## GEOTHERMAL CORROSION CASE STUDIES AT THE WAIRAKEI AND BROADLANDS GEOTHERMAL FIELDS USING THE 'CORROSOMETER' METHOD.

S. Soylemezoglu, K.A. Lichti, and H. Bijnen

Industrial Processing Division, Department of Scientific and Industrial Research, Petone, New Zealand.

### ABSTRACT

Instantaneous and continuous corrosion rates can be monitored by a 'Corrosometer' method. This method can readily be adapted to solve problems on corrosion in geothermal fluids. In this paper, a variety of geothermal case studies are presented, demonstrating the value of this rapid corrosion assessment. These include a study of the effect of pressure on corrosion rate in some geothermal fluids at Broadlands, an investigation of rapidly corroding bleed pipes and connections at Broadlands well BR 32, a study of the effects of geothermal steam condensate velocity on the corrosion rate of mild steel at Wairakei, and corrosion inhibitor monitoring of high pressure steam transmission lines at Wairakei.

## INTRODUCTION

The Corrosometer\* method for monitoring corrosion of carbon steel as described below has been extensively used in the geothermal fields of New Zealand. The Corrosometer system can be used independently of other geothermal corrosion monitoring techniques (Lichti and Soylemezoglu, 1979), though the interpretation of results can be more positive when additional information is made available from established techniques such as chemical analysis, coupon exposures etc. Carbon steel corrosometer probes are fully sealed, compact, and can be easily installed in high temperature (~200°C) high pressure (-30 MPa) geothermal fluids. The Corrosometer method provides continuous, reliable, instantaneous corrosion rate readings, and shows good sensitivity to the variations in conditions in a system.

The Corrosometer system consists of a probe and a meter. Operation of the probe is based on the increasing electrical resistance of an exposed sensing element as its cross-sectional area is reduced by corrosion. The instrument compares this increasing resistance to the constant resistance value of a protected reference element. By measuring the ratio of the two resistances, temperature changes that equally affect both elements are cancelled out. The resistance ratios, reported as dial readings are directly proportional to the thickness of the exposed element. Consecutive dial readings are

taken to generate a graph of dial readings versus time from which metal corrosion rates can be calculated.

The following corrosion case studies demonstrate the scope of the corrosometer probes as research tools, their use to assess trouble spots, and their value as corrosion control monitors in geothermal fluids.

## EFFECT OF PRESSURE ON CORROSIVITY OF GEOTHERMAL

### FLUIDS

The corrosion rates and the susceptibility to stress corrosion of turbine blade and rotor steels are presently being evaluated at Broadlands in condensate (20°C, 300 kPa), aerated condensate (20°C, 130 kPa), wet low pressure steam (104°C, 126 kPa, 10% wetness). These fluids contain geothermal gases such as H<sub>2</sub>S, CO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. The solubility of these gases in condensate and hence the chemistry of the corrosive fluid is affected by pressure, as well as by temperature, pH, and the partial pressure of the gases. A reduction in pressure would normally result in decreased gas solubilities and lower the corrosivity of the solutions. However, quantitative predictions can not at present be made from available knowledge of the corrosion chemistry.

Carbon steel corrosometer probes were selected to quantify the effect of reduced condensate pressures to atmospheric (100 kPa) and wet steam pressure to sub-atmospheric (13 kPa). For wet steam at this vacuum condition, the temperature at saturation was 50°C. In addition, the fluid velocity of the 13 kPa steam environ-ment was 34 ms<sup>-1</sup>, whilst that of the test at 12 ment was 34 ms<sup>-1</sup>, whilst that of the test at 126 kPa was 0.36ms<sup>-1</sup>. The experiments were conducted in the Broadlands corrosion rig and the Broadlands/ Ohaki geothermal pilot plant condenser 'S-Bend'. The description of the rig and the 'S-Bend', operation conditions and the detailed chemistry of these environments are published elsewhere. (Braithwaite and Lichti, 1979; Soylemezoglu, 1980). The probe exposures were up to 20 days, duration depending on the probes reaching a steady

ENVIRONMENT	CONOENSATE		AERATED CONDENSATE		WET STEAM	
PRESSURE ( kPa)	100	310	100	130	126	13
CORROSION RATE ( µmy 1)	120	190	4400	4350	45	< 2

The short-term exposures of carbon steel corrosometer probes in the above environments gave a rapid and reliable indication of the effects of reduced pressure on corrosivity.

