GEOTHERMAL CORROSION MONITORING TECHNIQUES

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1.0 INTRODUCTION

The direct use of geothermal fluid for power or heat generation requires the use of materials uhich are resistant to chemical conditions encountered in the field, Tho primary corrosive chemical species in tho New Zealand fields at Wairakei and at Broadlands ere H_2S end CO_2, with the level of H_2S at Broadlands being 10X higher than that at Wairakei. Extensive corroaion testing is being done at the Broadlands field to discover the effect of the higher H_2S levol. Tests were instigated to obtain engineering data on corrosion rates, corrosion fatigue properties, susceptibility to stress corroaion cracking end hydrogan effects.

Thio paper deals mainly with methods urad to obtain information on corrosion rater. these include coupon exposures, corrorometer probes, and hydrogon probes. Other methods used to evaluate corrosion properties will alro be discussed.

2.0 CORROSION RATE DETERHINATION

Currant methods of obtaining corrosion date ere outlined in Table 1. The table also provides a brief summary of advantages and disadvantages oncountered uith specific test methods in geothermal environments. figurer 1 to 10 rhow some of the equipment used to monitor corroeion end indicate typical results obtained in wet low pressure steam (125 KPa, 105°C, 10% wetness).

2.1 EXPOSURE Of COUPONS (1)

The exposure of insulated metal coupons to establish corrosion rates by loss in weight (figure 1) is e standard test, universally accepted for corrosion studies, end has been extensively used et Wairakei (2) (3) and et Broadlands (4). Experiments can be designed to provide either single exposures, or a semi-continuous record of corrosion from successive exposures. Short; exposures of 2 to 16 weeks permit e study of protection given by films which form initially whilst extmnded exposures of >30 weeks allow time for non-uniform effects such as pitting and phase selective corrosion to occur. Exposed coupons also provide material for identification of corrosion products, and matellographic examination of both internal corrosion and corroeion productr.

figura 2 illustrates the results of coupon weight loss determinations on a carbon steel after three exposure periods in wet low pressure steam. Tho apparent breakdown of the protective film et soma time after 13 weeks should be noted. The unexpectedly high material loss after 52 weeks coincided uith changing corrosion products (from iron sulphides to iron oxides and other sulphur containing species) end was shown to be due to onset of pitting corrosion.

Although nearly all corrosion rete determinations can be made by the coupon method, removal of coupons may disturb the environment end result. must always be historical. Evaluation procedures are lengthy and 'instantaneous' methods for semi-continuous monitoring of corroaion are often more desirable.

22 CORROSOMETER PROBES (5)

The corrorometer system consists of a probe and r meter that accurately measures the electrical resistance of the freely corroding sensing element of a probe. The corrosion rete can be calculated from the increasing probe resistance as material is lost by corrosion. Several probe models in use at Broadlands are illustrated in Figure 3, and a plot of results for carbon steel in wet low pressure steam is shown in Figure 4. Corrosometer prober ere available in carbon steel and types 304 and 316 stainless steel in e welded body 'special' form, Other materials are provided in 'tube' or 'wire' form as ahown in Figure 3. Consistent results (in both steam and condensate) which compare favourably uith coupon weight loss data have been obtained for carbon steel. Tho fully welded and epoxy filled probes (maximum temperate of 150°C) are considered to be the most suitable for use in geothermal environments.

23 HYDROGEN PROBES (6)

Corrosion of carbon steal in H_2S containing environment. results in the formation of atomic hydrogen which freely passes through. these steels and escapes as hydrogen gas. By providing e collection patch on the outside of a corroding pipe or by exposing a closed ended tuba of carbon steel the volume of liberated hydrogen can be collected and recorded. A hydrogan probe and gas collection unit are shown in Figure 5. A plot of cumulative volume collected vs time for such a probe exposed in wet low presaure steam io illustrated in figure 6. Tho hydrogen probr method typically provides qualitative corrosion information only. Tha system is however sensitive to changes In the environment end can be used to monitor established systems for chemical variations. The method is limited to carbon steels because of their high (compared to stainless steels) hydrogen permeation rates.

