JOURNAL OF APPLIED ELECTROCHEMISTRY 1 (1971) 19–26

The effect of oxygen and SO_3 on corrosion of steels in molten sulphates

A. J. B. CUTLER

Central Electricity Research Laboratories, Leatherhead, Surrey, U.K.

Received 16 July 1970

The corrosion of 18% Cr, 8% Ni steel has been studied in alkali metal sulphate eutectic melts as a function of the partial pressures of oxygen and SO_3 in equilibrium with the melt at 873°K. The rate of corrosion has been measured in terms of the corrosion current corresponding to the balanced rates of the anodic and cathodic processes at the unpolarized metal surface. The effect of SO_3 on the rate of corrosion is interpreted in terms of its role as an oxidizing agent and also in terms of its effect on the solubility of the corrosion products in the melt. The difference in the relative importance of oxygen and SO_3 as the oxidizing agent is interpreted in terms of their different solubilities in the sulphate melt.

1. Introduction

The limiting anodic and cathodic processes at inert metal (platinum) electrodes in alkali metal sulphate eutectic melts have been attributed respectively to the oxidation and the reduction of the anion [1, 2] represented by the charge transfer equations

$$SO_4^{=} \rightarrow SO_3 + \tfrac{1}{2}O_2 + 2e \qquad (1)$$

and

$$SO_4^{=} + 8e \rightarrow S^{=} + 4O^{=}. \qquad (2)$$

Since the overall cathodic process requires the transfer of eight electrons, we can expect that the mechanism of this process will involve several discrete steps. The sulphite ion and elemental sulphur have been identified as intermediate products at low current densities [2]. More detailed investigations of the mechanism have been carried out in terms of potential sweep studies of the cathodic polarization curve [3, 4]. It is suggested that the reduction of SO_3, derived either from the gas phase in equilibrium with the melt, or from the acid–base equilibrium for the sulphate anion,

$$SO_4^{=} \rightleftarrows SO_3 + O^{=}, \qquad (3)$$

can be regarded as the first step in the cathodic reduction process. It is significant in this respect that the residual cathodic current density at polarized inert metal electrodes remains appreciable, even in carefully purified alkali metal sulphate melts under an inert atmosphere, at potentials which are more negative than the potential at which SO_3 is reduced, whereas the residual current at less negative potentials decreases to relatively small values.

Chronopotentiometric studies of the reduction of SO_3 displaced from the sulphate anion dissolved in a chloride melt [5] have been interpreted in terms of the mechanism represented by the equation

$$\begin{tikzcd} SO_3 + e \arrow[r] & SO_3^{-}(\text{adsorbed}) \arrow[r, "\text{dimerization}"'] & S_2O_6^{=} \arrow[d, "\text{thermal decomposition}"'] \\ & & SO_4^{=} + SO_2 \end{tikzcd} \qquad (4)$$

although an alternative mechanism, which is represented by the equation

$$SO_3 + 2e \rightarrow SO_3^{=} \xrightarrow[\text{thermal decomposition}]{} SO_2 + O^{=}, \qquad (5)$$

can also be proposed for the reduction process. The products of these reactions are equivalent if the acid–base equilibrium (equation 3) is taken into account.

The significance of the reduction of SO_3 with respect to the corrosion of steels in sulphate melts is emphasized when metal–metal ion equilibria in sulphate melts are considered. Reversible metal–metal ion electrodes have been established [1, 2, 4] for couples such as Co/Co (II), Cu/Cu(I), and Ag/Ag(I) in alkali metal sulphate eutectic melts at potentials which are positive with respect to the potential at which SO_3 is reduced. Equilibrium metal–metal ion electrode potentials for metals such as iron and chromium however would be more negative than the potential at which SO_3 is reduced, since the standard potentials for these metal–metal ion couples would be more negative, and also because the ions are less soluble in the sulphate melt. The oxidation of these metals in alkali metal sulphate melts therefore takes place irreversibly in conjunction with the reduction of SO_3, and the reversible metal–metal ion equilibrium cannot be established. The potential of the metal is determined by the balance which is set up between the rates of the oxidation and reduction processes.

