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SKB

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Executive Summary

The proposed design for a final repository for spent fuel and other long-lived residues in Sweden is based on the multi-barrier principle. The waste will be encapsulated in sealed cylindrical canisters, which will then be placed in granite bedrock and surrounded by compacted bentonite clay. The canister design is based on a thick cast inner container fitted inside a corrosion-resistant copper canister.

During fabrication of the outer copper canisters there will be some unavoidable grain growth in the welded areas. As grains grow they will tend to concentrate impurities within the copper at the new grain boundaries. The work described in this report was undertaken to determine whether there is any possibility of enhanced corrosion at grain boundaries within the copper canister. The potential for grain boundary corrosion was investigated by exposing copper specimens, which had undergone different heat treatments and hence had different grain sizes, to aerated artificial bentonite-equilibrated groundwater with two concentrations of chloride, for increasing periods of time. The degree of grain boundary corrosion was determined by atomic force microscopy (AFM) and optical microscopy.

AFM showed no increase in grain boundary 'ditching' for low chloride groundwater. In high chloride groundwater the surface was covered uniformly with a fine-grained oxide. No increases in oxide thickness were observed. No significant grain boundary attack was observed using optical microscopy either.

The work suggests that in aerated artificial groundwaters containing chloride ions, grain boundary corrosion of copper is unlikely to adversely affect SKB's copper canisters.

Contents

1   Introduction

SKB have developed a copper-steel canister for the encapsulation of spent nuclear fuel and geological disposal. The canister consists of a steel or cast iron inner container, which provides physical strength, covered with an outer copper canister for chemical stability. The canisters will be placed in an underground repository and surrounded by a bentonite clay backfill. Shortly after the repository is sealed, it will become saturated with neutral to mildly alkaline groundwater from the surrounding geosphere and anoxic conditions will develop [1]. Corrosion processes are the major factors that will determine the period of time over which radioactive waste canisters will be able to prevent the leakage of radionuclides into the external environment. In the repository, pure copper should be immune to corrosion on thermodynamic grounds [2]. The copper used for the outer canister will be oxygen-free (UNS C10100, Cu-OF1) with an addition of 40–60 ppm phosphorus.

During the fabrication of the canister, it is inevitable that some grain growth of the copper will occur during welding operations. The initial grain size is expected to be between 180 μm and 360 μm and this may increase to 2 mm. As the grains grow, the boundaries will sweep through the body of surrounding grains and concentrate impurities within them. The larger the grains the greater will be the concentration of impurities at their boundaries. It is possible that this process may lead to the grain boundaries becoming anodic to the bulk and corroding preferentially, with the possibility of grain drop-out occurring.

To investigate whether this phenomenon occurs in reality the work described in this report was undertaken. The aim of the tests was to show whether the grain size of the copper or the chloride concentration in two simulated groundwaters had an effect on the intergranular corrosion of copper. The groundwaters chosen for the tests represented the extremes of the expected chloride contents. The extent of intergranular corrosion was assessed using atomic force microscope [3] and optical microscopy.

2 Experimental programme

The occurrence of grain boundary attack was investigated by immersing representative samples of copper in two artificial groundwaters and examining the exposed surfaces using atomic force microscopy (AFM) and optical microscopy. Trials with a custom-built scanning electrode technique were also carried out but they were unsuccessful.

2.1 Sample preparation

A sample of copper was provided by SKB. It had been cut from SKB's tube T 19, which was extruded by Wyman-Gordon (Livingston, Scotland) in 1998 using an ingot obtained from Outokumpu. The phosphorus content was 74–85 ppm (based on two samples taken from the top and bottom of the ingot) and the oxygen content was 2.3–5.2 ppm; the copper content was >99.99%. The sample was cut into pieces of two sizes:

- four pieces measuring $20 \times 20 \times 3$ mm, for optical microscopy examination after longer-term immersion experiments (specimens C and D);

- four pieces of dimensions $10 \times 5 \times 3$ mm, to fit in the AFM stage (specimens E and F).

Two pieces of each size (specimens D1, D2 and E1, E2) were annealed at 650°C for one hour in air, to grow larger grains simulating the heat-affected-zone of a weld. The identification of the specimens used in the tests is given in Table 1.

Table 1. Identification of samples used in experiments.

