# CORROSION IN ACIDIC GEOTHERMAL FLOWS WITH HIGH VELOCITY

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**SUMMARY-** Material corrosion tests were done in flowing two-phase fluid of an acidic geothermal well with high velocity in the range of 70 to 100 m/s. The results demonstrated that the effects of the **flow** turbulence on corrosion increased **as** the pH decreased, and **as** the temperature increased, and that the corrosion was further increased due to turbulence in an expanding flow situation. Duplex stainless steels and higher-alloyed materials gave superior performance to conventional stainless steel alloys.

### 1. INTRODUCTION

Geothermal wells have on occasion encountered acidic brines. In the Onikobe geothermal field in Japan (Abe, 1993) some acidic wells have been successfully used for production and some others for re-injection, but the majority have not been developed further for production and have been cemented shut for safety reasons. Similar experience has been reported in other fields (Lichti and Sanada, 1997).

Deep geothermal wells drilled recently also produce discharge water and steam with aggressive chemistries. For example they sampled supersaline and metal rich brine from the bottom of deep well, **WD-1** in the Kakkonda geothermal field in Japan, and confirmed that the borehole fluid contained magmatic substances (Ikeuchi, et al., 1996).

The utilization of such deep and acidic wells is increasing because of the need to increase the capacity of existing geothermal production systems. However, corrosion properties of the more aggressive fluids have not been fully defined, and there is a need to collect and evaluate materials results and experience relevant to the selection of materials for deep geothermal developments, as outlined in the objectives of the Materials Subtask of the IEA Deep Geothermal Program (Sanada, et al., 1997).

Reviews on materials performance in a range of geothermal fluids and guidelines for selecting materials have been published (DeBerry et al., 1978, Ellis, et al., 1981, Ikeuchi, et al., 1982). Data on corrosion resistance of titanium alloys, and Ni-Cr-Fe alloys in hyper-saline brines of the Salton Sea Geothermal Resource have also been

reported (Pye, et al., 1989, Moeller and Cron, 1997).

More recent work in Japan and the Philippines has concentrated on the corrosion properties and materials performance in acidic and aggressive fluids, (Abe, 1993, Maturgo, 1996, Sanada et al., 1997). The effect of fluid velocity on corrosion in flowing acidic two-phase fluid has been addressed by Sanada, et al. (1995) and Ikeuchi et al. (1997). The feasibility of acid fluid utilization has been asserted and the factors affecting the cost and risks have been defined (Lichti and Sanada, 1997). In addition, the chemical conditions occurring throughout a geothermal wellbore were calculated to discuss materials selection and corrosion control options, using thermodynamic models and a wellbore simulator (Lichti, et al., 1998).

This paper expands results discussed in a previous paper (Sanada, et al, 1995) on corrosion in an acidic two-phase flow with high velocity.

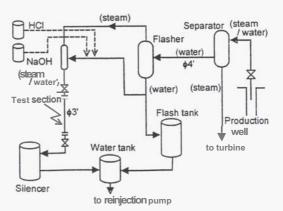


Figure 1. Schematic of two-phase flow apparatus for materials corrosion test at Onikobe geothermal field

Tablel. Typical chemical composition of Onikibe geothermal acidic brine.

рН	Cl <sup>-</sup>	SO <sub>4</sub>	Na <sup>†</sup>	Ca <sup>2+</sup>	Fe <sup>2+</sup>	Mg <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	SiO <sub>2</sub>	CO <sub>2</sub>	$H_2S$
3.2	4830	33	1733	580	167	149	0.11	11.4	. 92.1	28	trace

The aim of the work is to develop models of corrosion **as** a function of turbulence, pH value and temperature.

### 2. EXPERIMENT

Corrosion tests in flowing two-phase fluid were done at the Onikobe geothermal field using the apparatus shown schematically in Figure 1 (Ikeuchi et al., 1982). Hot water from a production well separator (35 t/h, at a temperature of 144°C, and the pH value 3.2) was available for the work (see Table 1).

The separated water was further flashed and all the steam directed into a mixing tank where hot water was remixed with the steam using a needle valve to give two-phase flow. The test apparatus shown in Figure 1 gave fluid velocities of 70 to 100 m/s and temperatures of 100 to 137°C. The injected water was treated with hydrochloric acid or sodium hydrooxide to control the pH in the range of 2 to 4.5. The flow quality defined as the ratio of steam mass flow rate to total mass flow rate, ranged from 0.4 to 0.6.