The solubility of corrosion products in the sulphate melt can be represented in the terms of the equilibrium

$$Fe_2O_3\ (\text{solid}) \rightleftarrows 2Fe^{3+} + 3O^{=}. \tag{6}$$

The solubility therefore depends on the oxide ion concentration in the melt, which is determined by the acid–base equilibrium for the sulphate anion (equation 3), and will therefore depend in turn on the partial pressure of SO_3 in the gas phase in equilibrium with the melt. Even when the metal ion concentration in the bulk melt is less than the concentration corresponding to the solubility product for the metal oxide, a solid oxide layer will still be formed on the surface of the metal due to the concentration gradients which are established as a result of the corrosion process. We can anticipate that the oxide layer will influence the kinetics of the corrosion process in a manner which is analogous to the effect of the oxide layer on similar gas phase oxidation processes, but in the sulphate melt this behaviour will be modified by the solubility of the corrosion products.

Thermodynamic data relevant to the corrosion of several metals in molten alkali metal sulphate environments have been summarized in the form of diagrams representing the chemical equilibria as a function of the potential and the oxide ion activity [6, 7].

2. Experimental

2.1. *Method*

The experimental procedure which was used to determine the rate of the corrosion process at 18 % Cr, 8 % Ni steel electrodes in the alkali metal sulphate eutectic melt is represented in Fig. 1. A linear sweep perturbation was imposed on the open circuit potential, E_0, of the steel electrode in the melt, and the current densities corresponding to the rates of the anodic and the cathodic charge transfer processes were determined as a function of the imposed potential. Even at relatively small overpotentials the rate of the charge transfer process favoured by the applied potential becomes much greater than the rate of the charge transfer process in the opposite direction, and a linear relationship is established between the potential and the logarithm of the

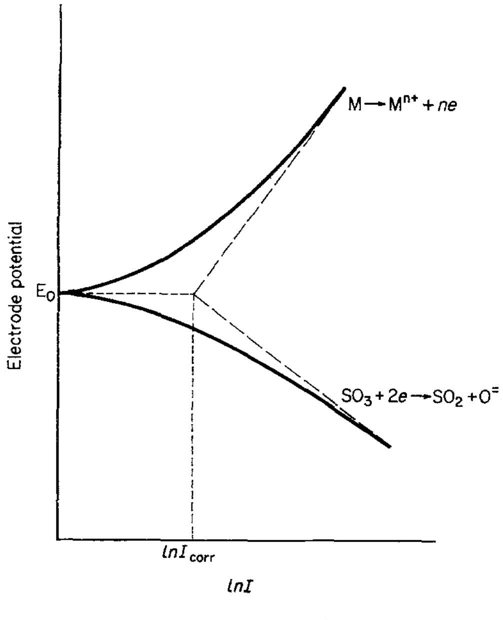

Fig. 1 Extrapolation of the E v log I relationships for the anodic and cathodic processes to obtain the corrosion current, I_{corr}.

current density. The E v. log I relationships established for the anodic and cathodic processes were extrapolated as shown in Fig. 1 to the point of intersection at the open circuit potential, E_0, to determine the corrosion current, I_{corr}, corresponding to the balanced rates for the oxidation of the metal and the complementary reduction process, which we have represented as the reduction of SO_3, at the unpolarized metal surface.

The interpretation of I_{corr} as the rate of oxidation of the metal implies that the oxidation of the metal is the only anodic charge transfer process taking place. This assumption is justified under the conditions of these experiments since no anodic charge transfer processes are observed at inert metal electrodes in the alkali metal sulphate eutectic melt in the relevant potential range. The technique does not depend on a precise identification of the mechanism of the cathodic reduction process which is complementary to the oxidation of the metal.

Since the technique involves a perturbation of the open circuit condition at the electrode surface, values of I_{corr} can only be determined at intervals during the corrosion process. The kinetics of the anodic oxidation process at steel electrodes can be investigated as a continuous function of time in terms of the current density at polarized electrodes maintained at constant potential, but it is not a simple matter to relate these measurements to the rate of corrosion at the unpolarized metal surface.