Sample	Annealing conditions	Comments
C1	as received	Prepared for immersion test
C2	as received	Prepared for immersion test
D1	650°C, 1 hour	Prepared for immersion test
D2	650°C, 1 hour	Prepared for immersion test
E1	650°C, 1 hour	AFM measurements – low chloride solutions
E2	650°C, 1 hour	AFM measurements – high chloride solutions
F1	as received	AFM measurements – low chloride solutions
F2	as received	AFM measurements – high chloride solutions

Table 2. Preparation and exposure period of large copper tile samples.

Copper Sample	Experiment	Exposure period
C1	Exposed to high chloride artificial BEA groundwater	1 month
D1	Exposed to high chloride artificial BEA groundwater	1 month
C2	Exposed to low chloride artificial BEA groundwater	2 weeks
D2	Exposed to high chloride artificial BEA groundwater	2 weeks

Before starting the experiments, the samples were polished to a quarter micron finish and etched using 100 g/l ammonium persulphate to reveal the grain structure [4]. The grain sizes in the un-annealed, small-grained material (C1, C2 and F1, F2) were of the order of 50–100 microns diameter and the grain sizes in the large-grained materials were a few hundred microns diameter. After the grain structure of the materials had been examined the tiles were re-ground and re-polished to remove the etching marks. Before the corrosion experiments the samples were chemically polished in 1:1:1 nitric / acetic / orthophosphoric acids for 1 minute at 70°C [5]. The samples for the AFM measurements were marked using a hardness tester to provide indexing marks.

2.2 Artificial groundwaters

The artificial groundwaters were based on bentonite-equilibrated Äspö (BEA) groundwater, which contained sodium carbonate (10 mM) and sodium chloride at two different concentrations. The high and low chloride concentrations were 20,000 ppm and 20 ppm respectively; these are the extremes of the chloride concentrations anticipated in a geologic repository. The alkalinity was adjusted to pH 10 by addition of NaOH. All tests were carried out at room temperature under naturally aerated conditions.

2.3   Atomic force microscopy

The atomic force microscope (AFM) is a type of Scanning Probe Microscope (SPM). It involves inspection of surface properties through the interactions between a sharp tip and the sample. There are several modes of Atomic Force Microscopy, the most common of which is the 'contact mode'. The contact mode involves moving the sample so that the force exerted on it by the tip is constant. The tip is supported on the end of a cantilever, whose deflection can be monitored using a laser beam optical lever and a photodiode. This enables extremely small changes in the position of the tip to be measured. By keeping the signal from the photodiode constant the force exerted by the tip on the surface can also be kept constant. The sample is then rastered horizontally and a three-dimensional image of the surface can be created. A schematic diagram of the AFM is shown in Figure 1.

An East Coast Scientific AFM instrument was used for the measurements. It was equipped with a piezoelectric tube scanner capable of scanning areas of 16 × 16 μm (512 × 512 pixels) with a vertical range of 1 μm and a vertical resolution of ~0.1 nm. The scanning tip was a standard micro-machined silicon nitride lever with a pyramid-shaped tip. The loading on the surface was 50–100 nN and the stylus contact area was ~20 nm^2. The lever arm and the sample could be viewed from above using a relatively long focal length microscope and video camera, which proved adequate to locate indent marks on the polished samples.
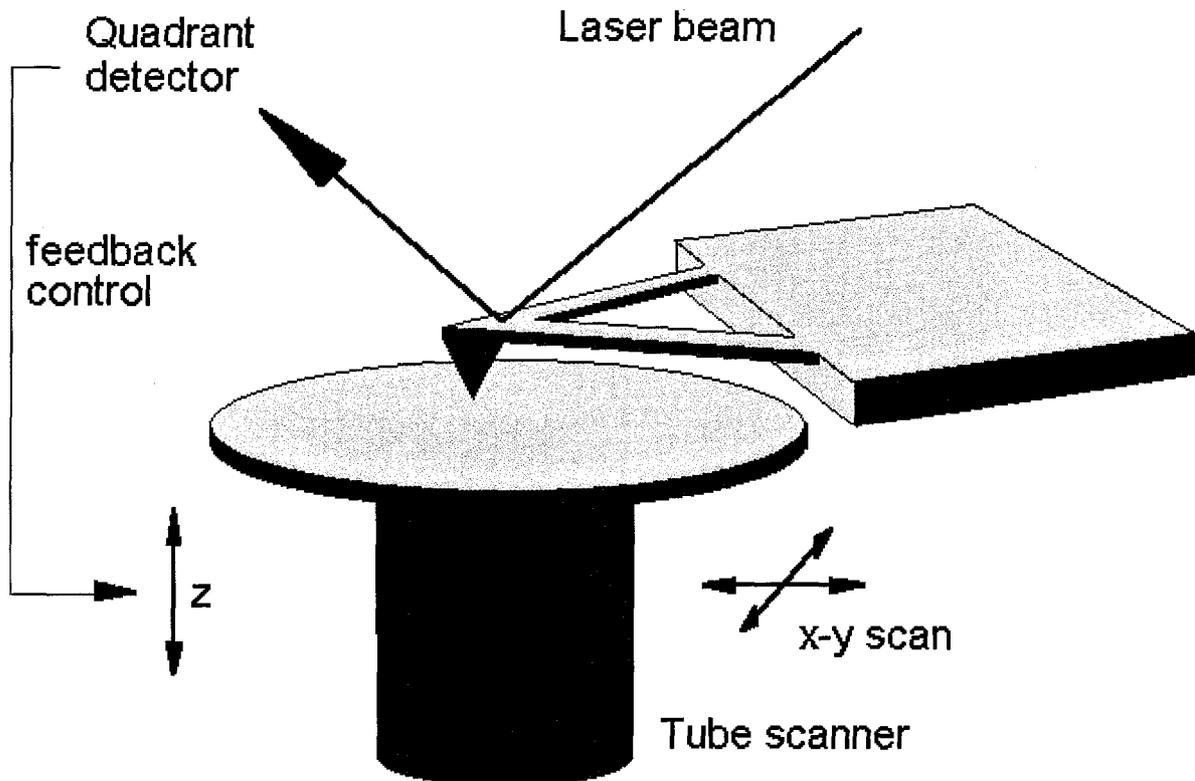
Figure 1. Schematic diagram of atomic force microscope (AFM).

