THE MATERIAL CORROSION TEST USING LOOP SYSTEM UNDER ACIDIC CONDITION AT GEOTHERMAL FIELD IN JAPAN

Norio Yanagisawa[1],Yoshio Masuda[2], Kazumi Osato[3], Masatake Sato[3], Kaichiro Kasai[3],
Koji Sakura[4], Toshihiko Fukui[4], Michihiro Akahori[5] and Keith Lichti[6]

[1] Renewable Energy Research Center, AIST, 2-2-9, Machiikedai, Koriyama, Fukushima 963-0298, Japan

[2] Research Institute for Chemical Process Techinology, AIST, 4-2-1, Nigatake, Sendai, Miyagi 983-8552, Japan

[3] Geothermal Energy Research & Development Co., Ltd.(GERD),1-22-4, Shinkawa, Cyuo-ku, Tokyo 104-0033, Japan

[4] TenarisNKKTubes, 1-10, Minamiwatarida, Kawasaki, Kanagawa, 210-0855, Japan

[5]Okuaizu Geothermal Co., Ltd.,1034-1,Kaminotaira,Sunakohara,Yanaizu, Fukushima, 969-7321,Japan

[6]Quest Integrity NZ Ltd., 69 Gracefield Road, Lower Hutt, Lower Hutt 5045, New Zealand

n-yanagisawa@aist.go.jp

Keywords: *Material corrosion, acidic fluid, HCl, small loop test, two-phase condition*

ABSTRACT

We carried out the material corrosion in acidic fluid under two-phase conditions at Yanaizu-Nishiyama, Okuaizu geothermal power plant using small loop test system in February of 2017.

We carried out several corrosion tests, 1 day, 4 days and 15 days testing under about pH 3.8 and 165 degreeC condition which gave us low corrosion rates. And we adjusted pH using H_2SO_4 or HCl to pH 3 and carried out one day test to determine the effect of a lower pH.

The loop-test system was about 2 meter high and 3 meter wide. The test coupons used were about 30 mm long and 8mm outer diameter and 5.2 mm inner diameter tube shape and inserted over a central rod with 8 test coupons in the loop system. A carbon steel, a low alloy steel and a 13% Cr stainless steel were tested in the loop system.

The corrosion rate was calculated from weight change of the coupons. This was compared to an estimation system for corrosion rate using previous corrosion data developed by AIST from 1980 to 2003 based on temperature, pH and metal chemical composition.

The corrosion rate of the pH 3.8 condition of carbon steel was from 0.1 to 0.3 mm/year and was lower than estimated using previous data which predicted 1.5 to 1.8 mm/year. The low alloy steel and the 13% Cr stainless steel showed the same trend as carbon steel. Two of the reasons for the observed differences were that the two-phase tests had a lower liquid/vapor ratio in the two-phase line than tested previously and the second reason was especially relevant on carbon steel, namely the precipitation of uniform layers of As and Sb metal was found.

In the pH control tests at pH 3 adjustment done using HCl acid showed a different trend. The corrosion rate of carbon steel was about 27 mm/year, and about 10 times larger than the estimated rate. The addition of HCl was proposed to have accelerated the galvanic corrosion under the deposited heavy metal.

1. INTRODUCTION

In the case of corrosive condition, geothermal power plant operators may have to replace surface facilities occasionally or use expensive materials for the surface facilities and borehole. Then, we need the solution for the problem of scaling and corrosion at surface facilities and borehole to reduce the plant risk of geothermal development. Then, New Energy and Industrial Technology Development Organization (NEDO) started the project “Research and Development of Geothermal Power Generation Technology” at FY2013.

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 proposal was accepted at FY2014 for a 4 year project. The concept of the project is shown in Figure 1 (Yanagisawa et al., 2016).

The project aimed to develop geochemical and flow simulation models to estimate erosion and corrosion of material and scaling at surface facilities and borehole. The results were intended to be compared to the existing database of material corrosion and scaling developed by previous research.

To check the results of new and historical simulations, field test and monitoring was undertaken. 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, Yanagisawa et al., 2017). From the results of these tesst, it was decided to check the long term behavior of materials (up to 15 days exposure) and to consider the influence of pH adjustment for control of corrosion.

Then we carried out one month of material corrosion testing in acidic two-phase fluid conditions at Yanaizu-Nishiyama geothermal power plant using a small bore loop test system in February of 2017.

