THE RELATIONSHIP BETWEEN CORROSION PRODUCTS AND CORROSION RATES IN GEOTHERMAL STEAM

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ABSTRACT

The successful use of mild and low alloy steels in geothermal steam depends on the formation and properties of corrosion product films which cover and protect the underlying metal. Significant corrosion takes place only in a layer of condensate formed due to heat losses, such as in steam pipes. The corrosion products and the corrosion rates depend on temperature and steam condensate chemistry. Corrosion rates have been obtained and corrosion products identified for coupons exposed at the Broadlands BR 22 corrosion test rig. Initially, on a corrosion-product film free surface, corrosion rates are unacceptably high but decrease, under certain conditions, with increasing exposure time as corrosion products begin to cover the surface and thicken. The high hydrogen sulphide content of the steam at BR 22, Broadlands, leads to the formation of a series of iron sulphides, mackinawite, cubic iron sulphide, troilite, pyrrhotite and pyrite. These compounds have been identified and characterised using X-ray diffraction and optical and electron microscopy. In steam and bore fluid environments there was a trend to sulphur rich iron sulphides with increasing time of exposure. A layer of magnetite adjacent to the metal was observed which was protected from the corrosive solution by the iron sulphides. The uniformity of the corrosion products was greatest in bore fluid compared with separated steam which corresponds with the lower corrosion rates observed in the former environment.

INTRODUCTION

The low cost of mild steels, their ready availability and ease of fabrication make them the primary building materials for geothermal power plants. The successful use of mild steel in geothermal fluids requires a low long-term corrosion rate. In coupon tests prior to the erection of the Wairakei station, Marshall and Hugill, 1957, showed that corrosion rates of mild and low alloy steels were acceptably low in separated steam provided oxygen was excluded. Up until recently, equivalent low corrosion rates were observed in the steam lines at Wairakei, the major use of mild steel. The patch type corrosion first noticed in 1977 and the subsequent investigations (Braithwaite 1979, Wilson and Lichti 1982) demonstrated that the low corrosion rates were dependent on the presence of a thin continuous adherent corrosion-product film, identified as magnetite.

Coupons have been exposed to geothermal fluids at Broadlands BR 22 in order to select materials for the Ohaaki station. Results from these tests reported by Braithwaite and Lichti, 1981 showed that corrosion rates of mild steel in steam were again acceptably low provided O_2 was excluded. However in Broadlands steam the corrosion products observed were identified using powder x-ray diffraction as the iron sulphides: mackinawite, troilite and pyrrhotite, compared with the iron oxide, magnetite observed at Wairakei. Lichti et al., 1981, and McAdam et al., 1981, have shown that the major portion of material loss due to corrosion occurs within the first weeks of exposure. Following the initial period, the corrosion rate stays at a very low level (apart from periods when the test vessels were opened allowing O_2 ingress). On the basis of these low long-term corrosion rates indicated by both coupons and Corrosometer probes, mild steel pipes having appropriate corrosion allowances have been specified for the steam gathering lines for the Ohaaki station. However the experience of the patch type corrosion in the steam lines at Wairakei suggested that a greater understanding of the significance of the role of corrosion products was required.

Iron Sulphides

Corrosion processes leading to the formation of iron sulphides are complex, partly due to the multiplicity of iron sulphide phases which can form and also because of the degree of non-stoichiometry of some of these phases, Table 1. Extensive studies of the corrosion products formed on mild steel in contact with aqueous solutions containing hydrogen sulphide have been carried out by Wikjord et al., 1980 and Shoesmith et al., 1979. These studies were carried out under conditions which are encountered in the Girdler-Sulphide process for separating heavy water. The temperatures range from 30-180°C, which are similar to those encountered in geothermal power stations, but at hydrogen sulphide pressures as high as 2MPa. Some relevant observations and conclusions from these studies are as follows:

1) Several phases were reported to co-exist in the same corrosion film leading to the conclusion

TABLE 1 : CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES OF IRON SULPHIDE AND OXIDE PHASES OBSERVED ON MILD STEEL COUPONS, Uyterbogaardt and Burkes, 1971.