24 ELECTROCHEMICAL TESTS

A system to provide polarisation resistance measurements in liquid dominated geothermal environments has been evaluated at Auckland Univerrity (7) and tests of this system will soon be undmrteken at Broadlands. The major limitation of the recommended system which usee three in-line probes of the same materiel io that a minimum fluid conductivity is required for occurata corroeion measurements. Very low corrosion rater em observed for stainless steels in cold condensate environments may also prove to be beyond tho scope of the instrument.

2.5 STRESS RUPTURE TESTS (6) (8)

Notched tensile test pieces are stressed in e static rig (see Figure 7) for exposure to geothermal environments where stress corroaion cracking or hydrogen induced cracking nay occur. Turbine rotor and blade materials ere currently under test at Broadlands in a variety of steam end condensate environments. The tests establish a critical stress below which no fracture occurs in a selected mxpooure period. Figure 8 shows e metallographic section through a notched specimen exposed in wet low pressure steam for 80 days. Extensive corroaion product formation is clearly ahown as is evidence of stress corrosion, however the specimen did not fracture under test.

26 CORROSION FATIGUE TESTS (9)

Goethermal corrosion fatigue results ere determined using loaded rotating bending Wöhler type specimens. Tests are conducted in wet geothermal steam and comparative data are obtained in air to establish the fatigue endurance limits up to 10^e cycles. Figure 9 illustrates the apparatus used to fatigue the specimens in air and Figure 10 gives a series of results for turbine blade stools. Comparison of a materials performance in geothermal steam to that in air provides a measuro of susceptibility to corrosion fatigue.

2.7 SUPPLEMENTARY METHODS

Methods listed ea supplementery in Table 1 are conaidered essential to promote better Understanding of the corrosion processes. If corrosion data ere obtained in the absence of this type of additional analysis, the ability to predict corrosion behaviour in similar but different environments cannot be developed. Costly retesting of selected alloys would be required in each new environment.

3.0 CONCLUSIONS

With the increasing number of proven corrosion monitoring methods the ability to identify euitable construction materials or to monitor corrosion in existing plant is greatly improved. Selecting the best monitoring method or combination of methods may however prove to be a difficult task. The use of complementary methods such as corrosometer probes and hydrogen probes together with coupons for metallographic and long term corrosion evaluation may provide ell the desired corrosion rate information about a particular environment when no single method would yield satisfactory results in a similar time period. Every applicable technique must be considered to obtain comprehensive corroeion data Cor very critical parts such as turbine blades and rotors. In many cases this requires collective action from a team of research scientists and engineers to give an unified approach to the corrosion monitoring problem.

REFERENCES

1. ASTM Recommended Practices G1-72 and G4-68
2. Marshall, T. and Braithwaite, W.R. Unesco, 1973. Geothermal Energy pp. 151-160.
3. Foster, P.K. and Tombs A.; N.Z. Journal of Science Vol. 5 No. 1 March, 1962 pp 28-42.
4. Braithwaite, W.R. and Lichti, K.A. ; OSIR - IPD To be published ASTM Special Technical Publication 1979-80.
5. Soylemetoglu, S.; OSIR - IPD To be published.
6. Marshall, T. and Tombs, A.; Australasian Corrosion Engineering, Vol. 13, No. 9, Sept., 1969, pp 1 to E.
7. Pound, B.G., Sharp, R.M. and Wright, G.A.; University of Aucklend Progress Reports on Geothermal Corrosion Research Project, Pert 2 and Part 3, 1979.
8. Borshevsky, H. and Marshall, T.; OSIR - IPD To be published.
9. Howard, R.; OSIR - IPD, To be published.