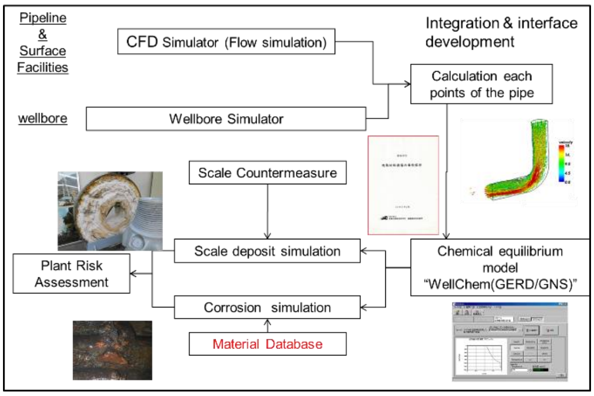


Figure 1: The concept of the project of Plant risk assessment.

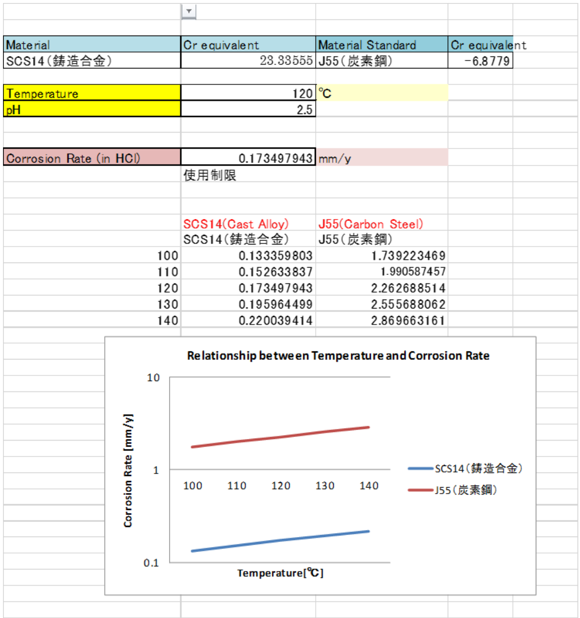
We carried out several corrosion tests, 1 day, 4 days and 15 days under about pH 3.8 and 165 degreeC condition using fluid produced by the test well. And we controlled pH using H_2SO_4 or HCl to pH 3 and carried out one day tests.

In this paper we show the estimation of corrosion rate under acidic conditions using previous test data and compare with the field test results.

2. ESTIMATION OF CORROSION RATE

From 1974 to 2002, AIST-Tohoku branch carried out the survey of erosion and corrosion in geothermal power plant pipelines and several laboratory tests were carried out. From these tests, the relationship between corrosion rate and corrosion environment for different alloy elements was summarized (Kurata et al., 1995, Sanada et al., 1995, Sanada et al., 1997, Sanada et al., 2000).

From the results of test data, the corrosion rate depsnds on temperature, pH and the chemical composition of the exposed material. For indexing of corrosion rate by material chemical composition, the idea of Cr equivalent was introduced (Kurata et al., 1992).



Material	Cr equivalent	Material Standard	Cr equivalent
SCS14（鋳造合金）	23.33555	J55（炭素鋼）	-6.8779
Temperature	120	℃	
pH	2.5		
Corrosion Rate (in HCl)	0.173497943	mm/y	
	使用制限		
	SCS14(Cast Alloy)	J55(Carbon Steel)	
	SCS14（鋳造合金）	J55（炭素鋼）	
100	0.133359803	1.739223469	
110	0.152633837	1.990587457	
120	0.173497943	2.262688514	
130	0.195964499	2.555688062	
140	0.220039414	2.869663161	

Figure 2: sample of the corrosion rate calculation system using Microsoft excel file

The ratio of the contribution to corrosion resistance of Cr and elements other than Cr was deduced from the experimental data. The Cr equivalent was calculated as follows:

$$Creq = Cr - 13.73\ C + 1.598\ Si - 0.433\ Mn + 27.28\ P - 51.12\ S + 0.237\ Ni + 0.712\ Mo - 1.060\ Cu\ (wt\%). \quad (1)$$

And the material corrosion rate (C.R, mm/year) was calculated using temperature, pH and Cr equivalent as follows:

$$\log (C.R) = 6.696 - 1930\ (1/T) - 0.622\ (pH) - 0.085\ (Creq) \quad (2)$$

An example list of calculation results of Creq is shown in Table 1. And based on the above equations, we make the calculations using a Microsoft excel spreadsheet. An example of this system is shown in Figure 2.