Eight types of materials were examined, including conventional steels, high-alloy stainless steels, nickel-base alloys and titanium alloys (Sanada, et al, 1995). Coupon type specimens (30 x 60 x t mm) were placed in parallel with the axis of the 3 inch pipe of the test section and were exposed to the two-phase flow for 23 to 72 hours.

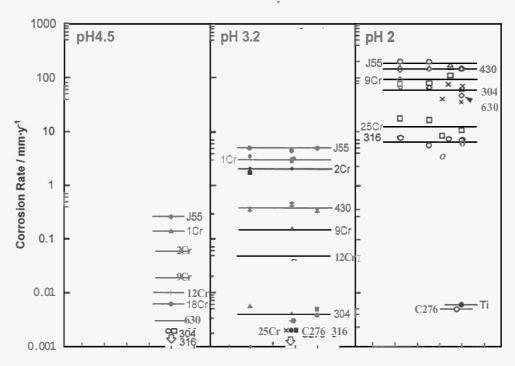
### 3. RESULTS AND DISCUSSION

In liquid dominated geothermal systems hot water which enters a geothermal well at a deep feed point rises to the surface and flashes to two-phase flow due to the pressure drop. Geothermal production well flows are therefore typically two-phase or multi-phase depending on the gas content.

Geothermal wells producing near neutral pH fluids are known to form iron-based corrosion product films or scales of silica and calcite or mixtures of these which slow corrosion to low acceptable levels (see for example Lichti et al (1997)). This study concentrates on the effect of lower pH on corrosion rate.

### 3.1 Effect of Flow Rate (70~100 m/s)

Figures 2 to 7 give results for corrosion in a twophase geothermal fluid flow where the water pH is acidic and describe the effects of the flow turbulence, pH and temperature on corrosion.



Two-phase Flow Velocity / m-s1

Figure 2. Corrosion rate in two-phase flow as a function of velocity. Temperature:  $100 \sim 110^{\circ}$ C, Quality x:  $0.4 \sim 0.6$ .

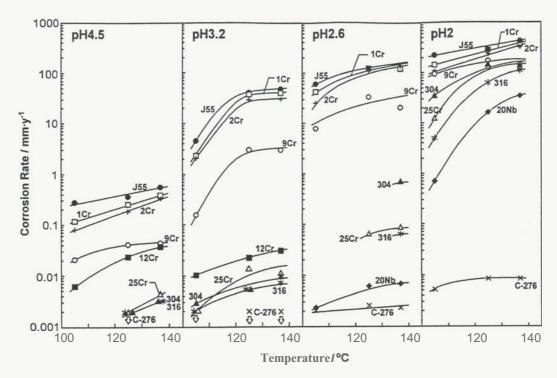


Figure 4. Effect of temperature on corrosion rate in two-phase fluid test. v: 70~100m/s, Quality: 0.4–0.6

was little difference in the corrosion rates observed under turbulent conditions in comparison to the autoclave test. That is, the corrosion of all the tested materials was independent of turbulence.

At pH 3.2 the corrosion of carbon and low-alloy steels was strongly dependent on the turbulence, being more severely corroded in the two-phase flow. Austenitic and duplex stainless steels and

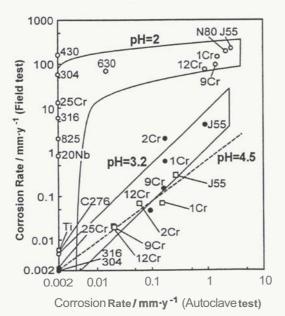
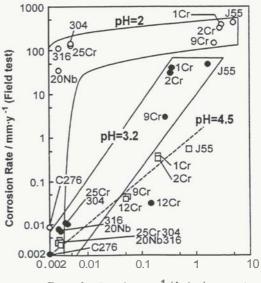


Figure 5(a). Comparison of corrosion rates in flowing two-phase fluid tests with static autoclave tests. <u>Temperature: 100 - 110°C</u>, velocity in field test: 70 - 100m/s. O: PH2, ●: pH3.2, □: pH4.5.

higher-alloyed materials did not show dependence on the turbulence, and low corrosion rates were observed.

At pH 2, almost all the metals and alloys experienced increased corrosion rates due to flow turbulence. For instance, 316 and duplex stainless steels had the rates of about 10 mm/y as they did not exhibit passivity effects. Only Hastelloy C276 and Titanium alloy showed



Corrosion Rate I mm·y -1 (Autoclavetest)

Figure 5(b). Comparison of corrosion rates in flowing two-phase fluid tests with static autoclave tests. <a href="Temperature: 137°C">Temperature: 137°C</a>, velocity in field test: 70 - 100 m/s. <a href="Dispersion-10">O: pH2</a>, <a href="Dispersion-10">D: pH3.2</a>, <a href="Dispersion-10">D: pH4.5</a>.

