ELECTROCHEMICAL AND CORROSION TESTING OF COPPER NUCLEAR WASTE CANISTERS
EXPOSED TO SULPHIDE ENVIRONMENTS

J. Smith
PhD Candidate
Department of Chemistry,
The University of Western Ontario,
London, ON, Canada, N6A 5B7

ABSTRACT

The mechanism and kinetics of Cu corrosion in anoxic aqueous chloride solutions containing sulphide (10^{-3} mol/L) have been investigated electrochemically and under natural corrosion conditions. Under these conditions Cu is thermodynamically unstable in anoxic water and the anodic growth of a chalcocite (Cu_2S) / digenite ($Cu_{1.8}S$) film is supported by the cathodic reduction of water. Electrochemical experiments at rotating disc electrodes and impedance spectroscopy show that the film growth occurs under SH^- transport control as stagnant conditions are approached. At this concentration, film growth can follow two distinct pathways. The initially formed film grows rapidly via an ion (or associated defect) transport process. If this film remains coherent, subsequent film growth / corrosion is extremely slow. If the development of interfacial stresses leads to film fracture then growth continues and a much thicker nodular deposit is formed. The primary goal of this research is to develop a mixed potential model which can be used to assess the performance of copper nuclear waste containers in granitic nuclear waste repositories.

INTRODUCTION

A proposed method of disposal of Swedish/Finnish/Canadian high-level nuclear waste is to place it in corrosion resistant containers and bury it approximately 500-1000m deep in granite environments.[1, 2, 3] The waste canisters would be buried in boreholes and backfilled with compacted bentonite clay. The primary candidate for the fabrication of these containers is copper, selected for its thermodynamic stability in the anoxic aqueous environment anticipated.[4] The design of these containers has been discussed elsewhere.[4] The key feature for present purposes is the proposed use of an outer copper shell (approximately 5 cm thick) and in inner liner of nodular cast iron.[3, 5, 6]

A model, based on mixed potential principles has been developed to predict container lifetimes under repository conditions.[7] This model predicts all O_2 in the repository will be consumed relatively early in the container lifetime (~2600 years).[8]

Possible components of the immediate vault environment include pyrite (FeS_2) and sulphate (SO_4^{2-}) both of which are potential sources of sulphide, the latter by reaction with sulphate-reducing bacteria (SRB) which can convert sulphates to sulphides.[9] Factors, such as the mechanical pressure from the swelling bentonite, the low water activity in the bentonite, γ-radiation and the heat from radionuclide decay processes should prevent microbial activity in the vicinity of the container. Remotely produced sulphide, however, could be transported slowly through the compacted buffer to the container surface,[9] Figure 1. Since the presence of sulphide films shifts the potential for copper dissolution to more negative values,[10] this could render copper susceptible to corrosion via the reduction of water.[11]

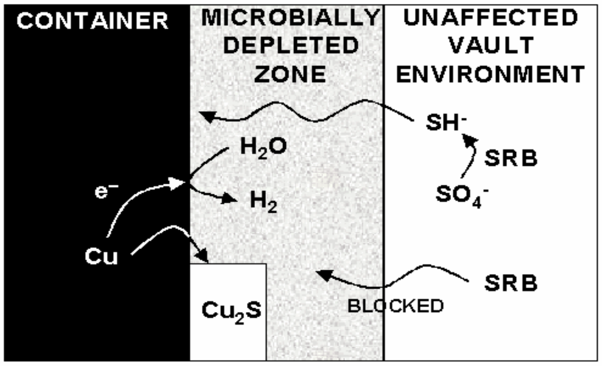

FIGURE 1: Schematic illustrating a possible scenario for copper corrosion under anticipated repository conditions.

$$2Cu + SH^- \rightarrow Cu_2S + H^+ + 2e^- \qquad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

Swedish/Finnish studies have found significant amounts of sulphide in repository sites, with predicted concentrations in the range of $(0\text{-}3)\times10^{-3}$ mol/L at vault closure to $(0\text{-}0.3)\times10^{-4}$ mol/L 10,000 years into the future.[13]

The corrosion of Cu-Ni alloys in polluted seawater has been studied extensively but much less research has been carried out on unalloyed Cu in sulphide containing environments.[14-23] In a relevant study, King and Stroes-Gascoyne[11] measured corrosion potentials (E_{corr}) on Cu covered with compacted clay under anaerobic conditions. As observed by others[13] in open solution, the presence of sulphide caused a drop in E_{corr} to values close to the redox potential for reaction (1). Based on available data, King[1] noted that while E_{corr} values were close to the equilibrium potential for reaction (1), it was not possible to decide whether E_{corr} was a redox equilibrium potential or a mixed potential due to the coupling of the anodic reaction of Cu (the forward step in reaction (1)) to the cathodic reduction of water.