# BROADLANDS WHL BR 32 CORROSION OF BLFED PIPES AND FITTINGS

Well BR 32 is located to the East of the Waikato River in the north-eastern sector of the Broadlands geothermal field, and appears to be on the boundary between hot and cold underground water. The well was drilled to 1100m and solid cased to 465m, with a slotted casing below this level. The downhole water temperature at 465m level is around 100°C, but the surface temperature of hot water drops to 90°C. A flow of 250 lmin<sup>-1</sup> of hot water at 90°C occurs on bleed discharge. The water chemistry down to the 600m depth at 90° to 100°C can be described as a slightly acid sodium bicarbonate water. Below 600m the water becomes increasingly more saline with chloride concentrations of 1050 ppm. After initial discharge the well was left on continuous slow bleed (about 40 lmin<sup>-1</sup>). The water discharged during the bleeding has very little hydrogen sulphide (about 2 ppm), and it comes entirely from the upper zone of sodium bicarbonate water. (Mahon, 1978).

Severe corrosion of the bleed pipes, reducers, joints and tee pieces were reported by the field maintenance staff after about 1 year on bleed, and these components had to be replaced. The form of even, general corrosion or wide, flat bottomed pits to a depth of approx-imately 1.5mm was observed on visual examination (Figure 1). This severe corrosion of the mild steel components appeared to be abnormally high for oxygen-free geothermal fluids, in which mild

steel corrosion rates of less than 100 µmy<sup>-1</sup> would be expected. The rapid corrosion was suspected to be either due to water velocity in the bleed pipes accelerating corrosion, or dissolved oxygen in ground water entering the bore and accelerating corrosion.

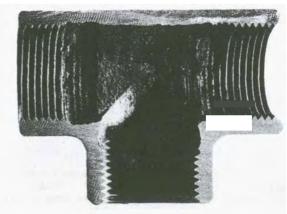


Figure 1: A tee piece removed from Broadlands
BR 32 bleed pipe connections showing
the severity of corrosion.

A carbon steel corrosometer probe was inserted into the well bleed pipe to determine the corrosion rates at various flow discharge rates. Test conditions and results of the corrosion rate determination experiments are given in Table 2.

	EXPERIMENT	(kPa-g)	TEMPERATURE (°C)	pΗ	FLOW RATE	FLOW VELOCITY	CORROSION RATE
	1	69	86	6.78	2500	3 · 0	900
İ	2	172	83	6.29	2100	2 • 5	870
		69	79	6 - 10	600	0.7	

On removal of the bore head after quenching of the bore, visual examination and measurement of the bore casing thickness at accessible locations indicated the absence of severe corrosion, thus eliminating the possibility of oxygen contamination. It was concluded that the velocity of the bore fluid was the main factor controlling the rate of corrosion. Low bleed water velocities were recommended as a method of controlling bleed pipe corrosion.

## WAIRAKEI SIEAM PIPELINES CORROSION - EFFECT OF CONDENSATE VELOCITY

Severe corrosion damage of 760mm (301nch) diameter high pressure (HP) steam transmission lines at Wairakei was first observed in 1977. The occurrance, nature, mechanisms and preventive measures of this corrosion have been studied by numerous workers. (Page 1978; Braithwaite, 1979; Giggenbach, 1979; James, 1980; Stacey, 1980; McAdam, 1980; Thain, 1980). Condensate velocity and turbulence were considered to have a role in the pipeline corrosion mechanisms. A corrosometer monitoring program using condensate from a catchpot of the HP L-line was initiated to investigate the effect of condensate velocity in a small diameter pipe on carbon steel corrosion rates.

One of the two steam traps on the condensate pot at Anchor 4/5 was isolated and condensate was drained through a collection pot, which provided a constant volume of flow. A special rig made out of mild steel steam pipes, with entry points for a corrosometer probe, and condensate inlet and outlet, was then connected to the collection pot. This arrangement allowed the test rig to be operated at HP line pressure of 900 kPa. Condensate flow direction in the rig was parallel to the corrosometer probe measuring element. Different condensate velocities were achieved by changing the size of the pipes around the corrosometer probe, and supplying a constant condensate flow at all times. Condensate velocities of 1.7, 3.4, 6.7, 13.5, 20.6 cms<sup>-1</sup> (maximum) were used during the tests. The circular nature of the test rig and central location of corrosometer probe permitted the Reynolds number to be computed for the velocities used during the tests. Re =  $d.v/\gamma$ , d = diameter of test rig corrected for loss of cross-sectional area due to presence of corrosometer probe, v = the condensate velocity and  $\gamma$  = kinetic viscosity of the condensate at test temperature). Carbon steel corrosion rates were determined at each velocity using corrosometer probes exposed for 20 days.

