The material corrosion test on pH adjustment condition by acid at geothermal field in Japan

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ABSTRACT

We carried out a pH adjustment test at the acidic hot water line at Kakkonda geothermal field in November 2017. And we compared the results with the material corrosion prediction equation using a Cr equivalent amount, as proposed by Kurata et al. (1992).

In the field test, the temperature was 145 ° C, the initial base case pH was 5.15, and then the pH was adjusted to 3 and 4 with sulfuric acid or hydrochloric acid. The test duration was 5 hours and K-55, TN80SS, TN80Cr13 and TN110Cr13S were used for the corrosion test. After the corrosion test, antimony and arsenic scales were attached to the test material and the corrosion rate was calculated after removing the scale.

According to the prediction equation, the corrosion rate at pH 4 was about 2 times that at pH 5.15 and 3 to 4 times that value at pH 3. But the measured value at pH 4 was about 1.2 to 1.6 times that at pH 5.15. And at pH 3, carbon steel and low alloy steel showed a high corrosion rate, but stainless steel showed lower values. The corrosion rate in the case of the addition of hydrochloric acid was higher than for sulfuric acid.

1. INTRODUCTION

In the case of potentially high acidic condition, geothermal power plant operators may have to replace surface facilities occasionally or use expensive materials for the surface facilities and borehole. Therefore, material corrosion behavior has been investigated by many researchers.

From 1974 to 2002, AIST-Tohoku branch carried out a survey of erosion and corrosion in geothermal power plant pipelines and laboratory tests were carried out. (Kurata et al., 1995, Sanada et al., 1995, Sanada et al., 1997, Sanada et al., 2000). The test data show that the corrosion rate depends on temperature, pH and the chemical composition of the exposed material. For indexing of the corrosion rate by material chemical composition, the idea of a Cr equivalent was introduced (Kurata et al., 1992).

After big earthquake at 2011, New Energy and Industrial Technology Development Organization (NEDO) started the project "Research and Development of Geothermal Power Generation Technology" at FY2013. And GERD, AIST and TenarisNKKTubes proposed a project on "Development of Geothermal Power Plant Risk Assessment System (Prediction, Measure and Management for Scale and Corrosion)".

The project aimed to develop geochemical and flow simulation models to estimate erosion and corrosion of material and scaling at surface facilities and borehole. And the first feasibility studies used one day field tests that were carried out at Kakkonda and Yanaizu-Nishiyama geothermal power plants in FY 2015 (Yanagisawa et al, 2016). The tests included 1-day, 4-day, 15-day tests with acidic two-phase fluid conditions at Yanaizu-Nishiyama geothermal power plant (Yanagisawa et al., 2017).

Then we carried out a pH adjustment test, using the single phase hot water line at Kakkonda geothermal field, by injecting sulfuric acid or hydrochloric acid. We also estimated the effect of pH adjustment by measuring the corrosion rate and applying SEM-EDS analysis.

2. ON SITE CORROSION TEST AT KAKKONDA GEOTHERMAL FIELD

2.1 Test Site

The pH adjustment corrosion test was carried out at the Kakkonda geothermal field. This geothermal field is located in the western area of Iwate Prefecture, in the north part of Japan. The main geothermal reservoir exists from 1,500 to 2,600 meters depth. The geothermal power plant at Kakkonda has 80MW capacity and was started in 1978.

At Kakkonda geothermal field, the test loop system was connected to a single-phase line that was connected directly to the acidic reinjection line. The geochemistry of the fluid sample was collected in the line on 10 November 2017, during the early stage short term corrosion test. The geochemistry of the fluid from this well was as follows; pH about 4.9, T-SiO2 1,100mg/l, Na 977mg/l, Cl 1,610mg/l, Ca 5.4mg/l, K 162mg/l, Total CO2 3.5 mg/l, H2S 0.5 mg/l, SO4 44mg/l and T-Fe 0.11mg/l.

2.2 Test loop system

In this project, a test loop design developed by Quest Integrity NZL Ltd (Quest Integrity) for GERD was used for the demonstration test. The corrosion test loop was designed for use in either single phase or two-phase systems directly at the geothermal fields.

In this test system, we try to measure the corrosion rate using the Corrosometer probes, LPR probes and cylinder coupon samples. For cylinder coupon samples, we prepared four types materials, K-55 (carbon steel), TN80SS (low alloy steel), TN80Cr13 and TN110Cr13S (Stainless steel) as shown in Figure 1. The coupon size is 30 mm length and 8 mm diameter. And the Cr equivalent of these materials are shown in Table 1.

Figure 1: Cylinder coupon sample of the corrosion test loop system.

