosion rate of the iron by interfering with the formation of a corrosion product layer.

The MCA specimen assemblies removed from deaerated Allard groundwater at 30 °C and 50 °C, exhibited shiny copper and black cast iron castellated nuts. No crevice corrosion was observed when they were dismantled.

4 Discussion

4.1 Effect of oxygen concentration and temperature

In the presence of oxygen, copper was the anode in the cast iron-copper couples. This is in agreement with published results for the galvanic corrosion of copper-iron couples in seawater. For example, reference [5] gives the galvanic series in seawater, in which the potential of mild steel or cast iron in flowing seawater is in the range -360 to –460 mV vs NHE and that of copper as -60 to –110 mV vs NHE. The potentials measured in the present work in deaerated conditions were considerably more negative than these values (e.g. see Figure 1), but the iron remained more negative than the copper, indicating that the iron would be the anode in any galvanic couple in deaerated conditions. The potential of the iron was below the hydrogen evolution potential at the pH of the groundwaters and so hydrogen evolution by anaerobic corrosion was possible.

Mansfeld and Kenkel [6] investigated the galvanic corrosion of a range of dissimilar metal couples, including 4130 steel and copper, over a period of 24 hours in naturally aerated 3.5% NaCl. They showed that the corrosion rate of steel was increased by a factor of ×13 when

Figure 6. Currents passing between cast iron and copper electrodes in bentonite slurry at 50°C - aerated initially then deaerated after 1200 hours - and potential of coupled electrodes (Test 8, Cell A).
coupled to a copper electrode. This was attributed to the copper being an efficient cathode for the reduction of oxygen. They showed that the increase in corrosion current due to galvanic coupling can be described by:

\[ i_g^A = i_a^A - i_{corr}^A \]  

where \( i_g^A \) is the increase in the dissolution rate due to galvanic coupling, \( i_a^A \) is the dissolution current density of the coupled anode material and \( i_{corr}^A \) is its corrosion current density when uncoupled (i.e. freely corroding). Similarly, Astley and Scholes [7] found that iron was the anode in copper-mild steel couples in aerated seawater with a corrosion rate, for a 1:1 area ratio of 270 µm/year, based on weight loss data. This represented an acceleration factor of \( \sim \times 3 \), compared to the corrosion rate of uncoupled mild steel. The enhancement in galvanic corrosion depends on the relative areas of copper and steel: the galvanic current is proportional to the area of the cathodic metal [7,8].

In the experiments reported here the galvanic corrosion current in aerated conditions was equivalent to an \( i_g^A \) value of \( \sim 100 \) µm/year (e.g. Figure 5), which is similar to the values reported for copper-mild steel couples in seawater. However, when the solutions were deaerated, the galvanic corrosion current was greatly reduced. For example, at 30°C galvanic corrosion rates as low as 0.02 µm/year for iron were observed after deaeration (Figure 3). There was a correlation between the amount of oxygen present and the galvanic corrosion current, as shown by the fact that oxygen transients, as shown by potential transients, led to transient increases in the galvanic corrosion current (Figure 3Figure 4). In deaerated conditions the cathodic reaction is the reduction of water rather than oxygen and the corrosion rate is determined by the kinetics, or the activation overpotential, of the hydrogen evolution reaction on the cathode (i.e. copper). Oxygen is a far more powerful oxidant for iron than water because of the greater separation in the thermodynamic equilibrium potentials and therefore the corrosion rates are higher in aerated conditions. Over time, there was a general reduction in the corrosion rate of iron coupled to copper in deaerated conditions and this was probably due to the slow accumulation of a corrosion product layer, as shown by the appearance of a black film on the surface of the iron electrodes. This corrosion product probably consisted of magnetite, as this was the composition of the black oxide observed in experiments to measure the expansion of a stack of copper and steel discs under anoxic conditions [9].

The galvanic corrosion rates measured in deaerated conditions were similar to the long-term anaerobic corrosion rates measured using barometric gas cells to collect hydrogen [10], which were of the order of 0.1 – 1 µm/year. Furthermore, gas generation experiments [11] using pieces of steel and copper wire spot-welded together failed to produce any increase in hydrogen generation rate. The increase in the galvanic current caused by increasing the temperature can be attributed to increasing the exchange current density for the water reduction reaction on the copper cathode.

4.2 Application of results to assessment of SKB canister performance

In terms of application of the results of this study to the evolution of the environment within the annulus of the canister the following scenario is envisaged. If water penetrates the annulus through a hole in the outer copper container a galvanic couple will be set up between the copper and the cast iron insert. The current passing between the copper and the cast iron will be concentrated at the contact points. If any residual air is present in the annulus the corrosion rate of the cast iron will be enhanced (i.e. the iron will be the anode and copper the
cathode). The measured galvanic corrosion currents passing to the iron in fully aerated artificial groundwater were equivalent to enhanced corrosion rates in the region of 100 µm/year. In the absence of oxygen in the annulus, as a result of oxygen consumption by corrosion of the cast iron insert or by reaction with the surrounding matrix, the galvanic corrosion currents will fall markedly. The galvanic corrosion rates of iron coupled to copper at low groundwater oxygen concentrations were measured as <0.1 µm/year at 30 ºC and <1 µm/year at 50 ºC. These are close to the values observed for the anaerobic corrosion of uncoupled iron.

5 Conclusions

The main conclusions from this work are as follows:

1. For copper-cast iron couples in artificial groundwaters simulating the SKB repository environment, deaeration leads to a marked decrease in the galvanic corrosion of iron.
2. Increasing the temperature from 30 ºC to 50 ºC led to an increase in the galvanic corrosion current by a factor of approximately \( \times 4 \).
3. The corrosion rates in deaerated conditions were comparable to those measured for iron corroding in the absence of galvanic coupling to copper.
4. No galvanically enhanced crevice corrosion was observed when copper and cast iron were coupled in deoxygenated conditions.

6 References

6. F. Mansfeld and J.V. Kenkel, Laboratory Studies of Galvanic Corrosion I. Two-Metal Couples, Corrosion 31(8), 1975.