Proc. 8th NZ Geothermal Workshop 1986

INHIBITION OF CORROSION BY PARAFFIN AT THE AIR-WATER INTERFACE IN GEOTHERMAL DOWN-HOLE HEAT EXCHANGERS

Ron Swisher[1] and Graham A. Wright[2]

1 Natural Sciences Department, Oregon Institute of Technology,
Klamath Falls, Oregon, USA
2 Chemistry Department, Auckland University, New Zealand

ABSTRACT

Down-hole heat exchangers (DHE's) are commonly used in the utilization of low temperature geothermal resources. The lifetime of DHE's is frequently determined by corrosion failure at the air-water interface. Paraffin or other hydrocarbons are sometimes put down the well to inhibit corrosion and appear to help, although little data is available. Experiments described here show that hydrocarbon floating on the air-water interface prevents formation of a thin aqueous film on the metal above the bulk fluid and that it is this thin film which promotes corrosion. Oxygen access is also critical. Even with the use of paraffin the corrosion rate in the bulk solution remains unacceptably high in the presence of air, whereas corrosion rates drop to low levels without the use of paraffin, provided air is rigorously excluded. Thorough sealing of the well head combined with the use of paraffin should eliminate or greatly reduce corrosion problems at the air-water interface.

INTRODUCTION

Low temperature geothermal resources are being exploited for direct use space heating in many parts of the world. Although these low temperature wells may be pumped, this frequently results in depletion of the hot water aquifer. An alternative method which uses the heat without removing the water is the use of a down-hole heat exchanger (DHE) in the well (Figure 1). These have been used successfully in Klamath Falls, Oregon (USA) and Taupo, New Zealand.

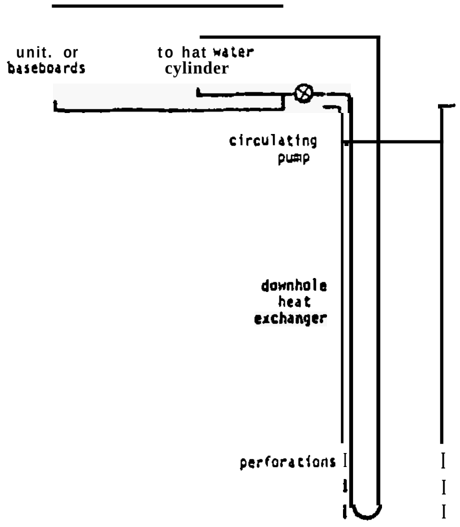

FIGURE 1. Down-Hole Heat Exchanger

The service life of these DHE's is frequently determined by corrosion and the most aggressive corrosion is commonly found at the air-water interface. It is common practice (Freeston. 1986; Lichti, 1985) to put paraffin, motor oil, or other hydrocarbon into the bore where it floats on the top of the air-fluid interface. Although this method is believed to provide protection to the heat exchanger pipe at the interface, there does not appear to be any published data actually confirming that this measure does provide protection.

The experiments described in this report were carried out:

a) to determine whether the paraffin layer does provide protection against corrosion at the air-water interface;
b) to provide quantitative estimates of how much protection is provided; and
c) to test whether the addition of a commercial corrosion inhibitor to the paraffin phase provides any additional protection.

MATERIALS AND METHODS

Metal coupons (25 mm x 125 mm x 2 mm) were made of mild carbon steel and all were from the same original plate. Simulated geothermal fluid was 1.2 mmol/l $NaHCO_3$, 4.3 mmol/l Na_2SO_4, 1.4 mmol/l NaCl, adjusted to pH 8.0. Metal coupons were cleaned after exposure to simulated geothermal fluid with Clarke's solution (2% $SbCl_3$, 5% $SnCl_2$ in concentrated HCl). Weight losses were measured and corrosion rates calculated in micrometers/year by the formula:

$$\text{rate} = w/dAt$$

where w is the loss of the metal mass in time t, A is the surface area exposed to corrosion, d is the density of the metal, and t is the time of exposure to the corrosive medium. Only surface actually exhibiting corrosion was used in these calculations. For partially immersed coupons with no paraffin this was the area of the whole coupon; for coupons partially immersed in fluid with paraffin on top it was the area of metal actually in the simulated geothermal fluid.

Two-liter beakers were each filled with 1.5 liters of simulated geothermal fluid. Paraffin wax or Ondina mineral oil 68 (Shell) was added as needed. Fluid was maintained at 78-80°C in a thermostatically controlled oil bath. Evaporation of fluid from beakers with no paraffin was controlled by placing a watch glass on top of the beaker and keeping the top of the watch glass filled with water. Distilled water was added to the beaker itself as needed to maintain a relatively constant water level (±3 cm).

A commercial corrosion inhibitor. CK 337 (Servo). was added to the paraffin layer at an initial concentration of 1% (v/v) in appropriate beaker. This corrosion inhibitor is an organic alkyl amine with a partition coefficient between hexane and water of 5:1.