Table 1: The Cr equivalent of several materials on pH adjustment test.

Material	Creq
K55(Carbon steel)	−6.9
TN80SS(Low metal alloy)	−1.7
TN80Cr13 (Stainless steel)	10.0
TN110Cr13S (Stainless steel)	15.5

The size of the cylinder coupon samples was about 30mm length with 8 mm outer diameter and 5.2 mm inner diameter. The set of nine samples and flow direction of hot fluid is shown in Figure 4 for the test loop system. Due to the use of two phase fluid, the loop system was set vertical at a height of about two meters. The temperature, pressure and the flow rate of test loop was controlled by the open ratio of valves at the entrance and exit of the test loop.

2.3 Test program and observation

Table 2 shows a list of the material corrosion tests. The first two tests were done using original acid fluid and the duration of tests were 20 days and 5 hours exposure under a pH of about 5.15 and 140 °C two phase conditions. After these tests, we controlled the pH using H2SO4 or HCl solutions and the target pHs were 4 and 3. The low pH tests were limited by the facilities available for neutralization and so the duration of the pH controlled tests was 5 hours.

After on-site testing, we observed the surface of the cylinder coupon samples and detected the composition of elements by SEM-EDS.

Table 2: The list of material corrosion test

	Test1	Test2	Test3	Test4	Test5
Test Date	2017/10/25～2017/11/14	2017/11/15	2017/11/16	2017/11/15	2017/11/15
Duration time(hour)	480	5	5	5	5
Temperature(℃)	150	142	141	149	150
Pressure(MPa)	0.47	0.46	0.44	0.54	0.54
Flow (L/min)	7.5	2.9	2.9	5.4	5.4
pH	5.5	5.15	4.05	3.05	3
Addition			H2SO4	H2SO4	HCl

After SEM-EDS observation, we removed the scale by washing using alternately DiHydrogen Ammonium Citrate (DiHAC) and NaOH and we measured the weight after and the final clean to calculate the corrosion scale thickness and corrosion rate for each test material. Cathodic protection was used during the cleaning stages to prevent additional corrosion of the base metals.

3. RESULTS AND DISCUSSION

3.1 Measured corrosion rates

From the weight change of the cylinder coupons, we calculated the corrosion rate (mm/year) from test 2 to test 5 and the results are shown in Table 3.

The relative corrosion rate of several pH adjustment test of carbon steel (K-55) compare with the base case of pH 5.15, used in test 2 were as follows; 1.6 times at pH 4 of H_2SO_4 solution, 3.2 times at pH 3 of H_2SO_4 and 5 times at pH 3 of HCl. And the corrosion rate of low metal alloy (TN80SS) shows a similar value as carbon steel.

The corrosion rate of stainless steel (TN80Cr13) are lower than for carbon steel. The relative corrosion rate for several pH adjustment test compare with the base case of pH 5.15 were lower than for carbon steel as follows; 1.2 times at pH 4 of H_2SO_4 solution, 2.4 times at pH 3 of H_2SO_4 and 2.8 times at pH 3 of HCl. And the corrosion rate of TN110Cr13 (Stainless Steel) shows similar value as TN80Cr13.

Table 3: The results of corrosion rate of several materials on pH adjustment test.

	Temperature (℃)	pH	Test Material	Measured C.R (mm/y)
Test2	142	5.15	K-55	2.14
			TN80SS	1.92
			TN80Cr13	0.69
			TN110Cr13S	0.64
Test3 (H2SO4)	141	4.05	K-55	3.51
			TN80SS	3.29
			TN80Cr13	0.86
			TN110Cr13S	0.75
Test4 (H2SO4)	149	3.05	K-55	6.94
			TN80SS	9.12
			TN80Cr13	1.64
			TN110Cr13S	1.13
Test5 (HCl)	150	3	K-55	10.62
			TN80SS	11.21
			TN80Cr13	1.96
			TN110Cr13S	0.93

3.2 Estimated corrosion rates using Cr equivalent

Table 4 shows the estimated corrosion rate and measured corrosion rate at pH adjustment tests for pH 3 and 4 using the addition of H2SO4 or HCl.

The corrosion rate at pH 4, based on the prediction equation, was about 2 times that at pH 5.15 and 3 to 4 times that value at pH 3. But the measured value at pH 4 was about 1.2 to 1.6 times that at pH 5.15. At pH 3, carbon steel and low alloy steel showed values close to the predicted values, but stainless steel showed lower values. The corrosion rate in the case of the addition of hydrochloric acid was higher than for sulfuric acid.