Name	Formula	Crystallographic structure	Colour of the polished surface	Reflectance	Anisotropy
Mackinawite	FeS_{1-x} $0 < x < 0.06$	tetragonal	Strongly varying, even in well polished sections. Usually pinkish or reddish grey.	22-45	Very strong. Completely crossed nicols: greyish white to dark grey or black. Not completely crossed nicols: bluish white to sienna brown.
Cubic Iron Sulphide	FeS	cubic	-	-	Isotropic
Troilite	FeS	hexagonal	as for pyrrhotite	-	Similar to pyrrhotite
Pyrrhotite	$Fe_{1-x}S$ $0 < x < 0.125$	hexagonal	cream with a faint pinkish brown tint	34-39	Very strong: yellow-grey greenish grey or greyish blue: intensity of anisotropy depends on orientation.
Pyrite	FeS_2	cubic	yellowish white	54	-
Magnetite	Fe_3O_4	cubic	grey	21	Isotropic

TABLE 2 : CORROSION PRODUCTS IDENTIFIED BY X-RAY DIFFRACTOMETRY

Environment	Exposure period (weeks)	Results from Lichti et.al 1981	Results from this study	Coupon Description	Material Loss* µm
Test Vessel 1**	4	T	T+P+(CIS+MAG)	Carbon steel	3.23
Bore fluid	13	T	P+(CIS+MAG)	1976/77	3.54
T = 160°C	52	T+(U)	P+(Py+U)		3.59
Test Vessel 3	4	T+(M+U)	T+CIS+(U)	Carbon steel	6.67
Separated steam	13	T	T+(U)	1978/79	9.95
T = 160°C	52	P+(U)	T+P+(U)		12.2
Test Vessel 4	4	M+U	M+(CIS+P)	Carbon steel	3.14
Wet steam	13	M+(P+Py+U)	P+(CIS+M+Py)	1978/79	3.27
T = 105°C	52	P+Py	T+P		6.14

M = Mackinawite	Py = Pyrite
T = Troilite	CIS= Cubic Iron Sulphide
P = Pyrrhotite	MAG= Magnetite
U = Unknown	( )= Minor Corrosion Products

* From Lichti et al., 1981

** This test vessel acts as horizontal separator. Consequently although the coupons will contact droplets of bore fluid they are not either continuously or intermittently immersed.

that non-equilibrium phases form for kinetic reasons and eventually transform to the stable phase.

2) Phase development progresses from iron-rich phases to eventual sulphur rich phases, the rate of transformation accelerating as the temperature is increased.

3) The initial metastable iron rich phase is usually mackinawite which offers the least protection.

4) The nucleation and growth of the more protective sulphur rich phases such as pyrrhotite and

pyrite can be retarded or prevented under conditions of rapid fluid velocity; these conditions rapidly remove ferrous ions from the vicinity of metal surface, (Tewari et al., 1979). This result was obtained at T = 120°C and is of major significance in respect to flowing condensate in steam pipelines.

5) Although the initial mackinawite layer, which appears as a fine grained film, probably forms by solid state reaction, the other phases appear as highly regular well-developed crystals, indicating slow growth by recrystallization from solution.

Another relevant study of iron sulphide corrosion products is that of Takeno et al., 1970 which showed that at room temperature cubic iron sulphide transforms gradually within a month to mackinawite after removal from a saturated H_2S solution in which it was grown. This observation contrasts with that of Shoesmith et al., 1979 who showed that the same transformation occurred within 100 hours. The only significant difference in the two experiments was the different temperatures 21°C (Shoesmith et al., 1979), 50°C (Takeno et al., 1970) at which the cubic iron sulphide was grown.