The samples for AFM examination were exposed to the test solutions for periods of 1 hour, 1 day, 5 days and 14 days. After each exposure period the specimens were placed under the AFM for examination (i.e. the same specimen was used throughout the test sequence and no repolishing was carried out before the specimen was re-immersed in the test solution). Once a sample was placed in the tube scanner and brought into contact with the stylus, the coarse micrometer stage was used to position the tip. Ten line scans of ten microns separation were taken along a line between the indexing marks. After each examination the sample was returned to the test solution for further exposure.

2.4   Immersion experiments

The immersion experiments were carried out by exposing small-grain and large-grain samples to the high and low chloride solutions, for 14 or 28 days. Half the surface area of each tile was masked with PVC tape so that a comparison could be made between exposed and unexposed surfaces. The tiles were either mounted in a glass dish or in a plastic matrix and placed in a glass immersion cell. Low or high chloride BEA was added and a glass cover loosely applied. The cell was then left at ambient temperature for the required number of days. At the end of the exposure period the surface was etched in 25% nitric acid to remove the oxide covering and to allow the surfaces to be examined using a stereomicroscope (magnification 70×). After optical examination, the specimen exposed for one month was etched with chromic acid to reveal the grain structure.

3 Results

## 3.1 Atomic force microscopy measurements

AFM examination of an etched material demonstrated that the AFM was capable of detecting attack at grain boundaries (Figure 2). The etching process was found to introduce pits at the grain boundaries. After re-polishing only polishing marks were detectable on the surface.

Samples F1 and E1 (small and large grain size respectively) were exposed to the low chloride solution for one hour, one day and ten days. AFM images indicated that there was no change in the grain boundaries or other significant topographical changes during the course of the experiments.


Figure 2. AFM image of grain boundary on etched copper (specimen F2, 16 μm × 16 μm image).