A cyclic potential sweep perturbation was imposed on the open circuit potential of the electrodes using a Chemical Electronics Linear Sweep unit in conjunction with a Wenking potentiostat. Current density was recorded as a function of the perturbed potential on a Hewlett–Packard X–Y plotter. A degree of compromise was necessary in the specification of the applied potential cycle. In order to minimize possible long-term effects of the potential perturbation on the corrosion process the perturbation was kept as small as possible, ±100 mV with respect to the open circuit potential E_0, consistent with the need to define the E v. log I relationship. For the same reason the period of the cyclic potential sweep was also kept reasonably short, 3 minutes for the complete perturbation cycle, although since the electrode takes a finite time to respond to the imposed potential change, the minimum time for the potential cycle was limited by the increasing hysteresis effect between the positive and negative going parts of the cycle which is represented in Fig. 2. The corrosion current, I_{corr}, was derived from the mean of the current–potential relationships for the positive and negative going parts of the cycle. The absence of any permanent effect on the corrosion process resulting from the potential perturbation was indicated by the continuity in the time dependence of the open circuit potential of the electrode before and after the perturbation.

2.2. *Materials*

The ternary alkali metal sulphate eutectic mixture [8] was prepared from Analar grades of lithium, sodium and potassium sulphates, and was dried and pre-melted in a muffle furnace. Experiments were carried out in a vertical tube furnace at 873±1K. The gas phase in equilibrium with the melt was prepared by mixing oxygen-free nitrogen, oxygen and SO_2 at measured flow rates. The gas mixture was dried by passing through $CaCl_2$ and P_2O_5 columns, and the equilibrium

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \qquad (7)$$

was established at the temperature of the experiment by passing the gases through a platinized asbestos catalyst just above the surface of the melt. The equilibrium between the gas phase and the melt was established by bubbling the gas into the melt at a rate of $1{\cdot}67\times10^{-6}$ m^3 s^{-1}.

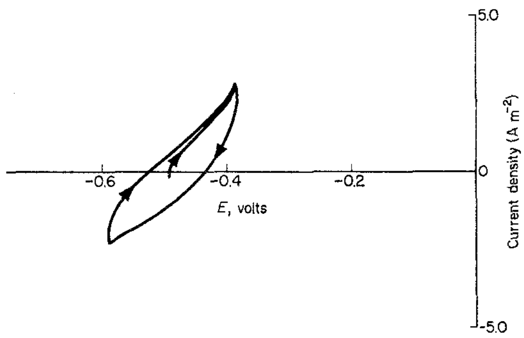

Fig. 2 Experimental cyclic polarization curve for the steel electrode in the alkali metal sulphate eutectic melt.

18 % Cr, 8 % Ni steel electrodes approximately 10 mm long were prepared from 2 mm O.D. rod. The surface of the metal was prepared by polishing with abrasive paper to grade 4/0 emery. No annealing or chemical polishing procedures were carried out. The electrodes were spot welded to platinum wire at one end, and supported at the end of a 2 mm I.D. alumina tube which minimized contact between the platinum lead and the sulphate melt. The relatively small effect of the spot welding on the exposed end of the electrode was removed by further polishing.

The potentials of steel electrodes in the sulphate melt were measured with respect to a Ag/Ag(I) (0·04 molal) reference electrode set up in a sealed Pyrex glass compartment.