Additional references and manufacturer information will be available on request.

TAELE 1: GEOTHERMAL CORROSION MONITORING TECHNIQUES

MAIN METHODS	BRIEF OESCRIPTION	ADVANTAGES	OISAOVANTACES
Coupon Exposure	Long term exposure of metal coupons. Monitor change in weight.	Test all materials. Can be in a remote site. Accurate and comprehensive corrosion information.	Long evaluation period Requires intensive labour. Multiple exposures often necessary
Corrosometer Probes	Changing resistance due to corroding metal elements.	Actual corrosion rat can be obtained in a short time. Continuous record of corrosion rate.	Can not distinguish type of corrosion. Limited material choic High cost. Requires daily monitoring.
Hydrogen Probes	Volumetrically measures hydrogen gas liberated by corrosion reactions.	Good warning means for a sudden change in e system. Continuous record of the corrosion.	Can not distinguish type of corrosion. Useful for carbon steel only. Requires daily monitoring,
Electro-chemical	Measures the corrosion rate by electro-chemical polarisation resistance method.	Instantaneous measure of corrosion rate. Provides rapid assessment of environments and material.	Applicable only to liquid dominated environments where the conductivity of the fluids is suitable.
Stress Rupture Teats -'U' Bend -Selected Stress	Testing the susceptibility of rotor and blade steels to stress corrosion cracking.	Indicates allowable stress levels.	Requires intensive labour. Sensitive to minor chemical changes.
Corrosion fatigue Test	Compare fatigue performance of turbine blade and rotor steels in geothermal fluids to that in air.	Indicates degradation of fatigue performarce due to geothermal environment.	Test is sensitive to exposure time.
Supplementary Methods			
Chemical Analyses	Measure concentrations of corrosive species and corrosion products.	Characterise specific environments for comparative purposes.	Sensitive to sampling and analyses techniques. Requires expertise.
Corrosion Product Analysis	X-Ray, Edax, and Electron Micro-probe. Identify major corrosion product species.	Suggest corrosion mechanisms.	Limited equipment availability. Sensitive to sampling and analyses techniques. Requires expertise.
Aetallographic Examination	Optical-Sem-(Tem) Microscopic examination of corrosion and corrosion products.	Reveals form and type of corrosion. Suggests history of corrosion.	Limited Equipment availability. Requires expertise.
Theoretical Evaluation	Potential pH Diagrams. Establish equations describing chemical equilibrium.	Indicates stable corrosion products. Suggests possible corrosion mechanisms.	Results generally apply to equilibria1 conditions only.

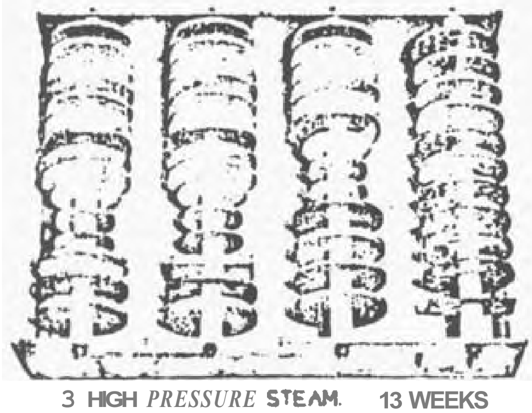

Figure 1: Corroded coupons on exposure rack.

