THE MEASUREMENT OF CORROSION RATES OF CARBON STEEL AND STAINLESS STEEL IN GEOTHERMAL MEDIA BY THE POLARISATION RESISTANCE TECHNIQUE

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ABSTRACT

The polarisation resistance method has been applied to the determination of corrosion rates of low carbon steel and 304, 316 and 410/420 stainless steels in geothermal media containing hydrogen sulphide. With electrolytes of low conductivity it was essential to design the three-electrode probes so as to minimise the contribution of the ohmic resistance. Galvanostatic step experiments demonstrated that the ohmic contribution was less than 5% of the polarisation resistance. Good agreement was found between weight-loss and polarisation resistance measurements of the corrosion rate for all the metals tested. In the case of the stainless steels the potential took about one hour to reach its steady-state value following the application of a constant current. For the 304 and 316 alloys the form of attack in H_2S solutions was observed to be pitting corrosion, but the polarisation resistance method still gave good agreement with weight loss measurements.

INTRODUCTION

A number of methods have been used to measure corrosion rates in geothermal media; these include the coupon weight-loss method, the corrosometer (resistance probe), the hydrogen probe and stress corrosion rigs.[1-3] Electrochemical techniques are attracting increasing interest for corrosion monitoring of metals and alloys in a variety of environments and appear to be quite promising for geothermal media.[4] One of these, the polarisation resistance technique, has, since its original development by Stern and Geary[5] in 1957, become widely accepted because of its capacity to provide a sensitive and instantaneous value of the corrosion rate. A comprehensive review of the polarisation resistance principle and its applications has recently been published by Mansfeld.[6] While the accuracy of the technique is usually quite adequate, it may be dependent on the situation in which it is applied. This study aims to provide an evaluation of polarisation resistance measurements on ferrous alloys in geothermal environments.

PRINCIPLE

The polarisation resistance technique involves measurement of the relation between current and potential between metal electrodes at potentials close to the corrosion potential (E_{corr}). The polarisation resistance, defined as

$$R_p = \frac{\partial E}{\partial I} \qquad .. (1)$$

can be determined rigorously only from the tangent to the polarisation curve at E_{corr}.[6] However, it is sufficiently accurate for most experimental data to linearise the curve,[7] particularly for data within a range of ±20mV about E_{corr}. Then

$$\frac{\Delta E}{I} = R_p \qquad .. (2)$$

A small current I is applied between a test electrode and an auxiliary electrode and the resulting change of potential of the test electrode, ΔE, is measured against a reference electrode. All three electrodes are usually made from the same type of metal. Equation 2 applies strictly only to solutions whose resistance is negligible. In general, the observed resistance consists of the polarisation resistance, associated with the corrosion reaction (R_p), and an electrolyte resistance (R_o)

$$\frac{\Delta E}{I} = R_o + R_p \qquad .. (3)$$

$$= R_o + B/I_{corr} \qquad .. (4)$$

The corrosion current I_{corr} can be calculated from measured values of $\Delta E/I$ of R_o can be neglected or a correction made.[8] B is a parameter derived from the kinetics of the electrode reactions. For iron and low alloy steels in acidic environments, B values are in the range 10-45 mV.[6,8] From the published data, we estimate B to be 25mV for carbon steel in cold geothermal condensates.

The corrosion rate (CR), defined as the mean rate of removal of metal (μm/yr) assuming uniform corrosion, is readily calculated from the corrosion current

$$CR = I_{corr}M/AzF\rho \qquad .. (5)$$

where M is the molar mass of the metal, z is the number of electrons transferred per metal atom, ρ is the density and F is the Faraday constant. Since R_p is inversely proportional to the electrode area, A, it is convenient to determine R_pA (Ωcm^2). Accordingly, for carbon steel in condensate at 20°C,

$$CR = 2.9\times10^5/R_pA \ \mu m/yr \qquad .. (6)$$

The electrolyte resistance depends on the geometrical arrangement of the electrodes in the probe used for the polarisation resistance measurements and the conductivity κ of the electrolyte

$$R_o = a/\kappa \quad ..(7)$$

where a is a constant dependent on the size and orientation of the electrodes and is therefore characteristic of a particular probe. Preliminary polarisation resistance measurements on carbon steel in condensates at a corrosion test rig at the Broadlands geothermal field and in condensate samples collected from a stream line at Wairakei were unsuccessful because of the low conductivity of the condensates (0.02 S m^{-1}). In these experiments the measured resistance was largely R_o and it was not possible to determine R_p.