DESCRIPTION OF EXPERIMENTS

Mild steel coupons which had been exposed to geothermal fluids derived from bore 22 at Broadlands in tests described by Lichti et al, 1981, were available for further studies of the corrosion products. Preparation of the coupons, their installation in the corrosion rig at BR 22 and their subsequent removal and storage has been described by Braithwaite and Lichti, 1980. It is worth repeating for the purposes of this paper that storage was at constant temperature (21°C) and at controlled humidity (over silica gel) in evacuated containers. The chemical composition and the physical characteristics of the geothermal fluid environment have been described by Lichti et al., 1981. Braithwaite and Lichti, 1980, and Lichti et al., 1981 had used x-ray diffractometry to identify the corrosion products scrapped from the coupons. For this study the corrosion products were left on a piece of coupon cut to fit into the x-ray diffractometer, a technique described as x-ray in situ. The morphology of the corrosion products were studied using scanning electron microscopy for which the specimens were gold-coated. Sections perpendicular to the face of the coupon were examined by optical microscopy using reflected polarized light. The sections were prepared by first vacuum impregnating with a low viscosity epoxy resin followed by pressurizing in an autoclave to assure penetration of the corrosion film, The samples were then recast in a harder epoxy resin. The surface was polished to a 1μm diamond finish. In polarized light sulphide and oxide phases were distinguished on the basis of reflectance and the anisotropy exhibited; the optical properties are listed in Table 1. An EDAX analyser on the scanning electron microscope was used to produce element density maps for iron and sulphur of one of the polished sections.

These techniques were used in combination to identify the corrosion products formed on the coupons.

RESULTS

The phases identified using x-ray diffractometry of the in-situ corrosion products are shown in Table 2 for various environments and exposure periods and compared with the results obtained by Lichti et al., 1981 using x-ray diffractometry of the corrosion products scrapped from the coupon. Included are the material loss results found by Lichti et al., 1981 for the particular coupon examined. This initial x-ray identification was supported by SEM micrographs of the habit of the larger crystals and the optical properties determined from the polished sections. These latter techniques were able to determine the location of various phases with respect to the underlying metal. A more extensive discussion of the optical properties of the corrosion products observed on these coupons is in preparation (Borshevska et.al).

Bore Fluid (T = 160°C)

X-ray diffraction of the in-situ corrosion products indicated that pyrrhotite was the major sulphide phase in all three exposure periods, Table 2, although the x-ray peak corresponding to the spacing for the 102 planes indicated increasing iron deficiency with exposure time, (Toulman and Barton, 1964). X-ray diffraction also indicated the presence of some cubic iron sulphide and possibly some magnetite.

Cross-sections of the coupons showed a quite uniform grey layer adjacent to the metal covered with layers of brighter crystals. On the face of the coupon, the sulphide corrosion products were a quite uniform crystalline layer, Figure 1 whereas on the edges this was not the case.

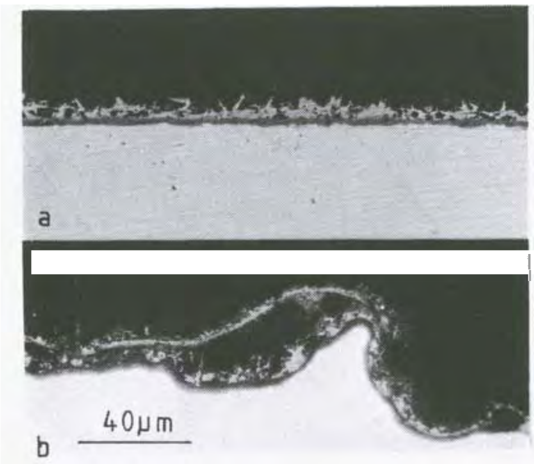

Figure 1: Cross-sections of a coupon exposed in vessel 1 (bore fluid) for 4 weeks. (a) face; (b) edge.(The difference in the profile of the underlying metal is due to initial surface preparation- the edges were only rough-machined).

The strong anisotropy in polarized light exhibited by the large crystals confirmed that they were the pyrrhotite identified by x-ray. The layer adjacent to the metal had negligible reflectance and did not exhibit any anisotropy which is consistent with it being magnetite as suggested by the x-ray data; the thickness of this layer, 2-4μm, did not increase significantly with exposure time. Its uniformity was maintained on the 13 week coupon but deteriorated on the 52 week coupon. The element density maps in Figure 2 confirm that the layer adjacent to the metal is an iron compound, and also that the layer of sulphide is significantly less than the total thickness of corrosion products - again suggesting a magnetite layer.