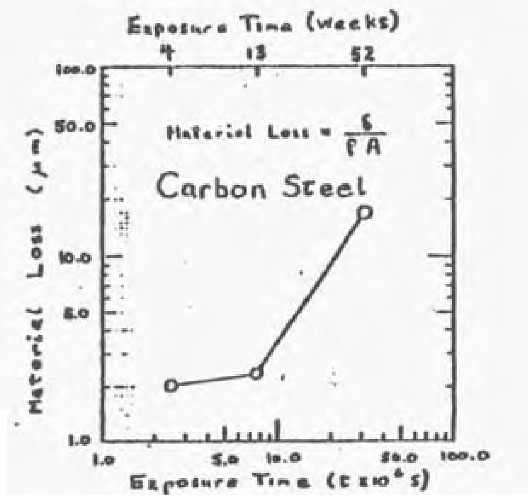

Figure 2: **Logarithmic** plot of corrosion **results** for coupons **exposed in wet low** pressure **steam.**

Figure 3: **Corrosometer probes.**

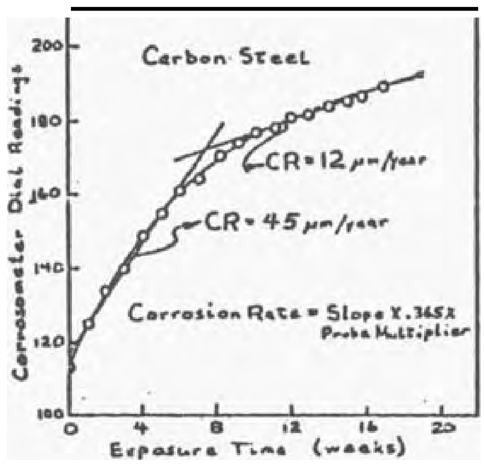

Figure 4: **Corrosometer** probe results obtained **in wet low pressure steam.**

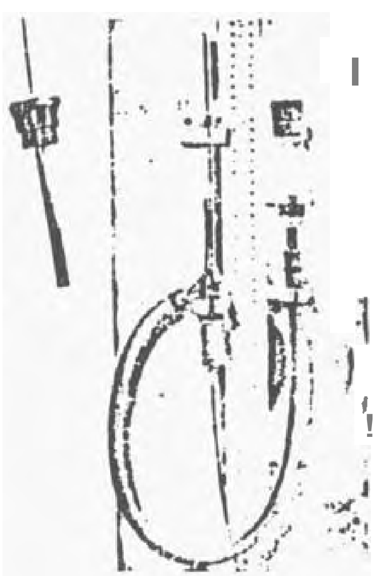

Figure 5: Hydrogen **probe and gas** collection **apparatus.**

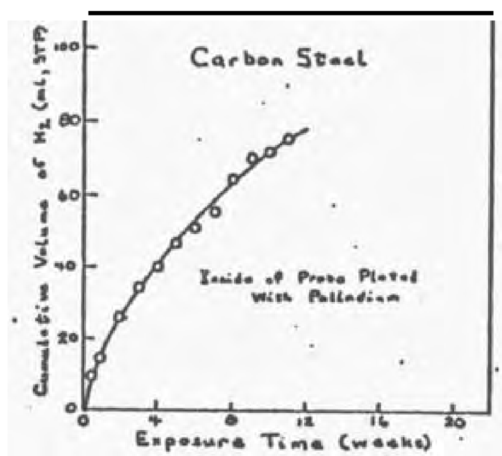

Figure 6: Hydrogen probe **results** obtained **in wet low pressure steam.**

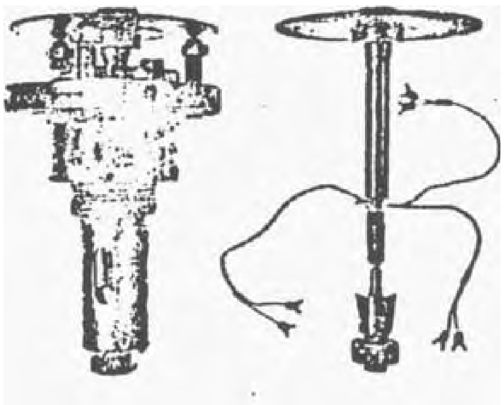

Figure 7: Stress rupture loading rig and loading system.