The primary goals of this research are; (i) to clarify the corrosion mechanism of Cu in sulphide solutions; (ii) to identify the nature of the phases formed; and, (iii) to determine the current-potential relationships for the anodic and cathodic reactions involved in the corrosion process. These relationships will form the basis of a mixed potential model for Cu container corrosion under waste disposal conditions.

EXPERIMENTAL DETAILS

All experiments were conducted using a three-electrode electrochemical cell consisting of a copper (5ppm phosphorous deoxidized) disc working electrode, a saturated calomel reference electrode (SCE; -241 mV versus SHE) and a platinum mesh counter electrode ($16cm^2$). Copper is polished successively with 220, 320, 500, 800, 1000 and 1200 grade silicon carbide paper and then to a mirror finish using 1 μm, 200 nm and 20 nm alumina suspensions. All solutions were prepared with 0.1 mol/L NaCl (99% purity) with various concentrations (10^{-5} to 10^{-2} mol/L) of sodium sulphide (98% purity) and de-ionized Millipore water (18.2 MΩ·cm) to mimic anticipated Scandinavian groundwaters.

Rotating electrodes were controlled using a Radiometer analytical rotator. Potentials were controlled using a Solartron 1287 potentiostat and electrochemical impedance spectroscopy was carried out using a Solartron 1254 frequency response analyzer. The Software used for the analysis of EIS data was Zview version 2.80 produced by Scribner Associates Inc.

To avoid O_2, the majority of experiments were performed in an anaerobic chamber in Ar-purged solutions, and electrodes were cathodically cleaned at
-1.3 V for 60 sec and -1.15 V for 60 sec prior to all experiments.

Electrochemical experiments were performed voltammetrically (2 mV/s) at rotating disc electrodes ($1 \leq \omega \leq 30$ Hz). Also, corrosion potential (E_{corr}) measurements were made with intermittent EIS measurements. EIS spectra were recorded using a potential input signal of amplitude ±10 mV over the frequency range 10^6 to 10^{-2} Hz. On completion of E_{corr} experiments, the extent of corrosion was determined by cathodically stripping the corrosion films using a potential scan from the measured corrosion potential to –1.6 V / SCE.

Scanning electron microscopy (SEM) was performed on samples corroded under open circuit conditions in 0.1 mol/L NaCl solution containing a sulphide concentration of 10^{-3} mol/L for various lengths of time. On completion of the corrosion experiment, specimens were removed from solution and rinsed with de-ionized water (18.2 MΩ·cm) to remove NaCl prior to examination using an S-4500 Scanning Electron Microscope.

RESULTS AND DISCUSSION

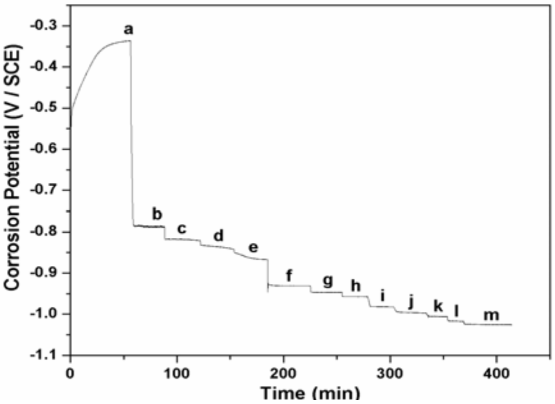

FIGURE 2: E_{corr} as a function of total sulphide concentration (in mol/L) and time (stagnant solution); (a) 0.00, (b) $3.32x10^{-5}$, (c) $6.62x10^{-5}$, (d) 9.90x10, (e) $1.32x10^{-4}$, (f) $4.59x10^{-4}$, (g) $7.84x10^{-4}$, (h) $1.11x10^{-3}$, (i) $2.69x10^{-3}$, (j) $4.23x10^{-3}$, (k) $5.71x10^{-3}$, (l) $8.55x10^{-3}$, (m) $1.12x10^{-2}$.

