ASSESSMENT OF CORROSION PERFORMANCE OF CONSTRUCTION MATERIALS IN GEOTHERMAL STEAM

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ABSTRACT

The reliability of geothermal power station performance depends to a large extent on the choice of appropriate materials for the various station components. Geothermal development in respect to materials "know how" is at a stage where many of the peculiarities of the corrosion processes have been identified. The corrosion rate and the cracking susceptibility of engineering alloys depends on the chemical composition of the geothermal steam, in particular the hydrogen sulphide content. Although it is possible to predict the stable corrosion products which form, there is no quantifiable relationship for corrosion rates or degradation in mechanical properties, as a function of steam chemistry. The approach which will be adopted for the Ngawha geothermal field (NZ) for materials testing and selection is to measure steam chemistry and relative and absolute corrosion performance and to compare these with the existing Broadlands database. In a 4 to 8 week test programe surface corrosion monitors - ASTM coupons and electrical resistance probes - will be exposed in test vessels specifically designed for geothermal fluids. Cracking susceptibility will be assessed using the Slow Strain Rate technique. By recording steam chemistry at the same time, the corrosion results obtained can be compared with materials performance from other geothermal fields. The programme described is suitable for any prospective steam field in the Pacific region. The results obtained will provide information relevant to the exploitation of the field of interest and also expand the database available to all users of geothermal steam.

INTRODUCTION

The expanding world wide database of materials performance in geothermal fluids has recently been summarised in a series of guidelines for geothermal materials selection. Generic types of materials have been identified as having certain applications limitations as broad functions of the corrosion chemistry to which the particular material may be exposed (Ellis and Conover 1981, Conover et al., 1980). Summaries of this type rely on the predictive capability of the corrosion specialist and offer only limited guidance to engineers. Worst case chemistries must be identified in both the database and the desired application to make effective use of this method of materials selection. Without a good understanding of the corrosion properties of new geothermal fields or new environments which arise from changes in exploitation techniques, a realistic comparison with the existing database becomes unduly speculative. Therefore, in many situations such as for new fields having hitherto unknown corrosion chemistries as is encountered at Ngawha Springs, New Zealand, some measure of surface corrosion and cracking susceptibility of commonly selected materials is essential to determine if the field is "exploitable" from a materials point of view.

In the Pacific region a number of countries are involved in developing systems to exploit their geothermal reserves. These reserves show a broad range of corrosion chemistries and many fields have not been characterised by in situ corrosion measurements or by an appraisal of their corrosion chemistries. To help in overcoming these problems a simple series of materials testing procedures have been designed. The aim of these tests is to establish a knowledge of the corrosivity of new and existing geothermal systems with a view to comparing these systems with the moderately well understood New Zealand fields of Broadlands and Wairakei (Lichti et al., 1981, McAdam et al., Jan 1981, McAdam et al., 1981, Braithwaite and Lichti 1980, Marshall and Braithwaite 1973). To make such comparisons it is necessary to reproducibly measure the corrosion chemistry of the geothermal fluids and the corrosion properties of "standard" materials exposed to these fluids. A range of techniques are available to assess surface corrosion:

- Potential-pH Pourbaix Diagrams (Biernat and Robins 1972)
- ASTM Weight Loss Coupons(ASTM G1-72,ASTM 64-68)
- Electrical Resistance Probes(Lichti et al.,1981)
- Hydrogen Collection Probes(McAdam et al.,1981)
- Electrochemical Polarisation Resistance Probes (Lichti and Wilson 1980)

and cracking susceptibilities:

- Stress-to-Rupture (Marshall and Tombs 1968)
- U Bend Specimens (ASTM G30-79)
- Rotating Bending Tests (Howard and Bijnen 1981)
- Modified Wedge Opening Load (WOL) Specimens (Wilson and Borsheveska 1980)
- Slow Strain Rate (ASTM STP 665 1977)

CORROSION CHEMISTRY OF GEOTHERMAL FLUIDS

The first stage of evaluation of the corrosivity of new geothermal fields is to compare the corrosion chemistry of such fields with that observed in characterised systems. Geothermal steam typically contains varying amounts of CO_2, H_2S, NH_3 and H_2 (see Table 1). These species as well as dissolved solids present in the steam as a consequence of carryover from steam/water separators and entrainment in discharge fluids from dry wells, together with small amounts of condensate arising from heat losses determine the corrosion chemistry of air free separated steam. The high temperature, high pressure water phase chemistry of separated water, condensate in equilibrium with steam, and steam condensate can be calculated from the measured 'concentrations of gases and dissolved ionic species (Glover 1980, Henley 1981). These calculated water phase chemistries characterise the corrosive electrolyte encountered by metals and alloys placed in these environments.