Samples F2 and E2 (small and large grain size respectively) were exposed to the high chloride solution for one hour, with no detectable change in topography. After exposure for a further day a fine-grained corrosion product (100 to 200 nm diameter), which is assumed to be copper oxide, was found to cover the surface of both specimens. The underlying polish marks were just visible (e.g. specimen F2, Figure 3). There was no evidence of thicker oxides at the grain boundaries. Figure 4 presents a height profile along a line scan on the same surface.
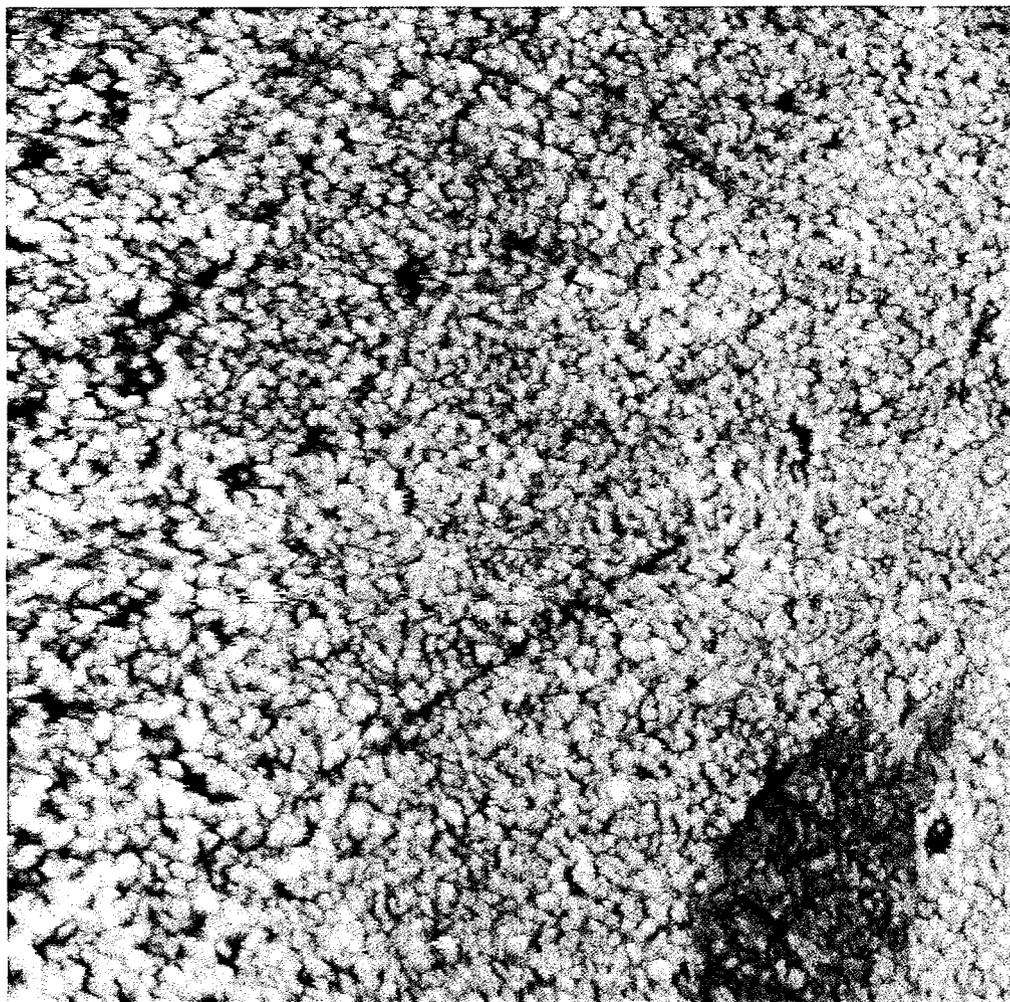
Figure 3. *Copper oxide on fine-grained copper in high chloride artificial BEA groundwater after 24 hour exposure (specimen F2, 16 μm × 16 μm image).*
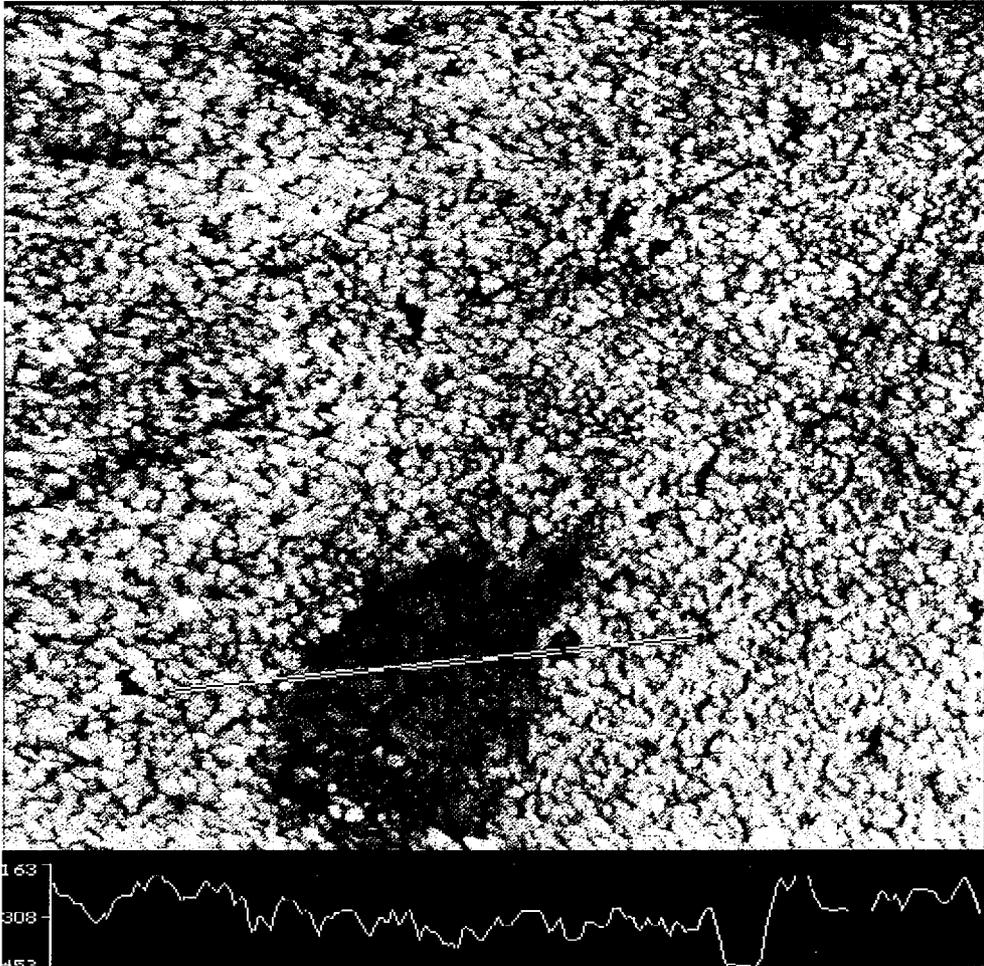
Figure 4. *Same sample as Figure 3. The line scan shows a depth profile (vertical height in Å).*