In this experimental work flow velocity, pH and temperature, were fixed at each test run, but flow quality (steam/steam+water ratio) which might affect corrosion (Nanjo et al., 1991), could not be controlled independently of flow velocity. For example, the quality varied from **0.4** to **0.6** at flow velocities of 70 to **100m/s** respectively.

Figure 2 shows corrosion rates of the materials exposed to two-phase flow at velocities of 70 to 100m/s for a temperature range of 100 to 110°C, for pH values of 4.5, 3.2 and 2. Firstly, it should be noted that for the conditions of the tests (70 to 100 m/s) the corrosion rate is independent of flow rate.

In pH 4.5 flow, carbon steel corroded at a rate of 0.3 mm/y which might be unacceptable in some applications, but many of the low alloy steels, stainless steels and high-alloy materials gave acceptable performance.

In pH 3.2 flow, carbon and low-alloy steels had unacceptable corrosion rates of several **mm/y**. Stainless steels having more than 9% Cr gave acceptable performance while austenitic and duplex stainless steel and Hastelloy C276 performed well at rates less than 0.01mm/y.

In pH 2 flow, carbon and low-alloy steels, 18 Cr ferritic and 304 austenitic stainless steels corroded at rates of more than 50 mm/y. 316 and duplex stainless steels also readily corroded at about 10 mm/y while Hastelloy C276 and Titanium alloy performed well.

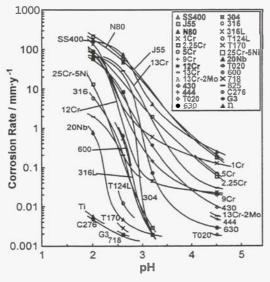


Figure 3. Corrosion data for two-phase flow with velocity of 70 to 100 m/s and temperature of 100 to 110°C. (Sanada et al., 1995)

### 3.2 Effect of pH (4.5 –2)

Figure 3 summarizes the pH effects on the corrosion at 100-110°C for tests done at pH 4.5, 3.2, 2.6 and 2. Carbon and low-alloy steels have unacceptable corrosion rates at pH values less than 4.5, but low-alloy steels having more than 9% Cr gave an acceptable performance down to pH 3.2. The ferritic stainless steel, 430, having 18% Cr gave a good performance pH 4.5 but was corroded at greater than 0.2 mm/y at pH 3.2. Austenitic and duplex stainless steels were severely damaged at pH less than 3.2. High-alloy stainless steels and Nickel-base alloys performed well at pH 2.6 but were severely damaged at pH 2. Hastelloy C276 and Titanium alloy gave acceptable corrosion rates even at pH 2.

# 3.3 Effect of Temperature (105 ~137°C) and pH (4.5 –2)

Figure 4 shows corrosion rate as a function of temperature in the range of 105 to 137°C. 105°C represents the mean value between 100 and 110°C for results described in sections 3.1 and 3.2 above.

Figure 4 shows that corrosion rates are significantly dependent on temperature and the effect is greatest for alloys which have intermediate performance, however pH remains the dominant effect.

The corrosion rate results show a strong dependence on alloy content at pH 4.5, especially for low alloy materials. The performance of all alloys tested at 105°C was acceptable but the low alloy material gave a marginal performance at 0.6 mm/year at the higher temperature. dependence on alloy content decreased for the low alloy materials, as the pH decreased to 2.6. The low alloy materials all have a similar high corrosion rate while the high alloy materials begin to show a strong dependence on alloy content. At pH 2 only Hastelloy C-276 shows a low, acceptable corrosion rate although performance of the high-nickel stainless steel 20 Nb is acceptable at the lower temperature tested.

## 3.4 Comparison of Flow Corrosion with Static Corrosion

Figures **5** (a) and (b) give a comparison of corrosion data obtained in a two-phase **flow** against static autoclave test results. The figures show how corrosion is increased due to the effect of turbulence.

Figure 5(a), which is revised **from** a previous paper (Sanada et al, 1995), shows the comparison of results obtained at 105°C. At pH **4.5** there

acceptable corrosion rates at pH 2, and the turbulence effects on their corrosion rates were negligible.

Figure 5(b) shows the comparison of flowing vs static results at 137°C. Corrosion of all materials was, again independent of the flow turbulence in pH 4.5 flow. In pH 3.2 and pH 2 flow, the corrosion rate increase due to the turbulence was more severe than at 105°C, however Hastelloy C276 and Titanium alloy again gave similar acceptable corrosion rate results.