Table 1 details measured gas concentrations and the calculated composition of condensate in equilibrium with steam at Wairakei, Broadlands and Ngawha in New Zealand. Potential-pH Pourbaix diagrams for the $Fe-H_2O-S$ systems for these fields are illustrated in Figure 1. The diagrams are based on the data of Table 1 and thermodynamic data which must often be extrapolated to the temperature of interest (Biernat and Robins 1972). The diagrams describe the equilibrium corrosion reactions of pure iron in contact with the condensate at the specified temperature. They do not include the sulphides, mackinawite and cubic iron sulphide because reliable thermodynamic data for these is not available. For systems where stable corrosion products have been collected, the predictions of these diagrams have been confirmed - see Table 1 and Figure 1. The diagrams give no indication of corrosion rates, however, we can correlate known corrosion results for the Broadlands and Wairakei fields with their corrosion chemistry and compare this with that of the new field under consideration. The corrosion chemistry of steam derived from the Kawerau, New Zealand 'field for example is similar to that of Broadlands with somewhat higher levels of carryover arising from differences in steam transmission systems. In broad terms this means that the corrosion behaviour database derived for Broadlands can with certain provisos be applied to the Kawerau system (Wilson 1982).

The condensate derived from Ngawha steam contains significantly higher concentrations of dissolved sulphides than that from Broadlands steam. The potential-pH diagram for Ngawha suggests that iron sulphides will form on carbon steel and may exhibit greater stability than at Broadlands. It is however difficult to predict the corrosion performance of carbon steel in this system particularly in view of the known tendency to pitting corrosion (Lichti et.al.,1981) in sulphide containing solutions and the complexity of corrosion products identified at Broadlands(Borshevska et.al.,1982). Corrosion measurements are therefore considered essential for the Ngawha system before the Broadlands database of corrosion results can be considered for this field.

TABLE 1: Gas phase chemistry and calculated composition of condensate in equilibrium with the steam phase.

		Wairakei HP Steam lines T=175°C	Broadlands BR22 Separated Steam T=160°C	Ngawha* (Anticipated) Separated Steam T=160°C
Gas fraction in steam				
wt%		0.1	2.1	15–16
Gas as a fraction of non–condensible gas				
mmol/	CO_2	930	952	950
mol	H_2S	57	21	12
(water	NH	12	4.6	10
free)	H_2	6	0.9	3
Calculated condensate composition				
mg/kg	CO_2	1.53	20.6	152
	HCO_3^-	0.49	11.1	125
	H_2S	0.25	1.3	5.4
	HS^-	0.056	0.48	2.9
	NH_3	0.53	4.2	39
	NH_4^+	0.32	3.6	70
Solution pH		6.35	6.5	6.6
Solids in steam derived from carryover				
mg/kg	Si02	~0.5**	-2	-0.5
of steam	Cl^-	-2.0	-4	-1.5
Stable corrosion products observed				
	Major	Magnetite	Troilite Pyrrhotite	??
	Minor	Pyrite	Magnetite Pyrite	??

*Gas fraction in steam - priv.comm. MWD Wairakei
**Concentration in condensate at final drainpot before station.

CORROSION MONITORING PROGRAMME

Surface Corrosion

Having established a need for corrosion measurements the second stage of evaluation is to select materials and techniques to monitor the corrosivity of the geothermal fluids. To establish the field as being exploitable the surface corrosion behaviour of typical construction materials in the expected geothermal environments must be evaluated. Initial measurements should be limited to no more than three materials. For most applications tests of a carbon steel AISI 1010, a martensitic stainless steel AISI 410 and an austenitic stainless steel AISI 316L would provide sufficient detail to quantify the field corrosivity and to compare that corrosivity with the existing database. Additional materials would expand the available database but would add little to the determination of field exploitability.