RESULTS

Aerobic Corrosion of Partially Immersed Coupons

Initial experiments were carried out with coupons partially immersed (70%) in simulated geothermal fluid. One beaker contained only geothermal fluid, the second had 2.5 cm of paraffin floating on top, and the third had 2.5 cm of paraffin with CK 337 corrosion inhibitor added to the paraffin phase at an initial concentration of 1% (v/v). Coupons were removed at 456 hours and 648 hours of exposure, cleaned with Clarke's solution. dried, weighed and the corrosion rate calculated in micrometers/year. The results are tabulated in Table 1.

TABLE 1

Corrosion rates (micrometers/year) of mild steel coupons partially immersed in aerobic simulated geothermal fluid at 80°C

	456 hr	648 hr
No paraffin	490	500
2.5 cm paraffin	310	300
2.5 cm paraffin + 1% CK 337	210	230

The data in Table 1 indicates that paraffin does indeed reduce the corrosion rate and that the commercial corrosion inhibitor CK 337 lowers the corrosion rate still further. Visual observation of the coupons provided additional information about the nature of the corrosion process. The coupons immersed in simulated geothermal fluid without paraffin had a thick black deposit, a few orange products and white crystals above the air/water interface. There was a thin black film of corrosion products below the water surface. Powder X-ray diffraction and magnetic properties confirmed that the black deposit was magnetite Fe_3O_4. After cleaning with Clarke's solution, several deep corrosion spots were noted on the portion of the coupon above the air/water interface, whereas the portion of the coupon below the interface was evenly corroded with no localized spots more deeply corroded than the rest of the surface. These observations suggest the simulated geothermal fluid forms a thin film on the coupon above the bulk fluid, which allows ready access to oxygen and promotes rapid corrosion. The presence of the white crystals shows that the film is continually evaporating and concentrating the dissolved salts of the geothermal fluid to the saturation level. The presence of this high concentration of salts (particularly chloride) would also promote corrosion.

Coupons partially immersed in fluid with paraffin floating on top of the air-water interface showed no corrosion either on the portion of the coupon in contact with paraffin or on the portion of the coupon above the paraffin which was exposed to air. The corrosion product on the coupon in contact with the simulated geothermal fluid was a black powder similar to that on the immersed portion of coupons in the geothermal fluid without paraffin. It was also noted that there was a thin layer of paraffin on the coupon above the paraffin layer.

A further experiment was carried out to determine if the nature of the hydrocarbon phase made any difference in corrosion protection. The corrosion rate of coupons partially immersed in Ondina mineral oil 68 (melting point = -15°C to -10°C) was compared with coupons partially immersed in paraffin wax (melting point = 55-60°C). There was no difference in the corrosion rates, indicating that the exact nature of the hydrocarbon layer is not critical. However, the paraffin wax with its lower vapor pressure would be likely to last longer and not vaporize away as quickly.

Coupons in the fluid with paraffin containing 1% (v/v) CK 337 were very similar to that with paraffin alone, but the corrosion below the interface was quite localized. Although 95% of the surface appeared virtually without corrosion, several deep localized corrosion spots were noted at the end of 648 hours. If corrosion at these localized spots continued for several more months, complete perforation of the coupon would result. The use of CK 337 does not appear to provide useful protection under the conditions found in geothermal DHE's and it was not investigated any further.

Aerobic Corrosion of Completely Immersed Coupons

Thus paraffin appears to provide protection from corrosion above the air-water interface by preventing formation of a thin film of solution above the interface. The previous experiments provide no information as to whether paraffin provides any corrosion protection below the surface of the liquid or whether the thickness of the paraffin layer has any effect. A second set of experiments were carried out with completely immersed coupons in geothermal fluid, fluid with 0.5 cm paraffin floating on top, and fluid with 5.0 cm of paraffin floating on top. The results are shown in Table 2.

TABLE 2

Corrosion rate (micrometers/year) of mild steel coupons completely immersed in simulated geothermal flujd at 80°C under aerobic conditions

	336 hr	480 hr
No paraffin	270	280
0.5 cm paraffin	270	270
5.0 cm paraffin	270	260

The data in Table 2 shows that the paraffin has no effect on the corrosion rate below the air-water interface. Thus, the paraffin does not act as a thermodynamic or kinetic barrier to oxygen dissolving into the bulk fluid, and the depth of the paraffin layer does not matter. This data is in agreement with published data on the solubility of oxygen in hydrocarbons which indicates that oxygen is approximately twenty times as soluble in hydrocarbons as in water at 80°C (Linke. 1965).

The corrosion rate of the completely immersed coupons (270-300 micrometers/year) is probably partially controlled by mass transport of oxygen to the metal surface. The rate of oxygen transport to the coupon surface is calculated from Fick's diffusion law:

$$\frac{dn}{dt} = \frac{A \times D \times c}{\delta}$$

Using A = 62.5 cm^2, D = 2 x 10^{-5} cm^2, c = 1.0 x 10^{-7} mole/cm^3 and δ = .02 cm. results in an oxygen mass transport rate of 6.3 (10^{-9}) moles/second. The oxygen consumption rate was calculated assuming all the product was magnetite, and resulted in an oxygen consumption rate of 5 (10^{-9}) moles of oxygen per second, which is the same magnitude as the mass transport rate.