Figure 2 illustrates the effect of changing condensate velocity on corrosion rate. The results are also plotted against the calculated Reynold's numbers in testing. The corrosion rate in almost stagnant hot condensate was extremely low, but it was found to increase linearly with increasing velocity and turbulence.

This simulated study indicated that actual condensate velocity in the HP lines (~1  $ms^{-1}$ ) and

the highly turbulent flows (Re = 30,000), (McAdam, 1979) had an important role on the rate of the severe corrosion. Hence reducing or limiting the flow of the condensate or inhibiting the corrosive condensate in the IP lines would result in reduced pipeline corrosion rates.

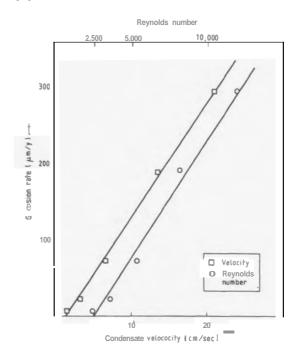


Figure 2: Effect of Wairakei steam condensate velocity and turbulence on corrosion rate of carbon steel.

## WAIRAKEI STEAM PIPELINES - CORROSION INHIBITOR MONITORING

Extensive evaluation of the corrosive conditions within the Wairakei HP pipelines and increased understanding of the corrosion mechanisms resulted in several proposals for the injection of synthetic and natural corrosion inhibitors as a viable means of controlling the observed corrosion. Methods used to monitor the effects of selected inhibitors included corrosometer probes, hydrogen probes, chemical analysis as well as visual examinations and ultrasonic 'D' meter thickness measurements. All of these methods were successful in identifying high metal corrosion rates, but only the corrosometer method proved capable of providing a quantitative instantaneous measure of the effect of particular inhibitors while the pipeline was in operation.

Carbon steel corrosometer probes were inserted into the HP L-line by using a special insertion rig which allows the probe to be placed into the line, whilst under full pressure. One third of the measuring element of the corrosometer probe was exposed to steam flow while the remaining portion was located in condensate. A typical corrosometer probe plot of the corrosion in the

Soylemezoglu et.al.

uninhibited pipeline is shown in Figure 3. An initial high rate of corrosion at 150 µmy<sup>-1</sup> decreased to 50 µmy<sup>-1</sup> after the formation of a protective film in 13 days.

Three types of inhibitors have been used. These were a filming amine (octadecylamine) supplied by Catoleum Ltd., under the brand name of Alfloc 190, a phosphate pH control chemical (tri-sodium phosphate), and bore fluid from the geothermal field itself.

Octadecylamine injections were conducted over a period of five months. Injection levels were set at 1 ppm (part per million by weight of the total flow of steam) and later changed to 0.4, 0.1 and 0.6 during the course of the tests. A typical corrosometer probe result obtained using 1 ppm injection level is illustrated in Figure 3. The initial corrosion rate of 120  $\mu my^{-1}$  decreased to a steady state level of 75  $\mu my^{-1}$ . Different injection levels had no effect on the steady state corrosion rate observed by the corrosometer probe. Chemical analyses of pipeline condensate indicated no significant change in pH, conductivity, ammonia, or dissolved iron concentrations. Visual examination on shutdown of the pipeline revealed little or no evidence of corrosion inhibition. (Stacey and Bacon, 1979). This confirmed the results obtained by corrosometer probes,

Tri-sodium phosphate injections were commenced in an attempt to provide pH control of the condensate. Initial pH was observed to be about

6.5. With a 0.5 kg day 1 injection rate of trisodium phosphate a pH of about 8 was achieved. Corrosometer probe results for two injection periods are illustrated in Figure 3. An initial corrosion rate of 125  $\mu my^{-1}$  decreased to a low value of 10  $\mu my^{-1}$  within 6 days of injection. When the injection was stopped after 10 days, the observed low corrosion rate continued for 2 days and was then followed by a rapid sharp increase in the corrosion rate to 270  $\mu my^{-1}$ . With the recommenced injection of tri-sodium phosphate, the same previous level of 10  $\mu my^{-1}$  was achieved. A section of the L-line used for these tests was then replaced because of excessive previous corrosion. The new section has been protected by continuing additions of tri-sodium phosphate at a rate of 0.5 kg day 1, and a corrosometer probe has again shown a long term steady state rate of less than 10  $\mu my^{-1}$ .