For surface corrosion studies ASTM coupons can be used to give some measure of the following aspects:

- weight gain - weight loss	material gain material loss	scaling rate corrosion rate
- pit density - pit depth	corrosion allowance	
- corrosion products - deposits	corrosion mechanisms scaling	

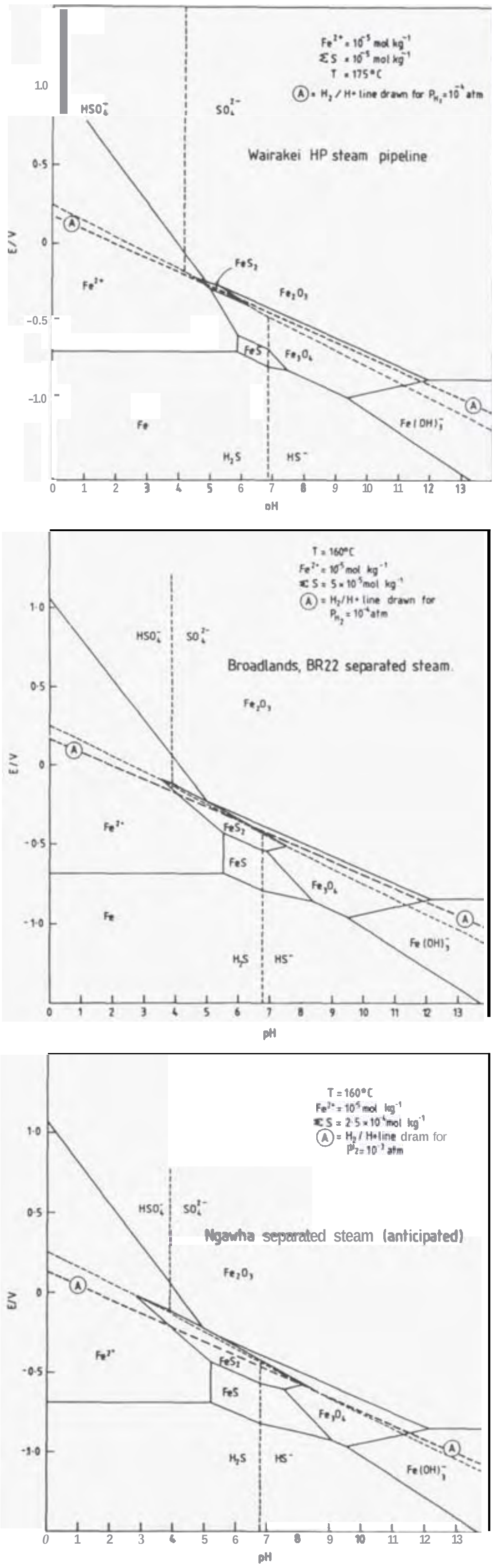

Figure 1: Potential -pH Pourbaix diagrams for separated steam at Wairakei, Broadlands and Ngawha, New Zealand.

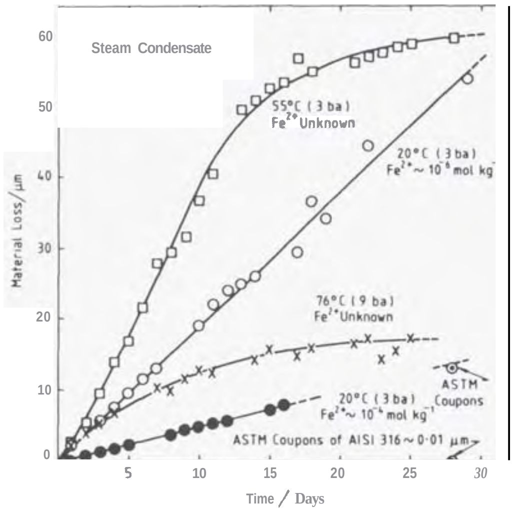

Figure 2: Carbon steel Corrosometer results for various condensate streams at Broadlands - BR 22.