The corrosion rate is calculated by firstly selecting the material and indicating the Cr equivalent and secondly by inputing the temperature and pH. And in this example, the estimated corrosion rate at 100 to 140 degree C is shown and a comparison is made for the corrosion rate a selected casing alloy and carbon steel.

3. ON SITE CORROSION TEST AT GEOTHERMAL FIELD

3.1 Test Site

The long term corrosion testing using acidic fluid, was done at the Yanaizu-Nishiyama geothermal field. This geothermal field is located in the western area of Fukushima Prefecture, in the north part of Japan. The main geothermal reservoir exists from 1,500 to 2,600 meter depth. The geothermal power plant of Yanaizu-Nishiyama has 65MW capacity was started 1995. And the EGS field test for water injection superheated region carried out by JOGMEC from 2013.

At Yanaizu-Nishiyama geothermal field, the test loop system was connected to a two-phase line connected directly to the production well 33P. The geochemistry of fluid sample was collected at the wellhead on 6 February 2017, during the early stage short term corrosion testing. The geochemistry of fluid from this well was follows; pH about 3.8, T-SiO_2 599mg/l, Na 5,770mg/l, Cl 10,900mg/l, Ca 581mg/l, K 1,210mg/l, Total CO_2 18 mg/l, H_2S 18 mg/l, SO_4 41mg/l and T-Fe 4.9mg/l. Gas concentrations in mmol/100mole H_2O were CO_2 708, H_2S 28.4 and NH_3 0.12.

3.2 Test loop system

In this project, a Quest Integrity NZL Ltd (Quest Integrity) GERD developed test loop the design was used for the demonstration testing（Osato et al., 2017）. The corrosion test loop was designed for use in either single phase or two-phase systems directly at the geothermal fields. The, GERD constructed test loop is as shown in Figure 3. The loop system has three test points, the electrical resistance Corrosometer (Rohrback-Cosasco system) was set at TEST Point 1, the LPR (Linear Polarisation Resistance) probe (Rohrback-Cosasco system) was set at TEST Point 2 and the several cylinder coupons were set at TEST Point 3 in Figure 3.

Table 1: The chemical composition of materials and Cr equivalent

	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Creq
K55（Carbon Steel）	0.45	0.24	0.96	0.022	0.025				0.01	-6.8779
TN80SS(Low Metal Alloy)	0.26	0.25	0.5	0.015	0.003	0.05	1.03	0.5		-1.73311
TN80Cr13(Stainless steel)	0.25	0.25	0.5	0.015	0.002	0.15	12.9	0		9.99301
TN110Cr13S(Stainless steel)	0.015	0.2	0.2	0.015	0.001	6	12.3	2	0.01	15.54173

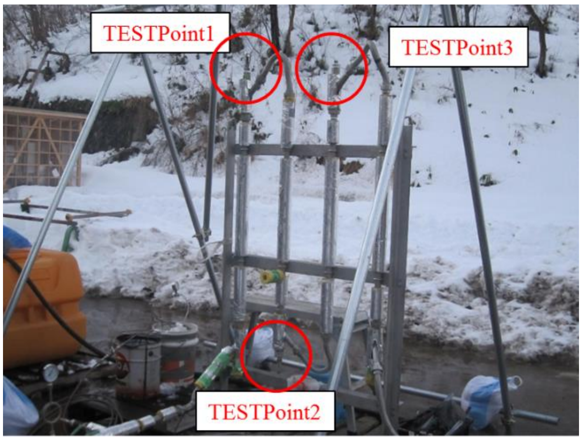


Figure 3: Corrosion test loop system at Yanaizu-Nishiyama geothermal field

Figure 4: Cylinder coupon sample of the corrosion test loop system.

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 materials, K-55 (carbon steel), TN80SS (low alloy steel), TN80Cr13 and TN110Cr13S (Stainless steel) and the chemical composition of materials and Cr equivalent are shown in Table 1.

The size of cylinder coupon samples was about 30mm length with 8 mm outer diameter and 5.2 mm inner diameter and the set of nine samples and flow direction of hot fluid is shown in Figure 4 for the test loop system. Due to two phase fluid, the loop system was set vertical about two meter height. And 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.