The use of bore fluid was also considered for corrosion inhibiting after a series of chemical analyses along the HP lines revealed an inverse relation between the presence of silica in condensate and pipeline corrosion, (Stacey, Scale samples collected from 1980). within the pipeline showed a similar trend (McAdam, 1980). Silica or other constituents in bore fluid could act as corrosion inhibitors in areas such as bore casings, well head equipment and transmission lines. Bore fluid injection tests have been conducted in HP J-line. Although corrosometer probes are not used for this experiment, a hydrogen collection patch (McAdam, 1980) at the outside of the pipe located opposite an

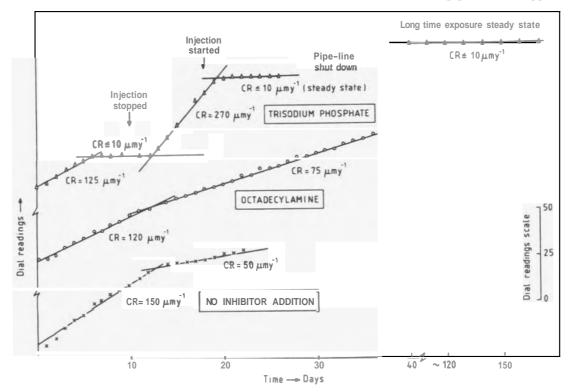


Figure 3: Graphical presentation of Wairakei HP L-line corrosion inhibitor monitoring results.

Soylemezoglu et.al.

active corroding area has produced qualitative results which are similar in trend to those of the L-line tri-sodium phosphate injection, indicating that bore fluid is a natural corrosion inhibitor in this system.

#### CONCLUSION

The cases cited in this report have demonstrated the unique ability of corrosometer probes to provide quantitative assessment of a variety of corrosion problems encountered in geothermal fluids. The corrosometer probe results are available as the experiments progress and changes in corrosivity are readily observed. It is for these reasons that the use of this monitoring technique is firmly established in the New Zealand geothermal power development areas, and it is recognised that it will continue to be a valuable method of corrosion monitoring.

#### REFERENCES

- Braithwaite, W.R. and Lichti, K.A. 1979. Surface corrosion of metals in geothermal fluids at Broadlands, New Zealand. ASIM special technical publication on 'Geothermal Scaling and Corrosion'. (in press)
- Braithwaite, W.R. 1979, Corrosion in the 30 inch steam pipelines at Wairakei geothermal field. ibid., (in press)
- Chen, K.Y. and Morris, J.C., 1970, Oxidation of aqueous sulfide by 02: General characteristics and catalytic influences. Proc. of 5th Int. Water Pollution Res.Conf. III 32/1-32/17.
- Chen, K.Y. and Morris, J.C., 1972, Kinetics of oxidation of aqueous sulfide by 02. Environmental Science and Technology, Vol. 6., 529-537.
- Giggenbach, W.F., 1979, The application of mineral phase diagrams to geothermal. corrosion. Proc. of the N.Z. geothermal workshop, part 1, 215-227.
- James, R. 1980, Supression of steam condensate corrosion at Wairakei geothermal project. Geothermal Energy Vol.8. No.3, p.11.
- iichti, K.A. and Soylemezoglu, S., 1979, Geothermal corrosion monitoring techniques, Proc. of the N.Z. geothermal workshop, part 1, 233-239.
- McAdam, D.G., 1979, Calculation of Reynold's number in the Wairakei HP lines. (Priv.com)
- McAdam, D.G., 1980, General injection of steam lines at Wairakei, DSIR report IPD 86/3.
- MacDonald, D.D., Roberts, B. and Hyne, J., 1978.
  The corrosion of carbon steel by wet
  elemental sulphur. Corrosion Science,
  Vol. 18, 411-25.

- Mahon, W.A.J., 1978, Chemical analysis: Water discharged from and residing in well 32 Broadlands. (Priv. com.)
- Page, G.G., 1978, Corrosion in the 30 inch steam pipelines at the Wairakei geothermal steam field (Unpublished DSIR report)
- Soylemezoglu, S. 1980, Report on corrosion experiments in the Broadlands/Ohaki geothermal pilot plant condenser. DSIR report IPD/TS/10.
- Soylemezoglu, S., and Harper, R., 1980. Oxygen ingress into geothermal steam and its effect on corrosion of mild steel, at Broadlands, New Zealand. (in preparation)
- Stacey, R.E. and Bacon, L., 1979, Report on the injection of Alfloc 190 into L-line, NZED internal memo (Priv.com.)
- Stacey, R.C., 1980, The inspection of the main steam transmission pipes during the 1979 shutdown of the station. NZED internal report, ref. 21/63/33.
- Thain, I.A., 1980, Wairakei The first twenty years, NZED report, Rutherford House, Wellington, N.Z.