Some type of continuous monitor is also required to realistically extrapolate the coupon weight loss results if a single short term coupon exposure is used. Electrical resistance "Corrosometer" ® (Rohrback Instruments of USA) probes of AISI 1010 and AISI 316L which are in the form of fully welded closed end tubes have been successfully used at Broadlands and are considered satisfactory for this application. Pitting characteristics (ASTM G46-76) and corrosion products formed on Corrosometer probes can be evaluated as for coupons however the cost of such probes dictates that they be reused as often as possible, Exposed coupons can be kept as permanent records or sectioned for metallographic examination of corrosion.

Corrosometer results for carbon steel in geothermal fluids have been given by Lichti et.al., 1981. They presented results for exposures of up to one year in separated steam when the majority of the information sought was in retrospect available at 4 weeks. Corrosion observed after 4 weeks was primarily due to test exposure variations. Carbon steel Corrosometers and electrochemical corrosion monitors are presently being used to evaluate corrosion in acidified separated water at Broadlands. Previously tests using only coupons were conducted for one year (Braithwaite and Lichti 1980) whereas realistic results are being obtained with continuous monitors in 3 to 4 weeks. Figure 2 illustrates a number of corrosion results obtained using carbon steel Corrosometer probes in geothermal condensates. The figure demonstrates how changing of the test conditions can significantly alter the corrosion results but more important for this discussion, how these differences are easily detected by carbon steel Corrosometer probes in 3 to 4 weeks.

If carbon steel corrosion rates on the order of those shown for condensate at 20°C in Figure 3 were obtained in steam then the use of this material for steam separation, transmission and power generation systems would be seriously limited. Alternatives to carbon steel such as stainless steel clad on carbon steel or new, perhaps unproven exploitation systems may need to be considered. In these situations more effort in corrosion monitoring and plant engineering would be required before the field could be declared as "exploitable".

Test Plant for Surface Corrosion Monitoring

Test plant for corrosion studies intended to establish field exploitability should be kept simple yet must provide a degree of flexibility. Test vessel configurations should allow independent control of physical test conditions without the need to alter well discharge conditions which must be selected to give typical fluid chemistry. Klyen, **1982**, has suggested the locations of 25mm diameter test fluid sampling points suitable for collecting geothermal fluids from wellhead equipment for chemical analysis. These same sample points can be used for obtaining corrosion test fluids as illustrated in Figure **3**. In situations where turbulence is not obtained in the main bore fluid discharge pipe more complex arrangements may be required to correctly sample this fluid. Use of sampling points on the vertical well piping has not always given reproducible chemical results and should if possible be avoided for obtaining corrosion test fluids.

A variety of test vessel designs and configurations have been used at Broadlands. Figure **4** illustrates a simplified test vessel for coupons, and Corrosometer probes which avoids many of the problems encountered during testing at Broadlands (Lichti et.al., 1981). The figure shows a 100mm diameter carbon steel test vessel which is flanged at both ends and which has been fitted with 50mm threaded ports welded into the side of the vessel. Fluid entry and exit is via the end flanges. The solid baffle and diffusor help to minimise fluid impingement on corrosion probes and give some fluid mixing. Steam piping to and from the vessel is again in small bore pipes with fluid control by manually set gate valves. The vessel can be located horizontally for tests using steam and vertically for two phase fluids (top entry - turbulent flow) and water (bottom entry). A horizontal vessel can also be used for tests in liquid environments however care must be taken to avoid air and gas pocket formation. Mass flow rates of 10 to 20 kg/hr are considered suitable for steam with somewhat higher flows for two phase fluid. For condensate, a flow rate of 10 kg/hr in such a vessel tended to erode carbon steel specimens and lower rates may be more appropriate. All pipework should be insulated and the vessels should be protected from the weather.

Pressure vessel codes should be used for all aspects of design, construction and testing of such test vessels and the associated pipework. A corrosion allowance of - 3mm on the test vessels will allow reuse of the vessels for a number of tests. Some form of overpressure safety device is essential.