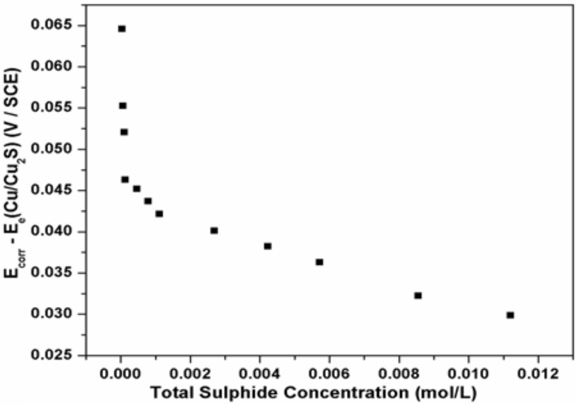

FIGURE 3: The difference between the observed corrosion potential (E_{corr}) and the calculated reversible potential (E_e) for the Cu/Cu_2S reaction as a function of total sulphide concentration.

Figure 2 shows E_{corr} as a function of increasing sulphide concentration ($[S]_T$) . The very negative E_{corr} value observed prior to the addition of sulphide is indicative of the anoxic conditions achieved within the anaerobic chamber. Comparison of this value to E/pH diagrams[24] clearly shows that, at this potential, copper is well below the threshold for copper oxide formation and is thermodynamically stable in water. However, the addition of even a small concentration of sulphide rapidly shifts E_{corr} to more negative values. Transition from E_{corr} value (a) to (b) requires approximately 1.5 minutes. Figure 3 shows that E_{corr} approaches the equilibrium potential (E_e) for the Cu/Cu_2S reaction (equation 1) as $[S]_T$ is increased. In calculating E_{corr} - E_e, E_e is given by the Nernst relationship,

$$E_{e(Cu/Cu2S)} = -1.13 - 0.030 \log[S^{2-}] \tag{3}$$

and the concentration of S^{2-} at any given $[S]_T$ and pH is determined from the dissociation equilibrium,

$$SH^{-} \Leftrightarrow S^{2-} + H^{+} \tag{4}$$

using a pKa value of 11.96.[25]

Considerable discussion has taken place on whether E_{corr} represents a redox potential for reaction (1) or a mixed potential involving the coupling of the anodic part of reaction (1) to the reduction of water.[17, 25] The approach of E_{corr} to $E_{e\,(Cu/Cu2S)}$ as $[S]_T$ is increased suggests control of E_{corr} by the Cu_2S redox reaction may be possible at high $[S]_T$. This would require that the sulphide film grow to an equilibrium state or constant thickness. E_{corr} values at lower $[S]_T$ ($< 4\text{x}10^{-3}$ mol/L) deviate significantly from $E_{e\,(Cu/Cu2S)}$ and, Figure 2, appear to be steady-state values; i.e., are not slowly approaching the redox potential. We conclude that, for the $[S]_T$ range of primary interest (10^{-3} to 10^{-5} mol/L), E_{corr} is a mixed potential, with reaction (1) potential-determining and the reduction of H_2O strongly polarized and rate-determining.

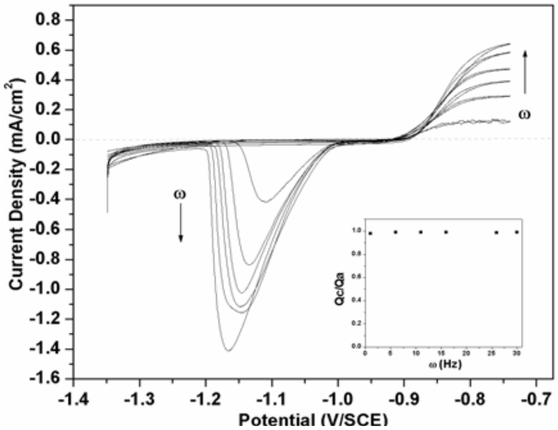

FIGURE 4: Voltammetric scans recorded at rotating disc electrodes for $[S]_T = 10^{-3}$ mol/L (from Figure 5) showing the peaks associated with the cathodic reduction of the copper sulphide film. Inset shows cathodic (Q_C) to anodic (Q_A) charge ratios obtained by integration of the anodic and cathodic sections of the voltammogram.

