ELECTROCHEMICAL STUDIES OF GEOTHERMAL CORROSION

B.G. POUND, R.M. SHARP and C.A. WRIGHT

Departments of Chemistry and Chemical and Materials Engineering,
University of Auckland

INTRODUCTION

Corrosion testing in geothermal systems is normally carried out to monitor the performance of existing plant or to guide the selection of materials and operating conditions in the design of new plant. A number of methods have been successfully used to measure corrosion rates in geothermal media; they include the coupon weight-loss method, the corrosometer (resistance probe), the hydrogen probe, stress corrosion rigs, and other methods.[1,2] Electrochemical techniques have not been widely used, although they appear to be quite promising.[3] The advantage of electrochemical methods is that they provide a direct measurement of the corrosion rate and it is possible to distinguish between active corrosion and passivation of the metal surface.

We have commenced a research project using electrochemical and related methods to determine the mechanism of corrosion of steel and other metals in geothermal fluids from the Broadlands field. This paper summarises some of our initial findings.

ELECTROCHEMICAL PHASE DIAGRAMS

Corrosion equilibria may be represented by potential-pH or Pourbaix[4] diagrams over the temperature range of interest. These diagrams indicate the thermodynamic limits of stability of a metal in relation to its ions and solid corrosion products, such as oxides and sulphides, as a function of pH and equilibrium potential of the electrochemical reaction.

By coupling potential-pH diagrams with corrosion potential data, it is possible to predict likely corrosion products of metal/environment combinations. The predicted products can in many cases be compared with actual corrosion products.

In constructing potential-pH diagrams, it is usual to calculate the free energy change of each reaction at the temperature of interest. The free energies of formation for species in the reaction at elevated temperatures are evaluated using a knowledge of the free energies of formation, entropies and heat capacities of the substances involved.

Geothermal equipment usually involves iron alloys in contact with fluids containing sulphide species and are at temperatures up to 573 K. Various potential-pH diagrams for the $Fe/S/H_2O$ system at elevated temperatures have been published.(3,5-9) We have assessed these publications and produced a set of diagrams applicable to Broadlands. These diagrams are based on potential-pH equations derived by Biernat and Robins.