For tests in condensed steam, condensed steam plus air or condensed steam/cooling water/air mixtures a test vessel similar to that shown in Figure 4 can be used. The corrosion rate of carbon steel in such fluids will however tend to be high. The vessel life may be very short due to corrosion and this corrosion may also add considerable quantities of Fe^{2+} to the test solution resulting in reduced corrosion rates, see Figure **3**. This same type of vessel can be made from AISI 316L stainless steel to avoid high Fe^{2+} in solution and to add to the life of the vessel. Austenitic stainless steels are however prone to stress corrosion cracking and high pressure (>2 ba) high temperature (>80°C) solutions containing significant concentrations of chloride or sulphide and air may initiate rapid catastrophic failure of the test vessel. Use of stainless steel clad onto carbon steel or epoxy coated carbon steel would reduce or avoid this danger. However for most test fluids of this type high pressures are not required and a simple open containment vessel such as that illustrated in Figure 5 would be suitable. The vessel is shown as it could be used with aerated fluids - valves labled 2 open. For non-aerated condensate tests a

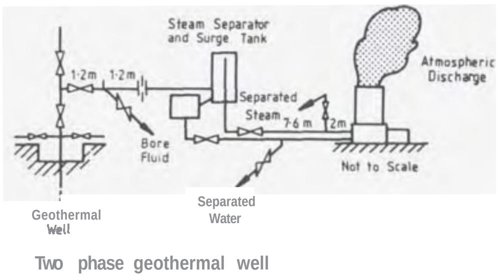

Figure 3: Geothermal fluid draw off arrangements for 200mm diameter pipes - Klyen **1982**

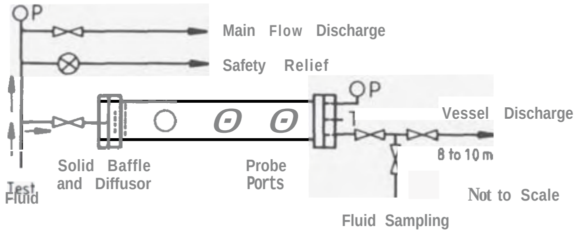

Figure 4: Carbon steel test vessel for steam, separated water and two phase fluids.

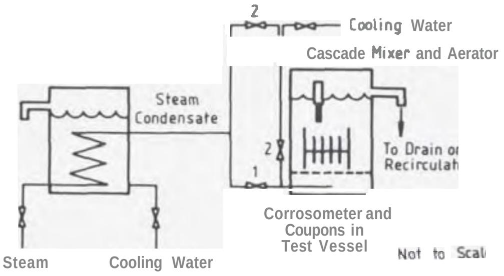

Figure 5: Stainless steel vessel for condensate/cooling water mixtures.

simple lid sealed with silicone rubber, fitted with a top drain and gas trap can be substituted for the side drain. Fluid discharged from the test vessel can be collected and selectively recirculated to similate fluids derived from a closed cycle steam condensing/cooling water system.

A prefabricated insert rack of AISI **316L** can be used for holding ASTM type metal coupons in the above test vessels (see ASTM G4-68). Coupons should be exposed parallel to the direction of fluid flow and no more than **4** should be placed across the vessel to minimise flow restrictions. Corrosometer probes are braught in via the side ports. In high pressure steam tests the probes can be used directly in contact with the test vessel while in low pressure wet steam and in liquid environments the probes should be insulated. Both nylon and some grades of TUFNOL® have been successfully used at Broadlands for this purpose (up to **130** kPa at 110°C).

Cracking Susceptibility

The long term reliability of geothermal power station components constructed in materials having suitable resistance to surface corrosion is determined by the materials resistance to corrosion induced cracking failure - Stress Corrosion Cracking (SCC). Cracking susceptibility is influenced by both materials parameters and environmental conditions which are present continuously, or which can arise intermittently. Testing for cracking susceptibility must firstly identify those materials which can withstand the environment which is present continuously. Secondly it must identify those environments which may occur intermittently and which can cause catastrophic failure of the materials which normally would perform successfully, Conditions occurring during plant start-up or shutdown are thought to be the most common examples of non-typical corrosion chemistry which may cause SCC.