3.2 Immersion tests and optical microscopy

3.2.1 Immersion experiments in high chloride solution

Both large-grained (D1) and small-grained (C1) copper samples developed a dark brown oxide. Figure 5 shows a photograph of sample D1 after immersion for 28 days in artificial high chloride BEA groundwater. The oxide was removed by a brief immersion in nitric acid. Microscopic examination indicated that there had been no preferential corrosion at the boundaries but generalised attack of the whole copper surface had taken place.
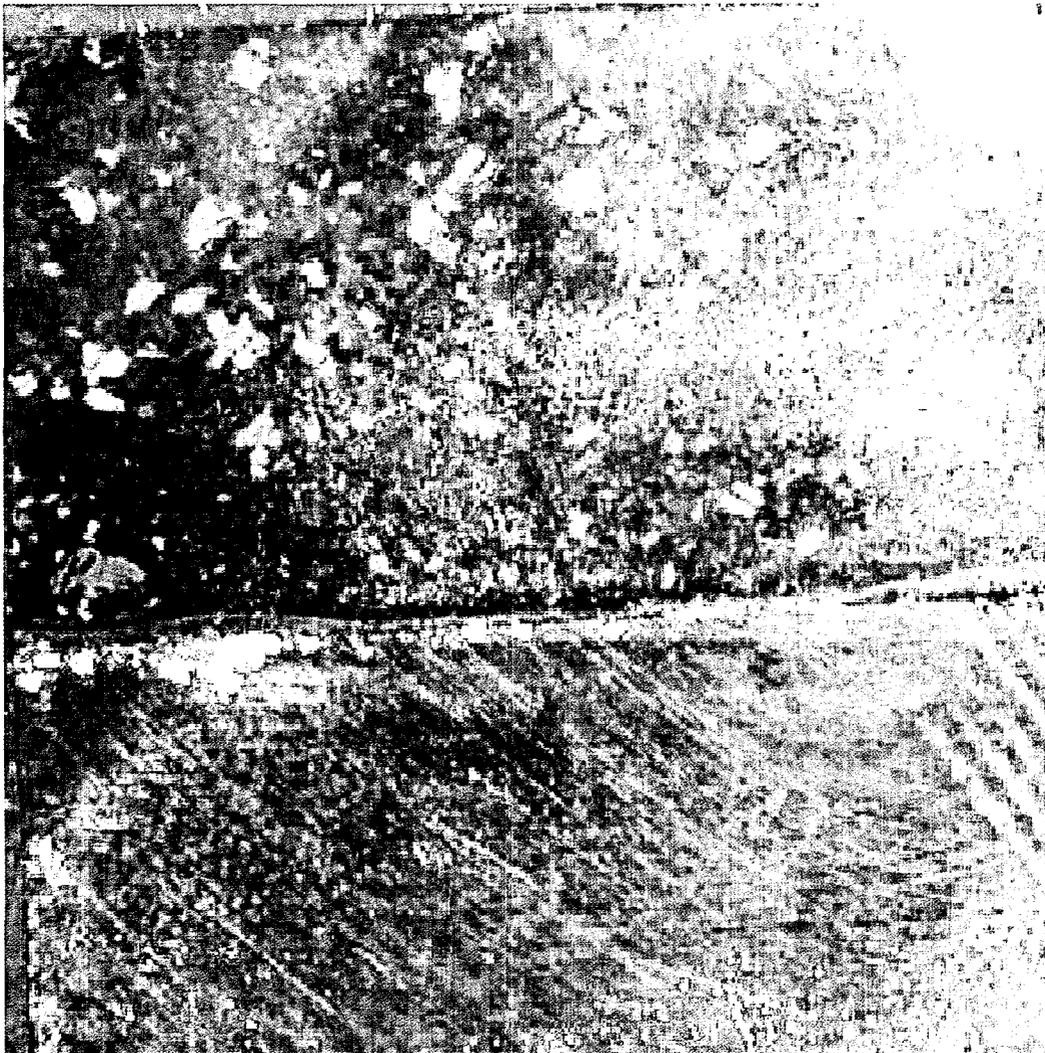
Figure 5. Photograph of large grain copper sample (D2) after 28 days' exposure to high chloride artificial BEA groundwater, showing masked area (bottom) and unmasked area (top).