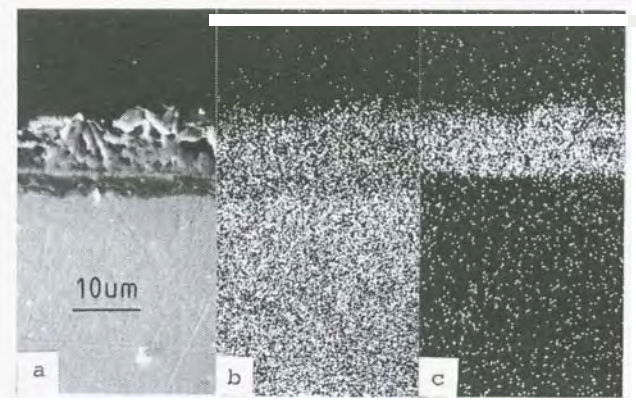

Figure 2: Element density maps for a cross-section of a coupon exposed in vessel 1 (bore fluid) for 13 weeks. (a) scanning electron micrograph ; (b) iron density; (c) sulphur density,

Scanning electron microscopy revealed that the pyrrhotite was present as hexagonal bypyramidal crystals of varying size depending on location on the coupon, Figure 3. Figure 3 also shows an underlying fine grained continuous film. The degree of perfection of the crystal also varied with position on the coupon and generally deteriorated with time of exposure. Increasing time of exposure also lead to an increase in size of the crystals which changed to hexagonal plates. Isolated colonies of cubic iron sulphide were observed on the 4 and 13 week coupon, but not on coupons exposed for 52 weeks. In the 52 week coupon isolated large needle like crystals were found of sufficient size to allow single crystal x-ray; they were identified as troilite.

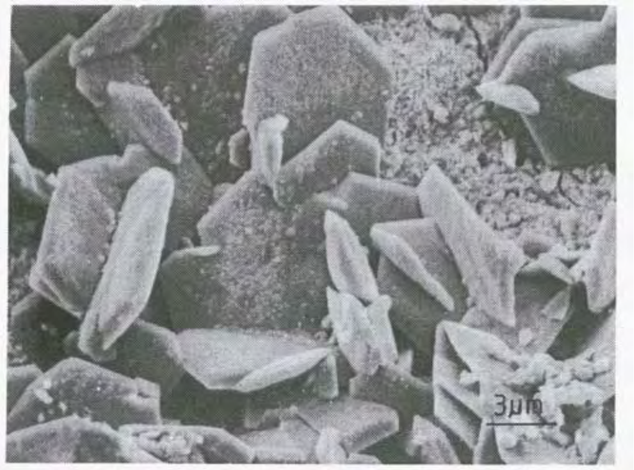

Figure 3: Pyrrhotite crystals on a coupon exposed in vessel 1 (bore fluid) for 13 weeks.

Separated Steam (T = 160°C)

Cross sections of the coupons from all 3 exposure periods revealed that although x-ray diffractometry had not indicated the presence of magnetite, a layer adjacent to the metal similar to that observed in bore fluid was formed in separated steam, Figure 4. However it did not have the same continuity or uniformity of thickness and it was not possible to determine whether the thickness changed with time. In reflected polarized light the iron sulphides showed the same anisotropy but more intense colours and higher reflectance than was seen with coupons exposed to bore fluid. The sulphide layer formed in separated steam appeared to be rather loosely packed, offering less protection to the underlying magnetite film compared with that formed in bore fluid. The morphology of the troilite crystals, identified as the major phase by x-ray diffractometry, is shown in Figure 5. Pyrrhotite was only observed on the 52 week coupon, as hexagonal plates.

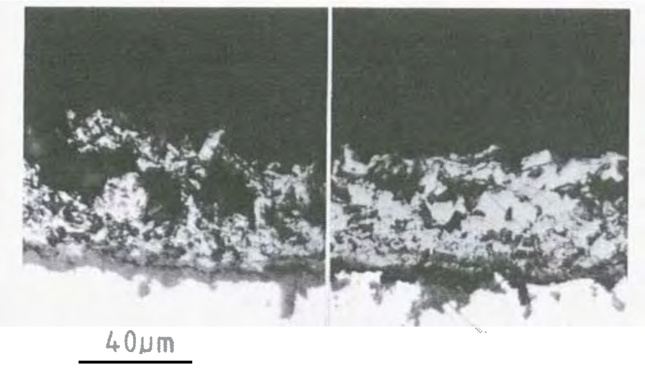

Figure 4: Cross-sections of a coupon exposed in vessel 3 (separated steam) for 52 weeks.