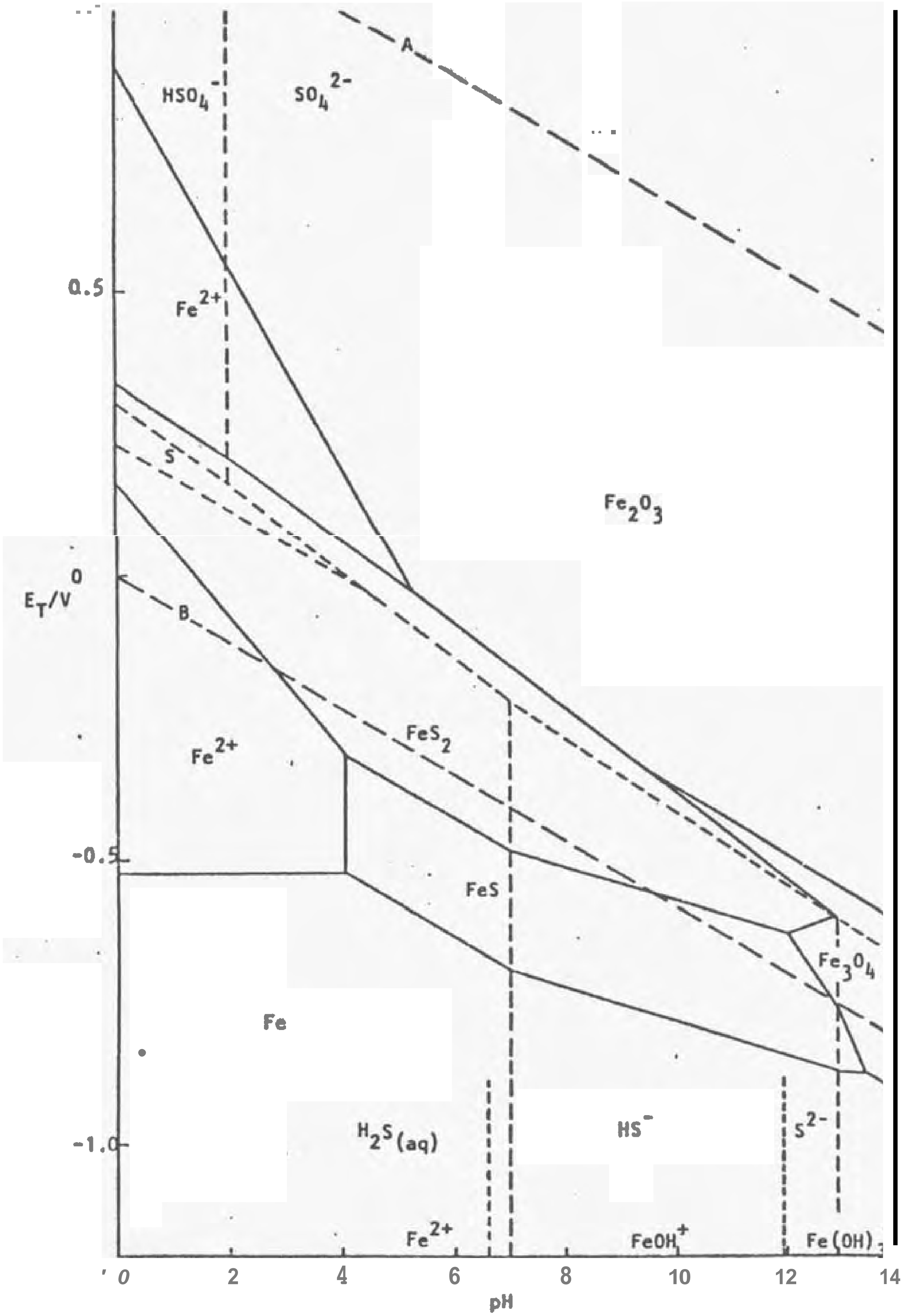

FIGURE 1: **Potential-pH Diagram for Fe/S/H_2O System at 298 K**

The conditions selected apply to cold condensate at the Broadlands Corrosion Test Rig.

$(Fe^{2+}) = 10^{-4}$ mol l^{-1}, $(H_2S + HS^- + S^{2-}) = 10^{-3}$ mol l^{-1}

$P_{H_2} = P_{O_2} = 1$ atm

A potential-pH diagram for the $Fe/S/H_2O$ system is shown in Figure 1. This diagram has been constructed for the conditions of the cold condensate chambers at the Broadlanda corrosion test rig.

In non-aerated condensate for example, the corrosion potential will lie between the region of Fe metal and line B which represents the discharge of H^+ to H_2. Since FeS is the predominantly stable species near neutral pH, it would be predicted that a sulphide of approximately this stoichiometry is likely to be the corrosion product. This is indeed consistent with the formation of Mckinawite ($Fe_{(1+x)}S$) on carbon steel in this medium as found from DSIR tests.[10]

The stability of FeS_2 is strongly dependent on temperature. Its region of stability in the potential-pH diagram decreases markedly with increasing temperature to the extent that FeS_2 does not appear at 573 K. At temperatures above 473 K the FeS region also diminishes but FeS and also Fe_3O_4 continue to be thermodynamically stable up to 573 K.

POLARISATION RESISTANCE METHOD

This technique involves applying a small current I between a test electrode and an auxiliary electrode and measuring the resulting change of potential of the test electrode ΔE measured against a reference electrode. All three electrodes are usually made from the same metal, but they must be insulated from one another. The observed polarisation resistance R_p is related to the corrosion current I_{corr}.[11]

$$R_p = \Delta E/I = B/I_{corr} \qquad \ldots \quad \ldots \quad \ldots \quad (1)$$

B is a parameter derived from the kinetics of the electrode reactions; for carbon steel at 20°C B is 0.025 V. The corrosion rate, defined as the mean rate of removal of metal (µm/yr) assuming uniform corrosion, is given by the following expression for carbon steel at 20°C.

$$\text{Rate} = \frac{2.9 \times 10^5 \ \mu m \ yr^{-1}}{R_p \ A/(\Omega \ cm^2)} \qquad \ldots \quad \ldots \quad \ldots \quad (2)$$

A is the surface area of the test electrode.