In order for the polarisation resistance technique to be successful, R_o must be reduced, and if possible, made negligible. This means that the proble should be designed so that the configuration of the electrode is optimised to make a as small as possible.

INFLUENCE OF PROBE GEOMETRY

The effect of three different probe designs was investigated, using low carbon steel as the test material in an aerated condensate of low conductivity, see Table 1. Constant currents in the range ± 30 µA were used to polarise the test electrode, and the change in potential ΔE was measured with respect to a reference electrode usually made of the same metal as the test electrode.

Table 1

POLARISATION RESISTANCE TESTS

Aerated condensate at 20°C (very little H_2S). Polarisation resistance RA in Ω cm^2. Corrosion rate CR in µm yr^{-1}. Conductivity 0.022 S/m.

	UNSTIRRED		STIRRED	
	RA	CR	RA	CR
Probe i	1850	157	1090	266
A = 1.51 cm^2	±200	±17	+50	±12
Probe II	1600	181	720	402
A = 1.51 cm^2	±50	±6	+20	±11
Probe III	1735	167	814	356
(Linear)				
A = 2.14 cm^2	±200	±19	±100	±44

Probe I was a concentric design with an exposed ring electrode and a central auxiliary electrode. The reference electrode was placed some 4mm to one side. The plots of ΔE versus I were quite linear, giving values for RA which are shown in the table. Oxygen is the cathodic reactant in these experiments and stirring of the test solution will increase the corrosion rate calculated by eq(6) because of the increased rate of mass transport of oxygen to the electrode surface.

Probe II was also a concentric design, with the reference electrode at the centre, surrounded by a ring-shaped test electrode mounted in a PVC holder, and the auxiliary electrode was a platinum ring outside the test electrode. Again good linear ΔE versus I plots were obtained, but the value of RA was lower than for probe I (see Table 1) because this design is expected to have a much lower ohmic resistance R_o. Galvanostatic experiments were used to determine R_o by application of a 30µA current step and following the potential-time transient on an oscilloscope, see Fig. 1. In order to facilitate the measurement of the ohmic potential drop IR_o a resistor R_1 = 100 Ω was placed in series with the test electrode. The total ohmic voltage drop $I(R_o + R_1)$ is given by the sharp vertical step at zero time ΔE = 4 mV approximately. Since IR_1 = 3mV, we find R_o less than 33 Ω which is less than 5% of the total measured resistance for this probe.

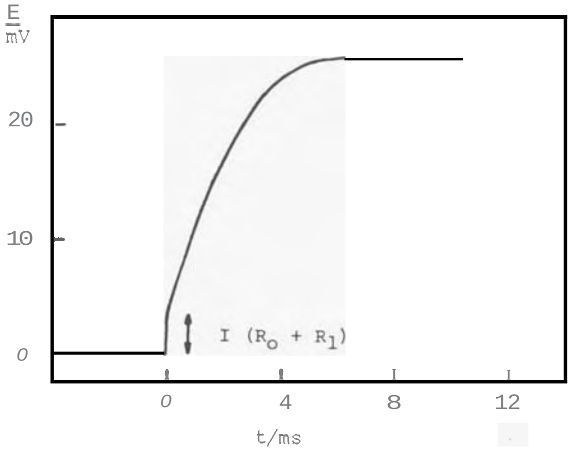

Fig. 1 Potential transient for carbon steel in aerated condensate.
R_1 = 100Ω series resistor.