Wet Steam (T = 105°C)

Cross sections of coupons again show a thin layer of optically inactive material adjacent to the metal , Figure 6 presumably magnetite. The layer was both discontinuous and where present of non-uniform thickness. There was an increase in amount and thickness of magnetite with exposure time, although never providing the continuous uniform covering of the underlying metal observed in bore fluid. The anisotropy shown by the corrosion products above the magnetite confirmed

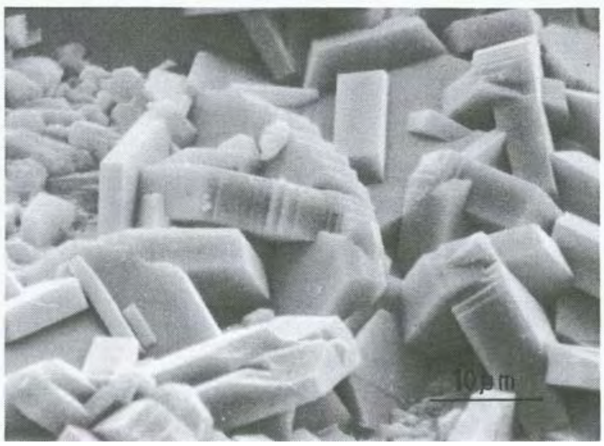

Figure 5: Troilite crystals on a coupon exposed in vessel 3 (separated steam) for 4 weeks.

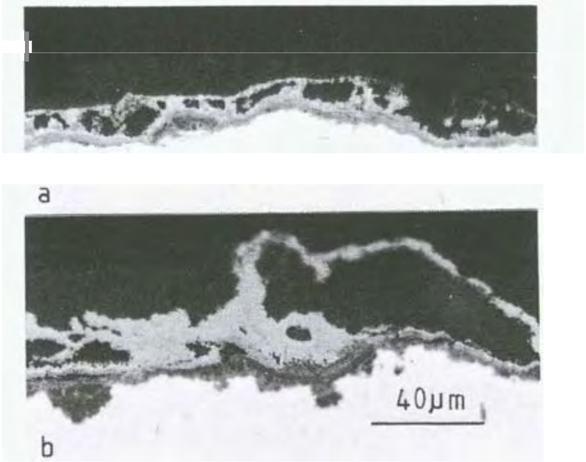

Figure 6: Cross-sections of coupons exposed in vessel 4 (wet steam) for (a) 13 weeks; (b) 52 weeks.

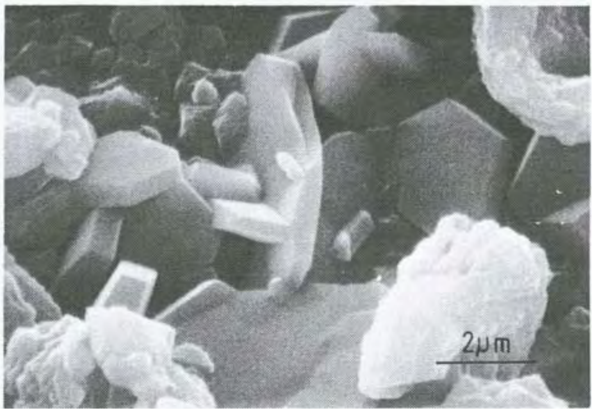

Figure 7: Mackinawite (bright semi-formed crystals) and troilite/pyrrhotite (hexagonal plates) on coupons exposed in vessel 4 (wet steam) for 4 weeks.