### 3.5 Corrosion in Expanding Flow

The above results demonstrate how flow turbulence can increase corrosion rates. This effect is of particular concern in geothermal wells where the casing size changes. In this section the results obtained under expanding flow conditions are presented and discussed.

Firstly, an expanding flow system was installed in a high speed, two-phase flow apparatus at Tohoku-NIRI (Nanjo, et al., 1992). The expanding flow section consisted of a rectangular pipe A of 20 mm x 50 mm in cross section followed by a rectangular pipe B of 50 mm x 50 mm. The flow conditions in the pipe A were; velocity 73 m/s, temperature 134°C, pH 3, steam quality 0.2. Obtained results for J55 and SS400 after 5 hours exposure test are shown in Figure 6. The corrosion rate was at a maximum within 100 to 120 mm downstream from the expansion point.

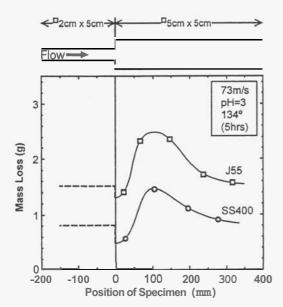


Figure 6. Corrosion mass loss downstream in expanding flow through the rectangular pipe of a laboratory apparatus.

Secondly, corrosion in an actual geothermal fluid was examined using an expanding pipe section attached to the apparatus in Figure 1. The pipes, which branched off from the main 4 inch pipe for the cyclone-separated hot water, consisted of a 4 inch dia. pipe and a following 8 inch dia. pipe. The flow condition was as follows; in 4 inch pipe, flow rate 35 t/h, temperature 144°C, velocity 1 m/s, steam quality 0, and in 8 inch pipe, temperature 109°C, velocity 30 d s, steam quality 0.04. Coupon specimens were placed in the center of the 8 inch pipe at 125 mm downstream from the end of the 4 inch pipe.

Results obtained from the field trials are shown in Figure 7 for a range of alloys. The carbon and low-alloy steel corrosion rates observed in the 8 inch pipe were 1.5 to 2 times as much as that in the 4 inch pipe. Alloy 630 and 304 stainless steels corroded at ten times the rate observed in the 4 inch pipe. The duplex stainless steel (25Cr-5Ni) and Hastelloy C276 had a similar performance.

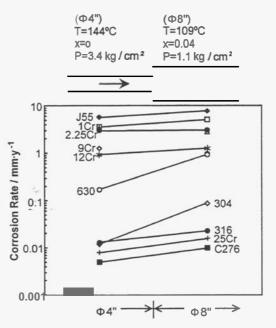


Figure 7. Corrosion acceleration in expanding flow. pH: 3.2.

### 3.6 Effect of Wall Shear Stress

Corrosion in flowing fluid is related to the mechanical and chemical behavior of a thin boundary layer at or near the material wall surface. Firstly a protective passive film can often be formed on the material wall surface. The shear stress on the wall surface induced by flowing fluid can prevent the film formation or may destroy films which have formed. Secondly a change in concentration of corrosive substances occurs in a layer near the wall, eg a change in pH.

Recently an analytical model of the behavior has been developed (Ikeuchi, et al., 1997), to describe the effect of wall shear stress in a producing well, and further work is continuing. The results will give an improved understanding of flow assisted-corrosion and will be of value in interpreting corrosion results obtained in the experiment described here for downhole conditions.

### 4. CONCLUSIONS

Material corrosion tests were done in flowing, two-phase fluid of an acidic geothermal well with high velocity in the range of 70 to 100 m/s. The results demonstrated the effects of the flow turbulence, pH value, temperature and material composition on corrosion.

- (1) Corrosion rates were independent of flow rate variation in the range  $70-100 \,\text{m/s}$ .
- Corrosion rates were strongly dependent on pH.
- (3) The influence of pH was most pronounced at the higher temperatures.
- (4) The effects of the flow turbulence on corrosion were significant in comparison to static autoclave tests for  $pH \le 3.2$ .
- (5) The effects of the flow turbulence on corrosion were the greatest at the lower pH, and at the higher temperature.
- (6) The corrosion was increased due to additional turbulence under expanding flow conditions; carbon and low-alloy steels corroded several times faster, 630 stainless steel was corroded ten times faster, duplex stainless steel (25Cr-5Ni) and Hastelloy C276 gave a similar performance in the expanding flow at pH 3.2.
- (7) Understanding of the effect of wall shear stress may provide a mechanism to apply the results of this work to downhole conditions.

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