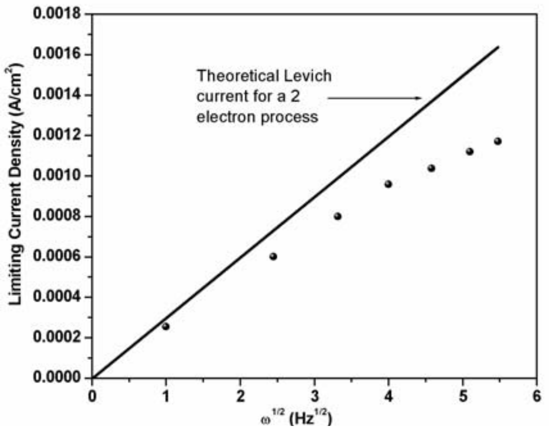

FIGURE 5: Limiting anodic currents (from the voltammograms in Figure 5) as a function of the square root of electrode rotation rate (ω) showing that the limiting current approaches the theoretical Levich limiting current as ω → 0.

Voltammetric scans on rotating discs, Figure 4, show the anodic formation of a copper sulphide film as well as peaks associated with their cathodic reduction. Sulphide film growth occurs reversibly, under partial transport control, and the presence of a single reduction peak suggests only one phase is present. Integration of the voltammograms yields cathodic to anodic charge ratios of ~99.9% (Figure 4 inset), i.e., regardless of rotation rate, all the charge injected on the anodic scan is available for reduction on the reverse cathodic scan, indicating negligible dissolution.

Diffusion limited anodic currents, Figure 4, approach the theoretical Levich limiting currents as the electrode rotation rate tends to zero, Figure 5. The deviations from predicted values as ω increases suggests a limitation on the anodic film formation rate due to the presence of a surface film.

Figure 6 shows EIS measurements in a 10^{-3} mol/L $[S]_{total}$ solution under natural corrosion conditions. The rapidly attained steady-state potential remains stable over the 46 hour duration of the experiment. The value for the phase angle (θ) at frequencies less than 10 Hz and the reduced slope of the log |Z| versus log frequency plot as frequency tends to 0 Hz indicate that the impedance behaviour cannot be represented by a simple parallel RC circuit, and can only be fitted using a circuit which incorporates a Warburg coefficient for diffusion effects, Figure 6 (inset). In this circuit, R_1 is the polarization resistance, C_1 is the interfacial capacitance and W is the Warburg impedance for diffusive transport.

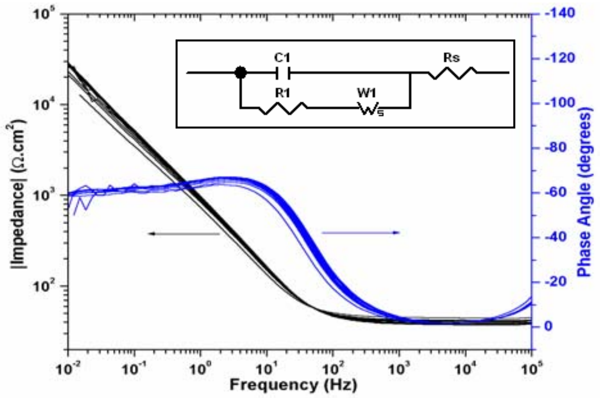

FIGURE 6: EIS data recorded during corrosion in a 10^{-3} mol/L sulphide solution. This plot includes 10 spectra recorded over the 46 hour duration of the experiment. The inset shows the equivalent circuit used to fit the data.

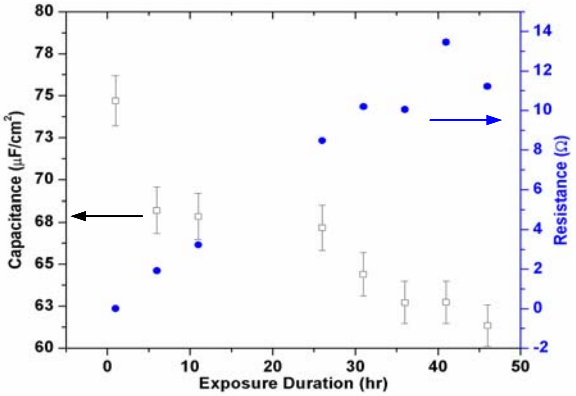

FIGURE 7: Total capacitance (C_1) and resistance (R_1) as a function of exposure duration for a copper electrode in 10^{-3} mol/L sulphide solution: values were obtained from a fit to the equivalent circuit shown in Figure 10.

A good fit to the data was obtained and Figure 7 shows the total surface capacitance (C_1) given by

$$(C_1)^{-1} = C_{dl}^{-1} + C_F^{-1} \tag{5}$$

, where C_F is the film capacitance and C_{dl} is the capacitance of the double layer, and the polarization resistance (R_1) as a function of the duration of exposure to the sulphide solution. Values of the Warburg impedance were also obtained but were very unreliable due to the large error involved in extrapolating the low frequency data to obtain the values. However, W is orders of magnitude greater than R_1, indicating control of the corrosion process by solution transport of SH^- under the stagnant conditions employed. This is consistent with the data in Figure 5 which shows that sulphide film formation becomes transport limited as $\omega \rightarrow 0$.