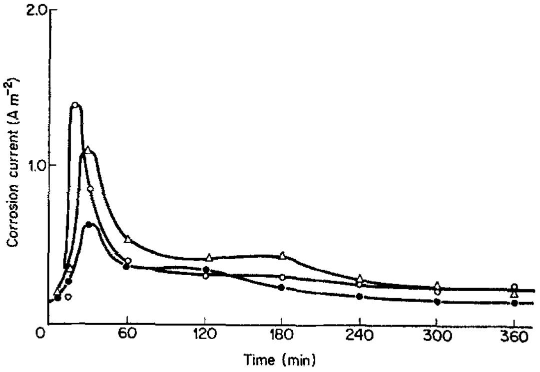

Fig. 3 The corrosion current as a function of time at steel electrodes in the alkali metal sulphate eutectic melt at 873K under an atmosphere of nitrogen containing controlled partial pressures of oxygen

●P_{O_2} = 1 N.m^{-2}
△P_{O_2} = 10^3 N.m^{-2}
○P_{O_2} = 10^5 N.m^{-2}

3. Results

3.1. *The effect of oxygen partial pressure*

The experimental values of I_{corr} which describe the rate of the oxidation process at the unpolarized steel electrode in the sulphate melt under an atmosphere of nitrogen containing controlled partial pressures of oxygen are plotted as a function of time for the different oxygen partial pressures in Fig. 3. The corrosion rates after 6 hours, and the integrated charge transfer during this period, $\int_0^t I_{corr}\,dt$, derived graphically from the experimental values of I_{corr} (t), are summarized in Table 1.

These data are correlated with the metal loss rate and the thickness of the oxide layer formed on the surface of the metal, which are more familiar parameters describing the corrosion process, on the basis of Faraday's laws. The correlation involves the densities of the metal and the oxide as well as the charge on the metal ion, and has been made on the simplified basis of the oxidation of iron to the three valent state and the formation of Fe_2O_3 on the metal surface. The effect of other components in the steel and the possible formation of lower valency ions will introduce an error into this simplified correlation but this will be small and systematic. We have assumed that the solubility of the corrosion products in the sulphate melt is negligible in the absence of SO_3 in the gas phase in equilibrium with the melt.

There is a moderate increase in the rate of corrosion after 6 hours with increase in the partial pressure of oxygen from 1N.m^{-2} to 10^3N.m^{-2}, but further increase in the oxygen partial pressure up to 10^5N.m^{-2} (pure oxygen)

Table 1. The effect of oxygen partial pressure on the corrosion current

P_{O_2} N.m^{-2}	I_{corr} A.m^{-2}	*Metal loss rate in. h^{-1}*	*Charge transfer* $\int_0^t I_{corr}\,dt$ (t = 3600 s) A.s.m^{-2}	*Oxide layer thickness* μm
1	0·15	0·52 . 10^{-6}	0·57 . 10^4	0·31
10^3	0·23	0·80 . 10^{-6}	0·85 . 10^4	0·46
10^5	0·24	0·84 . 10^{-6}	0·72 . 10^4	0·39

has hardly any further effect on the rate of corrosion. There is a corresponding increase in the total charge transfer and the derived thickness of the oxide layer with the initial increase in oxygen partial pressure from 1N.m^{-2} to 10^3 N.m^{-2}, but the total charge transfer during the experiment at 10^{3}N.m^{-2} is greater than during the experiment at 10^{5}N.m^{-2} of oxygen. This anomaly arises from the fact that the higher initial rate of the oxidation process was maintained over a longer period during the experiment at 10^{3}N.m^{-2} oxygen, and may reflect differences in the mechanical integrity of the oxide layers formed on the surface of the metal.

3.2. *The effect of SO_3 partial pressure*

Values of I_{corr} have also been determined for 18% Cr, 8% Ni steel electrodes in the alkali metal sulphate eutectic melt under atmospheres containing a constant partial pressure of oxygen of 10^{3}N.m^{-2} and controlled partial pressures of SO_3 in the range 0·5–400N.m^{-2}. The experimental data are plotted as a function of time for the higher partial pressures of SO_3 in Fig. 4. The rates of corrosion after 6 hours and the integrated charge transfer during this period are summarized in Table 2.