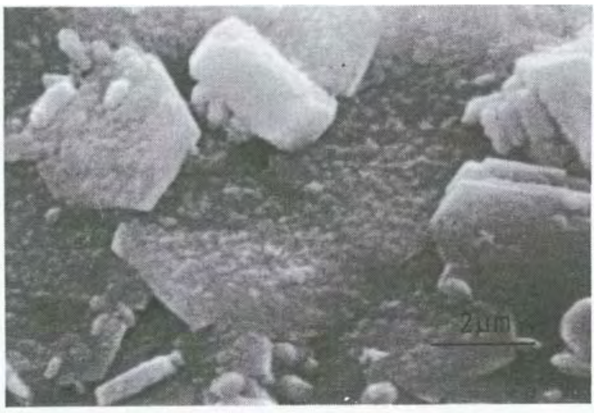

Figure 8: Well-formed hexagonal troilite or pyrrhotite crystals covered with fine-grained corrosion product on a coupon exposed in vessel 4 (wet steam) for 13 weeks.

the presence of mackinawite, troilite and or pyrrhotite. It was readily apparent from the cross sections that the crystals of sulphide were growing by recrystallisation from solution - Figure 6, but offering little protection to the underlying layers. Scanning electron microscopy showed areas of fined grained corrosion product in addition to patches of crystals of mackinawite, cubic iron sulphide and troilite/pyrrhotite Figure 7. It was not possible to distinguish between the latter two sulphides. In some parts of the coupons well formed crystals appeared to be covered with a fine grained corrosion product, Figure 8, a feature which was also common to other environments.

DISCUSSION

Before endeavouring to interpret the observations made of the corrosion products formed on coupons it is necessary to consider the objectives of coupon exposures. This is to determine the corrosion rates of materials when exposed to steam environments which are likely to be encountered in the working station which by necessity includes shutdown conditions. Consequently the coupons do not experience a completely invariant chemical environment for the duration of the test. As Lichti et al, 1981 have shown, that although shutdowns of the test vessels only occur infrequently, they contribute significantly to the corrosion which occurs and presumably to the corrosion products formed. Consequently it is necessary to use existing corrosion theory and results of experiments already described in the corrosion literature, e.g. Wikjord et al, 1980 to interpret what was observed.

In general the behaviour of the corrosion products is consistent with the pattern of behaviour described in the introduction as observed by Shoesmith et al, 1979 and Wikjord et al, 1980. During stages of corrosion, fine grained corrosion products (mackinawite) are expected to form. The nucleation and growth of well-formed crystals depends on temperature and on the degree of supersaturation of the solution with respect to ferrous and sulphide irons. Transformation of the initial iron rich sulphides to sulphur rich sulphides depends on temperature.

The initial corrosion product observed in wet steam (T = 105°C) was mackinawite. It is possible that it was the initial product formed in bore fluid and separated steam but had mostly transformed to pyrrhotite and troilite respectively by 4 weeks. This would be consistent with the observations of Wikjord et al., 1980 who did not find mackinawite after 1 day at T = 160°C and McAdam et al, 1981 who showed that the corrosion rate has decreased to a low level within 2 weeks.

Already at 4 weeks on coupons in wet steam, cubic iron sulphide and pyrrhotite had formed. Similarly pyrrhotite and troilite had formed on coupons in bore fluid and separated steam respectively, but underlying fine grained layers from which the crystals appear to be growing, were observed; by this time the corrosion rate had decreased to a lower level, (McAdam et al, 1981). The trend to sulphur rich iron sulphides does occur: mackinawite is not observed in bore fluid and separated steam and in wet steam after 13 weeks; the pyrrhotite in bore fluid becomes iron deficient with time; in some instances pyrite was observed; Table 2. There were however exceptions to this pattern. The behaviour shown in Figure 8 where well developed crystals appear to be buried in a fine grained corrosion product, probably arose following a vessel opening when acid formed by the oxidation of H_2S to H_2SO_4, caused a breakdown of the passivity of the film leading to a resumption of corrosion (possibly pitting), and production of this fine grained corrosion product. Subsequently an iron rich sulphide may recrystallize, such as the troilite crystal observed on the 52 week coupon in bore fluid. This sequence of events could explain the variety of corrosion products observed on coupons exposed to wet steam for 13 weeks although after 4 weeks at T = 100°C, Wikjord et al, 1980 observed a similar range of products.