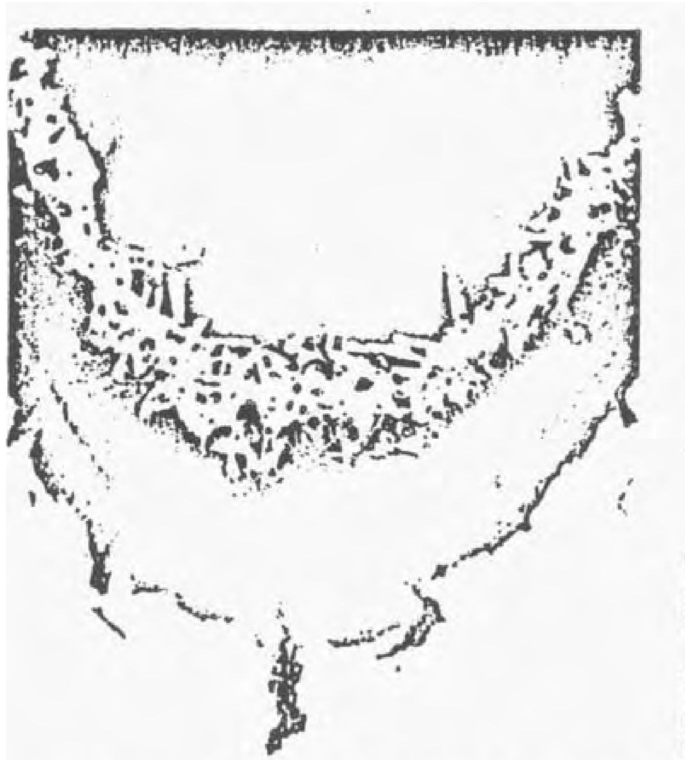

Figure 8 : Metallographic section of low alloy steel stress rupture' specimen exposed in wet low pressure steam.

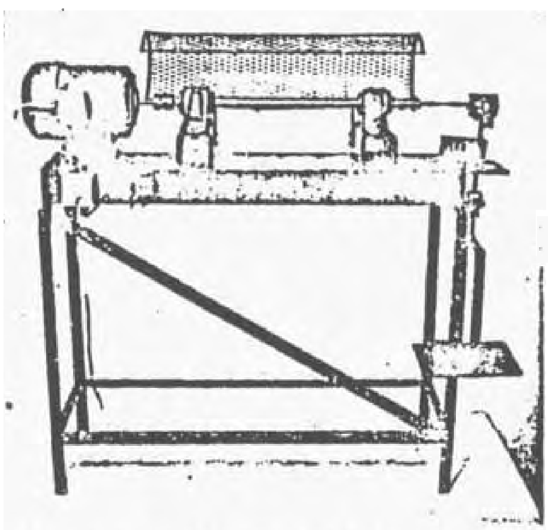

Figure 9: Fatigue test in air.

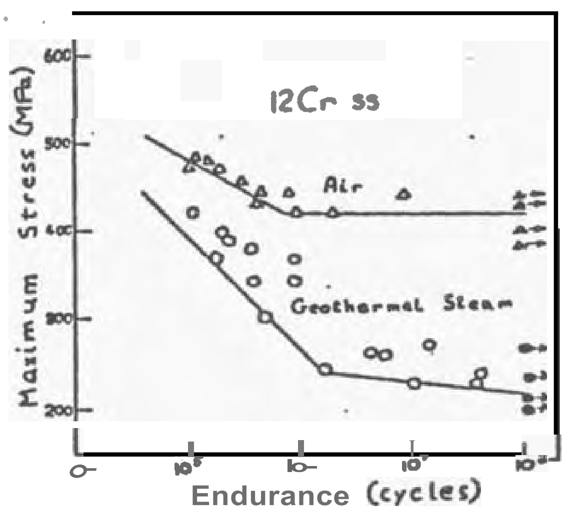

Figure 10: Typical corrosion fatigue results obtained in air and wet loo pressure steam.