The ratio of measured corrosion rate and estimated corrosion rate is shown in Table 4. The ratio, M/E, varies from 2.3 to 7.4. One of the reasons for this high ratio is the short duration time for the test, of about 5 hours.

Table 4: Comparison of the corrosion rate between estimation using data base and on-site testing.

	Temperature (℃)	pH	Test Material	Measured C.R (mm/y)	Estimated C.R (mm/y)	M/E
Test2	142	5.15	K-55	2.14	0.66	3.24
			TN80SS	1.92	0.48	4.00
			TN80Cr13	0.69	0.157	4.39
			TN110Cr13S	0.64	0.105	6.10
Test3 (H2SO4)	141	4.05	K-55	3.51	1.402	2.50
			TN80SS	3.29	1.02	3.23
			TN80Cr13	0.86	0.33	2.61
			TN110Cr13S	0.75	0.22	3.41
Test4 (H2SO4)	149	3.05	K-55	6.94	3.01	2.31
			TN80SS	9.12	2.18	4.18
			TN80Cr13	1.64	0.716	2.29
			TN110Cr13S	1.13	0.477	2.37
Test5 (HCl)	150	3	K-55	10.62	2.34	4.54
			TN80SS	11.21	1.51	7.42
			TN80Cr13	1.96	0.55	3.56
			TN110Cr13S	0.93	0.35	2.66

3.3 SEM-EDS analysis

The colors of the sample surface and elements detected by SEM-EDS are shown in Figure 2. In this figure, we show the results for a high corrosion –resistant material, Duplex 2507, for comparison with the test material. A cross-section image for carbon steel is shown in Figure 3.

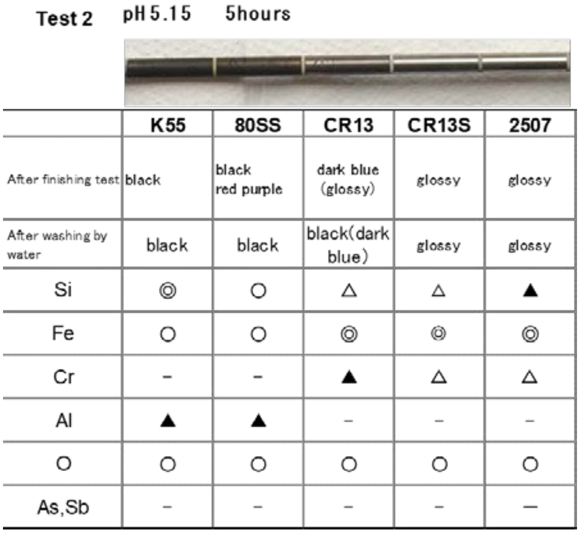
In this case, the color condition after testing are as follows;

・K55, TN80SS: Black (TN80SS is a little bit red)

・TN80Cr13: a small change in color

・TN110Cr13S, SAF2507: Glossy (not change color)

The silica is detected as a scale on the test material with Fe as shown in Figure 3. The volume of Si (scale) is decreasing in TN80Cr13, TN110Cr13S and Duplex and there are Fe、Cr、Mo on the surface as base metals.



Test 2 pH5.15 5hours

	K55	80SS	CR13	CR13S	2507
After finishing test	black	black red purple	dark blue (glossy)	glossy	glossy
After washing by water	black	black	black(dark blue)	glossy	glossy
Si	◎	○	△	△	▲
Fe	○	○	◎	◎	◎
Cr	-	-	▲	△	△
Al	▲	▲	-	-	-
O	○	○	○	○	○
As,Sb	-	-	-	-	—

Figure 2: The color and detected elements by SEM-EDS of several materials of Test 2.

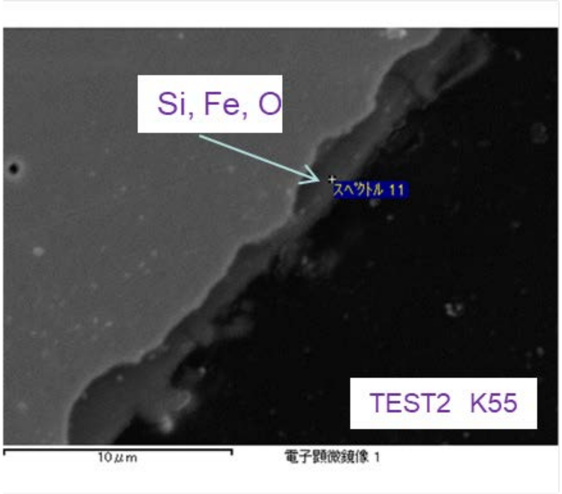


Figure 3: The cross-section image of carbon steel after Test 2.