Carbon and low alloy steels and ferritic/martensitic stainless steels having high fracture toughness, and sufficient resistance to SCC can be specified for service in H_2S containing environments. In the absence of oxygen and with low chloride levels austenitic stainless steels such as are used for fully sealed pipeline bellows also show good resistance to stress corrosion cracking. However, equipment suppliers and component selection engineers often tender or specify harder, higher strength materials which have a lower fracture toughness. Evaluation of materials of this type, which were proposed for use in Broadlands steam for the Ohaaki power station,for cracking susceptibility **has** to date concentrated on SCC in continuous operating environments. McAdam et.a1.,1981, for example, reported that the reduction in corrosion fatigue performance was much greater in steam from Broadlands BR22 than in Wairakei steam, the greater reduction being in the environment with the higher levels of H_2S (see Table **1**). More recent experiments involve **1-T WOL** specimens for identifying the reduction in fracture toughness of rotor steels exposed to geothermal steam, (Wilson and Borshevska 1980) and vibrating reed corrosion fatigue studies (Howard 1980). Results from these experiments will give a more complete database for the performance of blade and rotor materials in geothermal steam.

The problem of SCC in non-typical environments has only been addressed to a limited extent using worst-case fluids, **e.g. aera**ted steam.These tests have indicated the following species may be significant: H_2S, **S**, O_2, Cl^- (SiO_2 - possibly as an inhibitor); however the critical material strength levels at which cracking will occur and the concentrations of species required to cause SCC have not been quantified. Only a limited number of tests have been directed to potential problems in geothermal steam direct contact condensing systems where recirculating cooling water will contain oxidised products of sulphide and possibly excess chloride arising from carryover. Materials used for components such as gland steam condensers and oil coolers which utilise this cooling water must have sufficient resistance to SCC which could arise in this environment (Cragnolino and MacDonald 1982). Further effort to understand these problems is required even for the Ohaaki station.

As for surface corrosion if the corrosion chemistry is close to that of an established station or to that where a database of materials test results are available, then no further testing is required. Where the corrosion chemistry is substantially different, as has been shown for the Ngawha geothermal field compared with Broadlands BR22 - see Table **1**, then cracking susceptibilities must be determined. For Ngawha, the Slow Strain Rate testing technique which gives a rapid comparative measure of whether an environment will cause SCC,will be used (ASTM STP **665,** 1979). A limited range of materials, a turbine rotor low alloy steel, a blade steel AISI 410 and an austenitic stainless steel AISI **316L** are to be tested and their performance compared with that observed in Broadlands steam. The technique utilises a multi-specimen test-frame with a test duration of **3-4** days in which time a result is definitely found, c.f. stress rupture which requires a series of test specimens with an arbitrary 40 day time limit. The database which is already partly established for cracking susceptibility in Broadlands BR22 steam allows this very much restricted testing programme for cracking susceptibility in a new field, If the results found indicate a substantial increase in cracking susceptibility of the "standard" test materials in the new environment, then identification of materials having greater resistance to cracking may be required. Follow up testing using 1-T WOL fracture toughness specimens would be required to establish absolute data for component design in the new environment.

Developing countries can avoid testing for stress corrosion cracking by relying on manufacturer's recommendations. However the responsibility for power station reliability which depends on satisfactory materials performance rests with the steam users, who in fact are in control of steam quality which has been shown to have a major influence on cracking susceptibility. Additionally equipment suppliers must be able to demonstrate a knowledge of the peculiarities of geothermal steam compared to that of conventional power stations, and an awareness of problems which can arise during normal plant operation, An alternative approach is to rely on published literature showing materials performance in comparable environments. The weakness of this approach is that the published literature seldom includes materials of interest exposed to relevant environments. Hopefully, this problem will be partially remedied by the expanding Broadlands database. A third approach which is not beyond the capabilities of developing countries is to conduct SCC tests of the type outlined above for Ngawha. This does not involve an extensive programne and would be only a small cost compared to the total cost of a geothermal power station although personnel with some experience in corrosion testing would be required.

CONCLUSIONS AND RECOMMENDATIONS

The corrosion chemistry of the Ngawha geothermal field is significantly different from that of the Broadlands field. Surface corrosion and cracking susceptibility measurements of some standard materials are required in order to compare the corrosivity of the two fields. A simple series of short term tests suitable for assessing this corrosivity have been specified. Unless there are significant differences in the measured corrosivity then the Broadlands database of materials performance will be used to select materials for Ngawha. An evaluation of the corrosion chemistry and where necessary comparable corrosion tests to those specified for Ngawha should be considered for other geothermal fields in the Pacific region.

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