There is a gradual increase in the rate of corrosion represented by the value of I_{corr} after 6 hours with increase in the partial pressure of SO_3 up to 39N.m^{-2}, although at the lower partial pressures of SO_3 the corrosion rates are in fact less than that observed at the same partial pressure of oxygen in the absence of SO_3. At partial pressures of SO_3 greater than 39 N.m^{-2} in equilibrium with the melt the rate of the corrosion process increases more rapidly. Over the same range of SO_3 partial pressures the corrosion rates as a function of time, shown in Fig. 4, change from a conditon at the lower partial pressures of SO_3 where the rate decreases as corrosion proceeds, which is consistent with the growth of a protective oxide layer on the surface of the metal, to a condition at higher partial pressures of SO_3 where high corrosion rates are maintained throughout the experiment, which would be more consistent with the formation of soluble corrosion products.

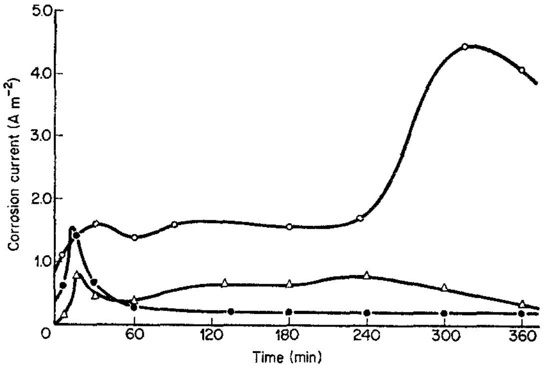

Fig. 4 The corrosion current as a function of time at steel electrodes in the alkali metal sulphate eutectic melt at 873K under an atmosphere of nitrogen containing a partial pressure of oxygen of 10^3 N.m^{-2} and controlled partial pressure of SO_3

●P_{SO_3} = 7·4 N.m^{-2}
△P_{SO_3} = 39 N.m^{-2}
○P_{SO_3} = 400 N.m^{-2}

Table 2. The effect of SO_3 partial pressure on the corrosion current

P_{SO_3} N.m^{-2}	I_{corr} A.m^{-2}	*Metal loss rate in. h^{-1}*	*Charge transfer* $\int_0^t I_{corr}\,dt$ *(t=3600 s) A.s.m^{-2}*	*Oxide layer thickness (corrosion products insoluble) μm*	*Metal ion concentration (corrosion products soluble) mole fraction $Fe_2(SO_4)_3$ 0·4 mole sulphate melt, electrode area 10^{-4} m^2*	*Ideal solubility of $Fe_2(SO_4)_3$ mole fraction*
0·5	0·14	0·49 . 10^{-6}	0·50 . 10^4	0·27	0·22 . 10^{-5}	2·6 . 10^{-11}
3·0	0·18	0·63 . 10^{-6}	0·59 . 10^4	0·32	0·26 . 10^{-5}	5·5 . 10^{-9}
7·4	0·22	0·77 . 10^{-6}	0·70 . 10^4	0·38	0·30 . 10^{-5}	8·3 . 10^{-8}
39	0·33	1·15 . 10^{-6}	1·28 . 10^4	0·69	0·55 . 10^{-5}	1·2 . 10^{-5}
75	1·02	3·5 . 10^{-6}	2·06 . 10^4	1·10	0·89 . 10^{-5}	8·6 . 10^{-5}
400	4·1	14·3 . 10^{-6}	4·86 . 10^4	2·62	2·10 . 10^{-5}	13·1 . 10^{-3}

Experimental evidence suggests that the effect of stirring on mass transport processes in the melt is an important factor influencing the corrosion rate at high partial pressures of SO_3 and this may account for the irregular behaviour of the corrosion rate as a function of time under these conditions. The corrosion rate measured in terms of I_{corr} at the steel electrode after 6 hours in the alkali metal sulphate melt with a gas phase containing a partial pressure of $400 N.m^{-2}$ flowing over the surface of the melt was an order of magnitude less than the value given in Table 2 for the same conditions but with the gas bubbling into the melt.