Preliminary experiments showed that the relatively low conductivity of some condensates (0.02 s/m) gave rise to an error due to the electrolyte resistance between the electrodes. This problem was overcome by designing the electrode probe so that the configuration between the test and reference electrodes was optimised. Another possible difficulty is that the presence of a film of corrosion product on the metal surface may cause an extra resistance in the circuit, leading to an underestimate of the corrosion rate. But in most cases the corrosion rate will be reduced in proportion to the amount of surface film, and there will be little error in the measurement of corrosion rate.

We have found that the polarisation resistance probe has performed satisfactorily in laboratory trials, giving results comparable to weight-loss measurements. It has the advantage of giving the corrosion rate directly from a single reading on a probe which can be permanently inserted into geothermal equipment. Field trials at Broadlands have been planned by DSIR.

ELECTROCHEMICAL POLARISATION

Cyclic voltammograms are extremely useful in predicting the. passivating behaviour of alloys in aggressive environments, in particular with regard to so-called active regions of potential in which a metal will undergo dissolution, passive regions when the metal becomes covered by a protective film, and film growth regions during which the film may thicken by further electrochemical reaction. The technique involves following the current response to a linearly-varying potential difference controlled between the working electrode and a reference electrode.

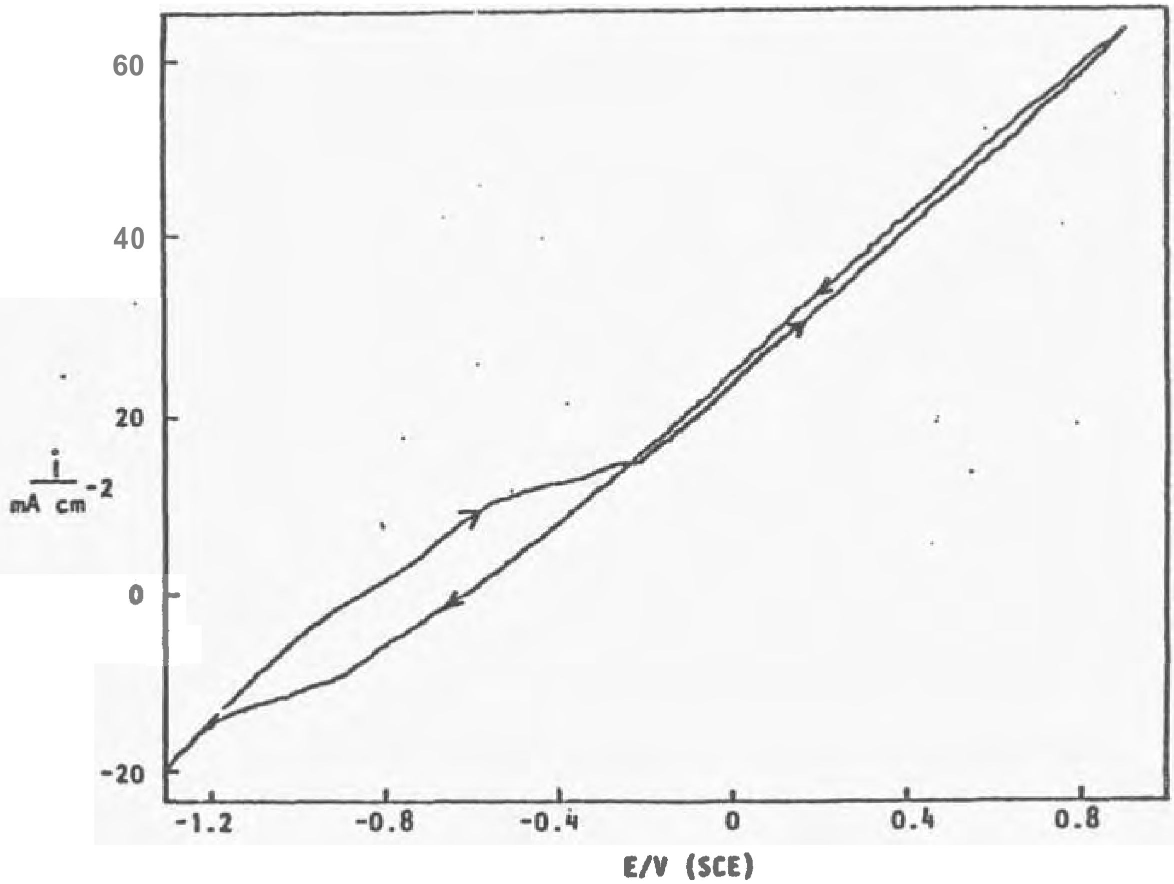

FIGURE 2: **Cyclic Voltammogram of Fa in Simulated Geothermal Liquid**

(Cl$^-$) = 0.032 mol l^{-1}, (HCO$_3^-$) = 0.003 mol l^{-1}

The solution was saturated with H_2S. Sweep rate = 100 mV s^{-1}

Note the apparent linearity in the high current region is an artefact of the system due to the low conductivity of the solution. This problem *can* be corrected *for* by using improved instrumentation.

A cyclic voltammogram of pure iron in a simulated geothermal fluid at 295 K is shown in Figure 2. The potential is swept from –1.3 V measured against a saturated calomel reference electrode. This potential lies in the region of hydrogen evolution as evidenced by the large cathodic (negative) current, As the potential becomes more positive, the hydrogen evolution current decreases. Eventually, a positive current is obtained probably as a result of Fe dissolution. The subsequent arrest in the current is associated