Probe III
In the third design of probe, the three electrodes were low-carbon steel rods arranged in line. The measure corrosion rates for unstirred and stirred condensates agreed with those obtained for the concentric arrangement of Probe 11, within experimental error (see Table 1). It is reasonable to assume, therefore, that R_o must be low for probe III also. Most of the current flows directly between the auxiliary and test electrodes, so that the IR_o drop to the reference electrode is small.

CORROSION RATE DETERMINATION - LABORATORY TESTS

Low-Carbon Steel

The corrosion rates of low-carbon steel obtained from polarisation resistance measurements were compared with weight loss results.[9] A simulated condensate was prepared containing 50 mmol/l NaCl. In half the tests, H_2S was bubbled through to saturation; in the other half no H_2S was added. A separate probe of the type III design was immersed in each condensate for a four week test period. Since the solutions were exposed to the air, the corrosion was caused by oxygen attack or combined oxygen plus H_2S attack when H_2S was present. On immersion in the solutions, the steel developed loose, non-adherent films which collected on the base of the test vessels. In the absence of H_2S, the corrosion product was red-brown rust, FeO.OH, while in the H_2S media, the material was one or more black iron sulphides probably with some iron oxide.

Polarisation resistance data showed that the current/potential curve for carbon steel in all four solutions was linear up to 25 μA (Figure 2) and hence the corrosion rate can be calculated on the basis of equation (6). The corrosion rates for steel in each condensate over the test period were approximately constant; this is associated with the lack of protection afforded to the steel by the loose films. Weight-loss experiments were also performed on low carbon steel in the same environments. The corrosion rates calculated from both methods are listed in Table 2. For these experimental conditions, the two methods give quite similar results. In particular, both methods show that the addition of H_2S causes a marked increase in the corrosion rate of steel.

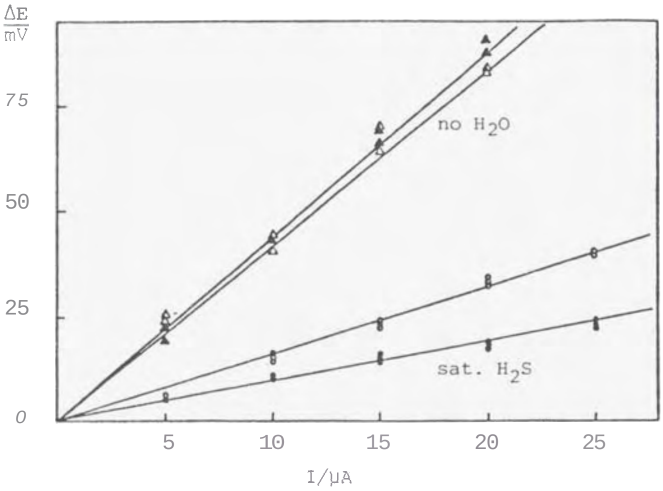

Fig. 2 Linear polarisation plots for carbon steel in aerated solution.

Stainless Steels

The corrosion rates of two austenitic (304 and 316) and two martensitic (410 and 420) stainless steels were obtained in deaerated solutions of 0.05 mol/l Na_2SO_4 saturated with H_2S. Table 3 shows that the polarisation resistance and weight loss methods agree satisfactorily. Probes of type III were used, and a corrosion rate meter based on the constant current principle was used to measure the polarisation resistance.[13] A steady value of ΔE was obtained after 1 to 1½ hours, and the resulting ΔE versus I graphs were linear up to ±30mV. The data were reproducible at different exposure times up to 28 days, indicating that the corrosion rate was fairly constant. The B values were determined by an analysis of the extended ΔE versus I data by the method of Mansfeld.[14]

The corrosion products observed include sulphur, and the martensitic alloys gave a black film of troilite, with small amounts of mackinawite, pyrite, haematitie and greigite. This is in accord with predictions.[11,12] The austenitic alloys 304 and 314 showed minute pits and no sign of general corrosion. The martensitic alloys, which had a much greater corrosion rate showed general corrosion accompanied by extensive pitting.