Examination of the electrodes and the sulphate melt showed that the electrode is covered by a black oxide layer after the experiments at the lowest partial pressures of SO_3 and although there were also traces of oxide floating on the surface of the melt, there was no discoloration of the bulk melt which would have indicated Fe (III) ion in solution. At higher partial pressures of SO_3 the electrode surface retained a relatively thick oxide layer, but no free oxide was observed on the surface of the melt, and the melt showed a pronounced yellow discoloration suggesting the presence of a significant concentration of Fe (III) ion in solution.

4. Discussion

4.1. *The relative importance of oxygen and SO_3 as oxidizing agents*

The fact that the rate of oxidation of the steel in the sulphate melt does not show a marked dependence on the partial pressure of oxygen in the gas phase in equilibrium with the melt in the absence of SO_3 suggests that oxygen may not play an important part directly as the oxidizing agent in the metal–metal oxide–sulphate melt interfacial region. The observation that the partial pressure of oxygen in the gas phase in equilibrium with alkali metal sulphate eutectic melts does not have a significant effect on the cathodic polarization curve at inert metal electrodes in the melt [3, 4] is consistent with this interpretation and contrasts with the behaviour of SO_3, which gives rise to a prominent reduction wave in the cathodic polarization curve. This suggests that SO_3 may be more important as the oxidizing agent at the metal or the metal oxide surface. The activity of SO_3 as the oxidizing agent in this region can therefore be proposed as one of the factors which account for the increase in the observed rates of the oxidation process with increase in the partial pressure of SO_3 in the gas phase in equilibrium with the melt.

The divergence between the relative importance of oxygen and SO_3 as the oxidizing agents is somewhat surprising in view of the similarity between the free energy changes [9] for the oxidation reactions represented by the equations

$$2Fe+3/2O_2 \rightarrow Fe_2O_3 \qquad (8)$$
$$\Delta G(873\ K) = -593{\cdot}5\ kJ\ mole^{-1}$$

and

$$2Fe+3SO_3 \rightarrow Fe_2O_3+3SO_2 \qquad (9)$$
$$\Delta G(873\ K) = -576{\cdot}8\ kJ\ mole^{-1}$$

but the difference in behaviour can be rationalized in terms of the solubilities of the gases in the sulphate melt. Since the solubility of gases in molten salts is generally small, oxygen from the gas phase will not be transported readily to the metal surface. The solubility of SO_3 in the sulphate melt is an exception to this generalization due to the chemical interaction which is represented by the sulphate–pyrosulphate equilibrium,

$$SO_3 + SO_4^{=} \rightleftarrows S_2O_7^{=}, \qquad (10)$$

and the transport of this species can therefore take place more readily in the melt.

Although it is apparent that oxygen is less important than SO_3 as the oxidizing agent in the interfacial region between the metal and the sulphate melt, we must recognize that the partial pressure of oxygen will still influence the corrosion process through the equilibrium between SO_2 and SO_3 in the gas phase (equation 7). We can also anticipate that oxygen may be more important as the oxidizing agent in regions where a three phase boundary between the metal, molten salt, and gas phases is established, and also at metal surfaces in porous solid sulphate environments.

4.2. *The solubility of corrosion products*

In addition to the role of SO_3 as the oxidizing agent at the metal surface, we have already considered the effect of the partial pressure of SO_3 on the solubility of the corrosion products in terms of the solubility equilibrium for the metal oxide (equation 6) and the acid–base equilibrium for the sulphate anion (equation 3) in the melt. These equilibria can be combined in the form represented by the equation

$$\underset{\text{(solution)}}{Fe_2(SO_4)_3} \rightleftarrows \underset{\text{(solid)}}{Fe_2O_3} + \underset{\text{(gas).}}{3SO_3} \qquad (11)$$

The ideal solubility of ferric sulphate in the alkali metal suphate melt in equilibrium with the solid ferric oxide can then be calculated as a function of the partial pressure of SO_3 in equilibrium with the melt in terms of the activity derived from the equilibrium constant, K, for equation (11),

$$K = \frac{a_{Fe_2O_3} \cdot P_{SO_3}^{\ 3}}{a_{Fe_2(SO_4)_3}} \qquad (12)$$

if we write for the pure solid oxide $a_{Fe_2O_3} = 1$. We have used the value $K = 4{\cdot}904 \times 10^9\ (N.m^{-2})^3$ at 873K derived from the data for the partial pressure of SO_3 in equilibrium with the pure solid ferric oxide and ferric sulphate phases ($a_{Fe_2O_3} = a_{Fe_2(SO_4)_3} = 1$), [10], and it has been necessary to assume that the solution behaves ideally with respect to pure solid ferric sulphate.