with the formation of a film on the electrode surface. The current then increases sharply and this fact coupled with the higher current after the potential is reversed indicates that pitting has taken place. Fine pits were observed extensively on the electrode surface on examination under the microscope. The form of corrosion which would be found on exposing steel to this medium would depend on the corrosion potential; above -0.2 V pitting would occur.

AC IMPEDANCE TECHNIQUE

A more sophisticated electrochemical method is to apply an AC potential to the electrode and measure its complex impedance with a phase sensitive detector. It is possible to obtain the resistive and capacitive components of the impedance over a wide range of applied AC frequencies. From this data one can determine separately the electrolyte resistance, the amount of surface film (from the capacitance), and the corrosion rate (from the resistance R_p). This method is known to be a useful method for corrosion monitoring,[12] but it has not been widely applied. We are investigating its application to the corrosion of metals in geothermal media.

ACKNOWLEDGEMENTS

We are grateful to the N.Z. Energy Research and Development Committee for funding this project. We also thank the Industrial Processing Division, DSIR for *their* co-operation.

REFERENCES

1. T. Marshall and W.R. Braithwaite, "Geothermal Energy" (Earth Sciences 12), Unesco (1973), p.151.

2. D.W. De Berry, P.F. Ellis, and C.C. Thomas, "Materials Selection Guidelines for Geothermal Power Systems", ALO-3904-1, U.S. Department of Energy, Washington (1978).

3. B.G. Syrett, D.D. Macdonald, H. Shih, and S.S. Wing, "Corrosion Chemistry of Geothermal Brines", 2 vols, Stanford Research Institute, Menlo Park, California (1977).

4. W. Pourbaix, Atlas of Electrochemical Equilibria, Pergamon Press, London (1964).

5. R.J. Biernat and R.G. Robins, Electrochim. Acta, 17, 1261 (1972).

8 R.C.H. Ferriera in Leaching and Reduction in Hydrometallurgy, A.R. Burkin (ed.), Institution of Mining and Metallurgy, London (1975).

7 P.T. Wilson in "Corrosion in the 30" Main Steam Lints - Wairakei Geothermal Field" by W.R. Braithwaite, DSIR (1978).

8 T.H. Seward, Amer. J. Sci., 274, 190 (1974).

9 D.D. Macdonald and B.C. Syrett, Corrosion, submitted for publication (1978).

10 W.R. Braithwaite and K.A. Lichti, "Surface Corrosion of Metals in Geothermal Fluids at Broadlands, New Zealand" (1979).

11 F. Mansfeld, Adv. Corrosion Sci. Tech., 6, 163 (1976).

12 I. Epelboin, M. Keddam and H. Takenouti, J. Appl. Electrochem., 2, 71 (1972).

- - - ooo0ooo - - -