Next, we show the results of Test4, with pH3 controlled by H_2SO_4. The colors and elements of surface are shown in Figure 4 and the cross-section image in Figure 5.

In this case, the color condition after testing are as follows;

・K55, TN80SS: Black,

・TN80Cr13: Dark Blue, TN110Cr13S: Light yellow

・SAF2507: Glossy

And the surface elements of carbon steel (K-55) and low metal alloy (TN80SS) are follows;

・As and Sb is higher than Si

・We can find Fe on the surface. That is almost same amount with O.

・We found As on the surface of coupon.

・White part in the SEM figure is As, as shown in Figure 5. This covered much of the surface.

In the case of TN80Cr13, TN110Cr13and SAF2507, we found mostly base metals. The amount of Si is low and we could not find As and Sb.

On the other hand, in the case of Test 5, with pH 3 controlled by HCl, the Sb content of the surface of K-55 is higher than the content of As. In the case of TN80SS, there is same trend between As and Sb as for Test 4.

Test 4 pH3.0 **H2SO4** 5hours

	K55	80SS	CR13	CR13S	2507
After finishing test	Black (Glossy)	light black (glossy)	dark blue	light yellow (green)	Glossy
After washing by water	Black (Glossy)	light black (glossy)	dark blue	light yellow (green)	Glossy
Si	△	△	trace	trace	trace
Fe	◎	○	◎	◎	◎
Cr	–	–	△	△	△
O	◎	◎	◎	◎	◎
Ni, Mo	–	–	–	Ni△	△
As, Sb	○As>Sb	○As>Sb	–	–	–
S	trace	–	–	–	–

Figure 4: The color and detected elements by SEM-EDS of several materials of Test 4.

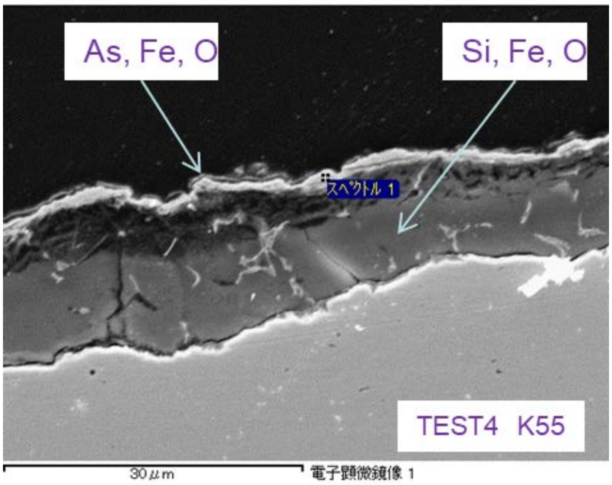


Figure 5: The cross-section image of carbon steel after Test 4.

It has been previously established that deposit layers of As and Sb on Carbon Steel can result in accelerated under deposit localized corrosion (Lichti et al, 2016). This was observed in pressure vessel trials with coated coupons where the deposit layers cannot be repaired by additional deposition. A metallurgical cross section of the deposited heavy metal scale on a carbon steel sample exposed in the corrosion test loop at low pH condition as shown in Figure 5.

The figure shows a continuously adhered deposit layer broken on occasion by shallow localized corrosion pits. The figure suggests that the low pH fluids continuously deposited heavy metals and thereby controlled the corrosion rate by blocking the corrosive fluid from attacking the metal surface. It is proposed that the lowering of pH accelerated the localized galvanic corrosion effect giving under-deposit corrosion and higher corrosion rates.

4. CONCLUSION

At Kakkonda geothermal field, the pH adjustment corrosion tests with sulfuric acid or hydrochloric acid were carried out. The test duration was 5 hours and K-55, TN80SS, TN80Cr13 and TN110Cr13S were used as test samples.

In the case of high corrosive material, carbon steel and low metal alloy, the measured corrosion rate compared with the base case of pH 5.15 for Test 2 were as follows; 1.6 times at pH 4 with H2SO4 solution, 3.2 times at pH 3 with H2SO4 and 5 times at pH 3 with HCl. Heavy metal, As and Sb, also precipitated on the test material.

In contrast, in the case of stainless steel, the measured corrosion rate compared with the base case of pH 5.15 at Test 2 were as follows; 1.2 times at pH 4 with H2SO4 solution, 2.4 times at pH 3 with H2SO4 and 2.8 times at pH 3 with HCl. These are lower than carbon steel rates of corrosion and no heavy metal was precipitated.

The heavy metal precipitation affected the corrosion rate at lower pH conditions.

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