The corrosion rates of the partially immersed coupons with no paraffin are actually averages of the corrosion rate above and below the surface. Calculation of the corrosion rate above the surface is possible, knowing the corrosion rate in bulk solution. The result of this calculation indicates that the corrosion rate in the water film above the surface is 830 micrometers/year compared with 300 micrometers/year in the bulk solution. Thus, the corrosion rate above the surface of the liquid is nearly three times the rate below the surface.

Although the use of paraffin at the air-water interface is clearly successful in eliminating corrosion above the interface, the corrosion rate below the surface is still unacceptably high. If oxygen levels can be kept at minimal levels within the well casing, the corrosion rate both below and above the interface should be much lower. The anodic oxidation of iron will not occur without a corresponding cathodic reduction and oxygen is the major. if not only. cathodic reductant in these experimental conditions.

Anaerobic Corrosion of Completely Immersed Coupons

In order to obtain an idea of the relative corrosion rate under fairly strict anaerobic conditions, the experiments described in Table 1 were repeated under anaerobic conditions. This was accomplished by sparging the simulated geothermal fluid for twenty minutes with oxygen-free nitrogen and using beakers sealed at the top with ground glass fittings. After sparging. the coupons were quickly inserted, the gas space above the liquid was filled with nitrogen, the top fittings were sealed, and the beakers placed in the 80°C bath. The results are shown in Table 3.

TABLE 3

Corrosion rate (micrometer/year) of mild steel coupons completely immersed in simulated geothermal fluid at 80°C under anaerobic conditions

	360 hours
Partial (70%) immersion	11
Complete immersion	8

The results show that there is a major reduction in corrosion rate achieved by fairly rigorous exclusion of oxygen. The corrosion rate in the film above the solution can be calculated and is 18 micrometers/year at 360 hours, about 2% of the film corrosion rate when air was available (830 micrometers/year). The corrosion rate in the bulk fluid is reduced from 280-300 micrometers/year in the presence of oxygen to eight micrometers/year when air is excluded.

The corrosion rate in the film above the bulk solution is higher than that below the surface under both aerobic and anaerobic conditions, but the corrosion rate of the film under anaerobic conditions is less than that of the bulk solution with access to air. Geothermal fluid itself is completely anaerobic and, hence, if air is effectively prevented from entering the well head, corrosion rates should be quite low. These experiments emphasize the desirability of having the well casing tightly sealed to prevent ingress of atmospheric oxygen into the well.

CONCLUSIONS

These experiments indicate that paraffin or other hydrocarbons floating on the air-water interface of geothermal wells can dramatically reduce the corrosion rate occurring above the interface. They also indicate that the exact nature of the hydrocarbon is not critical, nor is the depth of the paraffin layer. As long as some hydrocarbon layer is present above the water layer, formation of a thin film above the bulk solution is prevented, and it is this thin water film which promotes rapid corrosion rates. The use of paraffin should not be regarded as a panacea, however, as corrosion rates are still very high if oxygen is present. .The use of paraffin combined with rigorous exclusion of oxygen should produce low corrosion rates of ten micrometers/year or less.

Corrosion failure at the air-water interface in DHE's in geothermal wells has been extremely variable with some wells suffering corrosion failures in a few years, while other wells have lasted 40 years without corrosion failure (Newcombe. 1976). One likely explanation of this phenomenon is not variations in fluid temperature or chemical makeup, but access of oxygen from the air into the geothermal well. Wells with a tight seal at the top of the well casing are less likely to have corrosion failure at the air-water interface than wells with poor seals that admit a slow but continual replenishment of oxygen. The highest corrosion rates will occur if air is actively pumped into the well. This process, air lifting, has actually been used in some non-flowing wells in Rotorua to pump hot water up the well, but the corrosion rates are very high, as has been noted (Wells and Lichti. 1985). Air lifting hot water from geothermal wells over any substantial length of time is likely to produce unacceptably high rates of corrosion failure. A DHE can produce adequate heat with minimal corrosion problems.

The data of these experiments suggest that the use of paraffin in geothermal DHE's combined with rigorous exclusion of oxygen from the interior of the well casing should reduce or eliminate problems of corrosion failure at the air-water interface.

ACKNOWLEDGEMENTS

Ron Swisher would like to thank the Geothermal Institute and the Chemistry Department of Auckland University for their hospitality during a sabbatical 1eave.

REFERENCES

1. Freeston. D.H. (1986), private comunication.
2. Lichti, K. (1985), private communication.
3. Linke, W.F. (1965), Solubilities: Inorganic and Metal-Organic Compounds, 4th ed.. American Chemical Society.
4. Newcombe, J. (1976), "Maintenance Problems and Solutions in Geothermal Well Plumbing". Geo-Heat Utilization Center Quarterly Bulletin, Vol. 1, No. 4, pp. 4-6.
5. Wells, D.B., and Lichti. K. (1985), "A Corrosometer Study of Corrosion in Rotorua Geothermal Fluids , Proceedings of the 7th New Zealand Geothermal Workshop, pp. 91-96.