The stability after removal from the test environment of cubic iron sulphide continues the trend indicated by the results of Shoesmith et al, 1979 and Takeno 1970. That is as the temperature at which the cubic iron sulphide is formed increases its stability increases; for formation at 21°C the transformation to mackinawite occurred in 200 hours; for formation at 50°C the transformation to mackinawite occurred in 1 month. In these tests the cubic iron sulphide formed at T = 105°C seems to be stable indefinitely.

The difference in the major corrosion product formed in bore fluid compared with separated steam suggests that some factor associated with the bore fluid environment favours the formation of pyrrhotite. The higher pH of the bore fluid, 7.4 compared with 6.3 leads to an eighty fold increase in the concentration of HS^- which is likely to be significant. However whether these crystals are troilite or pyrrhotite does not appear to be significant with respect to controlling the corrosion rate; as Figure 3 shows there shape and orientation precludes any protection of the underlying layers.

The corrosion products identified by Lichti et.al, 1981 differ in some instances from those found in this study. Principally the difference is where pyrrhotite and troilite are interchanged. Troilite is the stoichiometric end member of the solid solution range of non-stoichiometric pyrrhotites. It was distinguished from pyrrhotite by the position of the x-ray peak arising from the d_{102} spacing. The distinction is often difficult to make especially if only a small amount of corrosion product is available for x-ray examination. The results of this study also demonstrated that the distribution of the corrosion products formed on coupons exposed to geothermal fluids is more complex than the simple model assumed by Lichti et. al., 1981, of an iron sulphide film of uniform thickness and density.

The feature of the corrosion products which was significantly different from the results in the published literature was the presence of a magnetite layer adjacent to the metal and underlying an iron sulphide layer. Its identity was established by virtue of its reflectance compared with iron sulphides (Table 1), its optical isotropy, and the indication of its presence by x-ray diffractometry. The thickness of this layer on the 4 and 13 week coupons in bore fluid corresponds very closely to the material loss for these coupons found by Lichti et al., 1981 i.e. 2-4μm.

It would be a reasonable deduction based on:

a) the material loss suffered by the coupons;
b) the continuity of the magnetite films formed on the coupon;

that this magnetite layer has a major influence on the long term corrosion rate. (The difference in corrosion rates shown by the Corrosometers and the coupons in the bore fluid test vessel has been explained by Lichti et al., 1981). However it is apparent after comparing the continuity of this magnetite film formed in steam environments to that formed in bore fluid, that it requires a protective overlying layer of iron sulphides. These iron sulphides which are slowly recrystallized from solution, act as sinks for H_2S or HS^- which will consequently be reduced in concentration to a level at which thermodynamically, the formation of magnetite would be expected. In some instances, Figure 1, there was a continuous protective layer of iron sulphide. Consequently in order to obtain a low long term corrosion rate it is necessary firstly to form a protective iron sulphide film under which a magnetite film develops. It is apparent that this was achieved more readily in bore fluid than in separated steam - the causal factor, possibly pH and a higher HS^- concentration or some other bore fluid component such as SiO_2 has yet to be determined.

The coupons in this study were exposed to an almost static liquid environment, arising from condensation of steam on to the coupon surface and perhaps impingement of condensate droplets. Although these results characterize the corrosion product phases which allow low long-term corrosion rates, the experiments of Tewari et al, 1979 indicate that the processes which control the formation of protective corrosion products are strongly influenced by fluid velocity. Consequently these results are only a guide to what may occur in the practical situation of condensate flow in steam lines or heat exchanger tubes.

CONCLUSIONS

The behaviour of the iron sulphide phases observed on coupons exposed in geothermal steam from Broadlands well BR 22 can be explained using, or is consistent with the published literature on the corrosion of steel in aqueous sulphide solutions. The significant new observation is the presence of a thin magnetite layer adjacent to the metal, underlying a layer of iron sulphide which for the most part is re-crystallized from solution. The outer layer of sulphide acts to protect the magnetite layer from the sulphide solution. The results indicate that a greater degree of protection is obtained where dissolved SiO_2 is present or the condensate in contact with the coupon has a higher pH.

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