The very small values of R_1 indicate the surface sulphide film does not significantly impede corrosion. The increase of R_1 with time, Figure 7, is consistent with a minor thickening of the film as suggested by the slight decrease in C_1 over the same period, if we assume the C_{dl} remains constant and attribute the change in C_1 completely to the thickening of the film. The fact that the capacitance changes little after the first ten hours, a period over which E_{corr} has not yet established a steady-state value, suggests rapid film formation at short exposure times with slow to negligible growth thereafter.

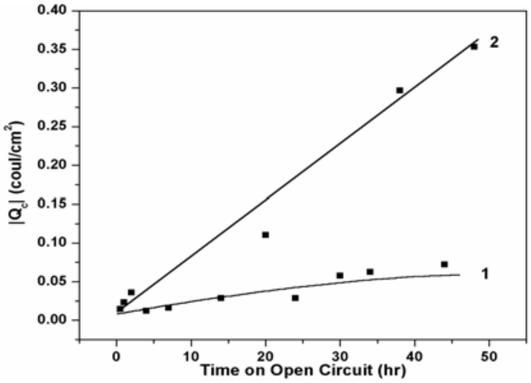

FIGURE 8: Plot of cathodic charge (Q_C) as function of exposure to a sulphide solution (10^{-3} mol/L).

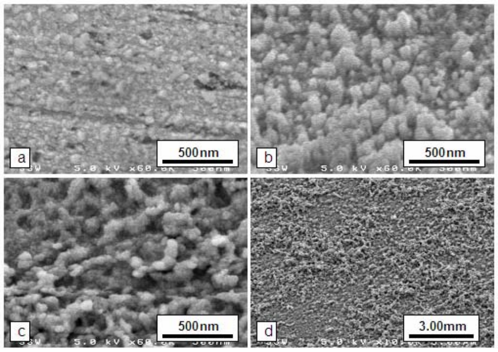

FIGURE 9: Scanning electron micrographs of copper sulphide films formed by corrosion in a 10^{-3} mol/L sulphide solution for a duration of (a) 1 hr, (b) 8 hr and (c,d) 24 hr.

In a second series of corrosion experiments, the sulphide films were cathodically stripped after various periods of exposure. The E_{corr} values in these experiments agreed closely with those measured in the impedance experiments described above, making the two sets of data comparable. Cathodic stripping voltammograms (CSVs), recorded after corrosion, fall into two categories; those which exhibit a small reduction charge generally associated with a single reduction peak; and those which exhibit a significantly greater reduction charge often associated with two reduction peaks. No apparent correlation between the E_{corr} value measured and either of these two behaviours is observed.

These observations indicate two distinct film growth patterns, a suggestion supported by the charge time plots, Figure 8, obtained by integrating the charge under the CSV film reduction peaks. Initial film growth would be expected to occur by ionic or defect transport through the growing sulphide film. Along this pathway, the film would be expected to approach a limiting thickness as suggested by line 1 in Figure 8. This would be consistent with the impedance data for the experiment described in Figures 6 and 7, which shows that the corrosion process leading to the formation of this film is rapid.

However, compressive interfacial stresses and film fracture may occur allowing for subsequent growth by transport through fractures (or pores). The film would then be expected to grow substantially thicker, line 2 in Figure 8. This second process would lead to the observation of the dual film reduction process observed in one trend of CSVs. It would be expected that, for natural corrosion conditions, this second pathway would be more prominent than the first.

Scanning electron micrographs of corrosion products were also performed. Samples were prepared under open circuit conditions in a 10^{-3} mol/L sulphide solution and removed after 1hr, 8 hr and 24 hr. The E_{corr} values were consistent with those observed previously. SEM shows the surface to be covered by a nodular deposit, Figure 9a-d, suggesting growth of the outer layer occurs by a nucleation and growth process. It appears that the film becomes much thicker with time in solution. At the end of 24 hours, an extremely flawed and porous, sponge-like deposit can be seen, Figure 9c,d, indicating the on-going accumulation of a thick outer layer of deposit. These observations are also consistent with an on-going film growth process following pathway 2 in Figure 8.