3.2.2 Immersion experiments in low chloride solution

Thinner oxide films were grown on the specimens in the low chloride BEA. Again, there was no evidence of material loss from the grain boundaries. There was no difference in reflectivity between the exposed and masked-off copper surfaces. If there had been, it would have been an indication that the grains or their boundaries had been affected by the test solution.

4   Discussion

The work has shown that it is feasible to study the corrosion of copper samples using the AFM. In the case of the high chloride artificial groundwater, once an incubation period had passed, it was possible to follow the corrosion in real time.

The results show that in aerated alkaline solutions containing chloride ions, there is no preferential attack and dissolution of copper at the grain boundaries, regardless of grain size. AFM analysis of grain boundaries showed no increase in 'ditching' for low chloride media and no increases in oxide thickness at grain boundaries for the high chloride media.

This result is supported by the optical microscopy examination of copper exposed to high chloride solution, in which no significant grain boundary attack was observed in the photograph taken at the end of the exposure.

5   Conclusions

The main conclusions from this work are as follows:

1. There was no observable grain boundary corrosion of oxygen-free copper canister material in aerated artificial bentonite equilibrated groundwater at 20 ppm or 20,000 ppm chloride, after exposure periods up to 28 days.

2. Uniform corrosion and oxide formation occurred more readily on the copper surface in high chloride concentrations.

3. No effect of grain size on the susceptibility to corrosion of copper in aerated artificial bentonite equilibrated groundwater was observed.

6 Recommendations

To date, experiments have only been carried out at room temperature in aerated artificial bentonite-equilibrated groundwater over a range of chloride concentrations. It is recommended that a review of other relevant environments should be carried out to determine whether they are likely to be any more aggressive.

Preliminary trials with a scanning reference electrode (not reported here) were unsuccessful because the custom-built equipment did not have the necessary resolution, but in principle the technique has the capability to detect grain boundary corrosion and may warrant further investigation using commercially available equipment.

7 References

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2   N. de Zoubov, C. Vanleugenhaghe and M. Pourbaix, *Copper,* Section 14.1 in 'Atlas of Electrochemical Equilibria in Aqueous Solutions', M. Pourbaix (ed.), 2nd edition, National Association of Corrosion Engineers, Houston, Texas, USA, 1974.

3   G. Barkleit, F. Schneider, K. Mummert, *Application of Atomic Force Microscopy for Characterization of Intergranular Corrosion of SS 304L*, presented at Eurocorr '98, Utrecht, 1998.

4   G.F. Vander Voort, *Metallography Principles and Practice*, McGraw-Hill, pg. 622, 1984.

5   ibid., pg.554.