Table 2

COMPARISON OF CORROSION RATES
OBTAINED FROM POLARISATION
RESISTANCE AND WEIGHT-LOSS METHODS[11]

50 mmol/l NaCl, with and without H2S (sat), at 17°C.
Weight loss w, in time t, for a sample of
Area A, gives CR = w/Atp

	Time hours	Weight-Loss μm yr^{-1}	Polarisation Resistance μm yr^{-1}
Condensate	500	33	27
	600	32	28
Condensate +	500	172	158
H_2S (satd.)	600	165	185
Condensate	300	30	18
	500	29	21
Condensate +	300	176	219
H_2S (satd.)	650	181	193

CORROSION RATE DETERMINATION - FIELD TRIALS

Tests were carried out at the Broadlands geothermal field in collaboration with staff of the Industrial Processing Division, DSIR.[16] The corrosion rate meter[13] was combined with Petrolite M-510-E probes (DSIR[16]) and some results are shown in Table 4. The corrosion rate of carbon steel was independent of time and agreed with earlier weight-loss measurements.[16] The 410 stainless steel also showed consistent polarisation resistance behaviour with B = 25 mV, but the corrosion rate is much greater than the weight-loss measurements taken over 4 weeks by Lichti and Braithwaite.[3] Our values do agree with the laboratory measurements by weight-loss shown in Table 3.

CONCLUSION

The results presented in the tables demonstrate that the polarisation resistance method agrees well with the weight-loss determination of corrosion rate. It is clear that the ohmic resistance of the electrolyte solution has a negligible effect in these relatively low conductivity solutions, provided the probe is designed so that the reference electrodes is placed on the side of the test electrode opposite to the auxiliary electrode, for three-in-line probes. The advantage of the polarisation resistance method is that it gives an immediate read-out of the corrosion rate, and our results show that this rate was independent of the time at which the measurement was made, within about ±10% (see Table 2).

Less previous work has been done on the polarisation technique applied to stainless steels, compared with carbon steels. We find that the method gives satisfactory results, although it is necessary to allow 1 to 1½ hours for ΔE to reach its steady-state value for an applied constant current. The results agree well with the weight-loss method (see Table 3) even though the mode of attack involves pitting. In pitting corrosion the anodic area is localised to the interior of the pits, but there is no reason why the theoretical principles of the method should not apply to this situation. The results given in Table 3 are of course corrosion rates averaged over the whole surface, since there is no way the true area of the pits can be determined. Both the polarisation resistance and the weight loss methods suffer the same disadvantage in giving only an average corrosion rate, and not revealing the density or depth of the pits. But if the occurrence of pitting corrosion is first established for a given alloy in the corrosive medium, the polarisation resistance jives a useful measure of the rate of attack (expressed as an average corrosion rate) and would be expected to give a useful response to any change in the rate of attack on the metal.

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Table 3 CORROSION RATES OF STAINLESS STEELS

De-aerated 0.05 mol ℓ^{-1} Na_2SO_4/H_2S (satd),

pH = 4.6, $\kappa = 0.72$ S m^{-1}, T = 18-20°C.

	POLARISATION RESISTANCE			WEIGHT-Loss	
AISI	$R_n A/cm^2$	B/mV	CR/μm yr^{-1}	Time/days	CR/μm yr^{-1}
304	31000	19	7.2	28	6.6
316	85000	22	3.0	28	2.7
410/420*	9200	30	38	28	41

* 410 and 420 were used for polarisation resistance and might-loss measurements respectively.

TABLE 4 CORROSION RATES OF CARBON STEEL AND 410 STAINLESS STEEL NON-AERATED CONDENSATE "" AT BROADLANDS

Probe : Petrolite M-S10-E (3-in-line)(DSIR)16

H_2S $5x10^{-3}$ mol/kg, pH 4.7, K = 0.028 S/m (DSIR)[15]

	Corrosion Rate/μm/yr	
Time/hrs	Carbon Steel	410 s.s.
2	139	37
3	--	32
5	144	--
23	142	

Weight-loss : 170 ± 5 μm/yr[16] 0.916 μm/yr[3]

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