SUMMARY AND CONCLUSIONS

(i) In anoxic aqueous conditions containing dissolved sulphide, copper is thermodynamically unstable and the anoxic growth of a copper sulphide film is supported by the cathodic reduction of water.

(ii) On a clean copper surface, film growth occurs rapidly and is controlled by the diffusive transport of SH^- to the electrode surface under stagnant conditions.

(iii) At a sulphide concentration of 10^{-3} mol/L film growth can follow two distinct pathways. The initially formed film grows via the transport of Cu^I ions (or an associated defect) through the sulphide film. If this film remains intact, then film growth is limited and a steady-state thickness is achieved. If the development of interfacial stresses leads to film fracture, then growth can continue and much thicker nodular deposits, confirmed by SEM, are formed.

(iv) When an intact sulphide film is present the corrosion potential achieves a value very close to the equilibrium potential for the sulphide formation reaction. This, and the observation that the cathodic current for H_2O reduction is very small and potential independent, shows that the latter reaction is rate-determining.

ACKNOWLEDGEMENTS

This research has been funded by the Swedish Nuclear Fuel and Waste Management Co (SKB), Stockholm. In addition, the authors would like to thank Dr. Roberta Flemming and Tatiana Karamaneva of the Dept. of Earth Sciences in the University of Western Ontario for XRD analyses, and Surface Science Western for use of their scanning electron microscope.

REFERENCES

1. F. King, Swedish Nuclear Fuel and Waste Management Co. Technical Report, TR-02-25 (2002).
2. J. McMurry, Evolution of a Canadian Deep Geologic Repository: Base Scenario, Ontario Power Generation Report No: 06819-REP-01200-10092-R00 (2003).
3. J. McMurry, Evolution of a Canadian Deep Geologic Repository: Base Scenario, Ontario Power Generation Report No: 06819-REP-01200-10127-R00 (2004).
4. I. Puigdomenech and C. Taxen, SKB Swedish Nuclear Fuel and Waste Management Co. Technical Report, TR-00-13 (2000).
5. C. Andersson, SKB Swedish Nuclear Fuel and Waste Management Co. Technical Report, TR-02-07 (2002).
6. P Maake, Used Fuel Container Requirements, Ontario Power Generation Report No: 06819-PDR-01110-R01 (2001).
7. F. King and M. Kolar, Ontario Power Generation, Nuclear Waste Management Division Report, 06819-REP-01200-10041-R00 (2000).
8. F. King, Canadian Nuclear Society, Proc. Int. Conf. on Deep Geological Disposal of Radioactive Waste, 5-39 (1996).
9. K. Pederson, SKB Swedish Nuclear Fuel and Waste Management Co. Technical Report, TR-00-04 (2000).
10. F. King and S. Stroes-Gascoyne, Proc. 1995 Int. Conf. on MIC, NACE International and American Welding Society, Houston, TX and Miami, FL, 35/1 – 35/14 (1995).
11. M Pourbaix and A. Pourbaix, Geochim. Cosmochim. Acta, **56**, 3157 (1992).

12. P. Pitkanen, A. Luukkonen, P. Ruotsalainen, H. Leino-Forsman and U. Vuorinen, Posiva Oy, Report 98-10 (1999).
13. H. Yamada and T. Nakamura, J. Japan Foundrymen's Soc., **36**, 470 (1964).
14. B.C. Syrett, Corrosion, **33**, 257 (1977).
15. L. Giuliani and G. Bombara, Br. Corr. J., **8**, 20 (1973)
16. H.P. Hack and J.P. Gudas, Corrosion, **79**, Paper 234 (1979).
17. D.D. MacDonald, B.C. Syrett and S.S. Wing, Corrosion, **35**, 367 (1979).
18. B.C. Syrett, Corros. Sci., **21**, 187 (1981).
19. L.E. Eiselstein, B.C. Syrett, S.S. Wing and R.D. Caligiuri, Corros. Sci., **23**, 223 (1983).
20. D.D. MacDonald, B.C. Syrett and S.S. Wing, Corrosion, **34**, 289 (1978).
21. B.C. Syrett and D.D. MacDonald, Corrosion, **35**, 505 (1979).
22. B.C. Syrett and S.S. Wing, Corrosion, **36**, 73 (1980).
23. E.D. Mor and A.M. Beccaria, Brit. Corr. J., **10**, 33 (1975).
24. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd Edition, NACE International, Houston, TX (1974).
25. M.R. Gennero de Chialvo and A.J. Arvia, J. Appl. Electrochem., **15**, 685 (1985).