Calculated values of the ideal solubility of ferric sulphate in the melt in equilibrium with solid ferric oxide at the experimental partial pressures of SO_3 are given in Table 2. These values are compared with the concentrations of ferric sulphate corresponding to the integrated charge transfer during the oxidation experiments. At the lower partial pressures of SO_3 the limit imposed by the solubility is much less than the concentration corresponding to the total charge transfer, and the principal effect of the oxidation process must therefore be the formation of an oxide layer on the surface of the metal. Transport processes through the oxide layer will determine the kinetics of the oxidation process, and the gradual increase in the rate of oxidation with increase in the partial pressure of SO_3 under these conditions can be attributed to the increasing activity of SO_3 as the oxidizing agent in the metal–metal oxide–molten sulphate interfacial region. At higher partial pressures of SO_3 the ideal solubility of ferric sulphate in the alkali metal sulphate melt in equilibrium with solid ferric oxide is greater than the concentration corresponding to the total charge transfer, and we can attribute the more rapid increase in the rate of the oxidation process with increase in the partial pressure of SO_3 in this range to the dissolution of the corrosion products. We can assume that the rate of the charge transfer process will be fast compared with the rates of mass transport processes involved, and concentration gradients will therefore be established which will maintain the oxide layer on the surface of the metal, but at the higher partial pressures of SO_3 the thickness of this layer will be less than the calculated values given in Table 2 which are derived from the total charge transfer. The thickness of the oxide layer, and therefore the rate of the oxidation process, will be determined under these conditions by the rates of the transport processes for SO_3 and the metal ion in the sulphate melt.

5. Conclusions

The high rates of corrosion which are observed in molten sulphate environments at high partial pressures of SO_3 can be attributed to the role of SO_3 as the oxidizing agent, and especially to the effect of SO_3 on the solubility of the corrosion products. Corrosion by sulphatic environments in industrial plant will also be influenced by thermal gradients in the system, and by the factors which determine the melting point of the environment [11, 12], but these aspects have not been considered in this work.

Acknowledgment

This work was carried out at the Central Electricity Research Laboratories and is published by permission of the Central Electricity Generating Board.

References

[1] C. H. Liu, *J. Phys. Chem.* **66**, 164 (1962).

[2] K. E. Johnson and H. A. Laitinen, *J. Electrochem. Soc.* **110**, 314 (1963).

[3] A. J. B. Cutler, A. B. Hart, M. J. Fountain, and N. H. Holland, *A.S.M.E.* Publication 67-WA/CD-4 (1967).

[4] B. W. Burrows and G. J. Hills, *Electrochimica Acta* **15**, 445 (1970).

[5] D. M. Wrench and D. Inman, *ibid.*, **12**, 1601 (1967).

[6] A. Rahmel, *ibid.*, **13**, 495 (1968).

[7] G. Bombara, G. Baudo, and A. Tamba, *Corrosion Science* **8**, 393 (1968).

[8] E. K. Akopov and A. G. Bergman, *Russ. J. Inorg. Chem.* (Eng. trans.) **4**, 520 (1959).

[9] Joint Army–Navy–Air Force (JANAF) Thermochemical Tables (Dow Chemical Company, Michigan, U.S. 1966).

[10] 'High Temperature Properties and Decomposition of Inorganic Salts', Part 1, Sulphates (National Bureau of Standards, Washington D.C., 1966).

[11] A. W. Coats, D. J. A. Dear, and D. Penfold, *J. Inst. Fuel* **41**, 129 (1968).

[12] A. W. Coats, *ibid.*, **42**, 75 (1969).