3.3 Test program and observation

Table 2 shows the list of material corrosion tests. The first three tests were done using flow directly from well 33P, the original acid fluid and the duration of tests were 1 day, 4 days and 15 days exposure under about pH 3.8 and 165 degreeC two phase conditions. After these tests, we controlled pH using H_2SO_4 or HCl solution and the target pH was 3.

Due to using H_2SO_4 or HCl solution to the test solution was required to be neutralized before discharge to the injection pool. The low pH tests were limited by the facilities available for neutralization and so the pH control tests were less than 1 day (24 hours), especially the HCl test duration was limited 0.3 day (8 hours).

After on-site testing, the weight difference of cylinder coupon samples at TEST Point3 was determined after removasl of all deposits and corrosion products. Scales including amorphous silica and heavy metal require differing cleaning methods and so prior to clening the scales present were chemically analysed.

Figure 5 shows the spectrum of surface deposits present on Carbon Steel by SEM-EDS. The spectrum shows the existence of As and Sb precipitation on the analysed test sample. These deposit metals were present on Carbon Steel but also on TN80SS (low alloy steel), TN80Cr13 (stainless steel) and TN110Cr13S (Stainless steel), namely As and Sb . 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.

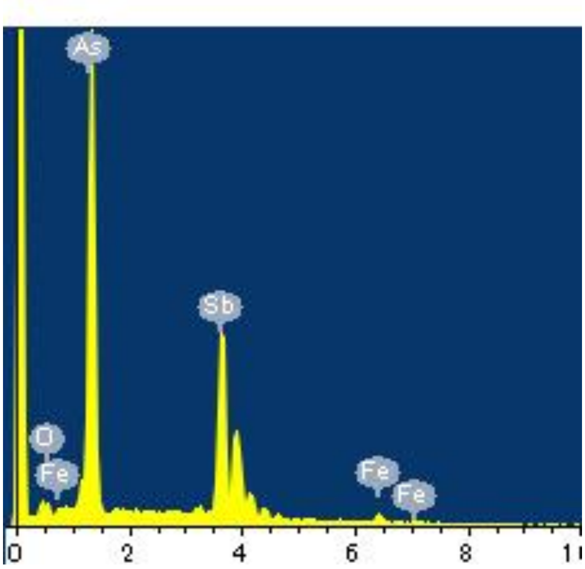


Figure 5: The spectrum of SEM-EDS. As and Sb exists on Carbon Steel (K-55) Cylinder coupon sample before NaOH and DiHAC Cleaning

Table 2: The list of material corrosion test

	Units	Test 1	Test 2	Test 3	Test 5	Test 7
Fluid		33P Original	33P Original	33P Original	pH3.0 by H2SO4	pH3.0 by HCl
Time Start		2017/2/2 10:45	2017/2/3 12:10	2017/2/7 14:35	2017/2/25 11:20	2017/2/27 10:25
Time End		2017/2/3 10:30	2017/2/7 12:00	2017/2/22 14:50	2017/2/26 8:00	2017/2/27 16:30
Duration	day	1.0	4.0	15.0	0.9	0.3
Well Head Pressure	MPaG	0.75	0.76	0.76	0.76	0.76
Inlet Temperature	deg.C	171.3-172.1	168.4-169.1	170.7-173.5	172.2-173.2	170.6-170.2
Inlet Pressure	MPaG	0.74-0.74	0.71-0.73	0.74-0.76	0.76-0.76	0.76-0.76
Outlet Temperature	deg.C	168.2-168.5	160.5-160.6	165.9-170.0	171.9-173.1	168.8-168.6
Flow Rate	L/min	4.5	4.8	4.6	4.6	4.6
pH		3.74-3.72	3.85-3.89	3.69-3.86	3.00-3.58	3.05-3.03

3.4 Measured corrosion rates

From the weight change of cylinder coupons, we calculated the corrosion rate (mm/year) and the results are shown in Table 3. The measured corrosion rates decreased with duration as shown in Figure 6. These rates decrease as a linear extrapolation method was used while parabolic or logarithmic kinetics may be occurring.

Table 3: The results of corrosion rate of several material on the test, 1,4 and 15 days.

	Duration (day)	pH	Inlet Tempreture (Degree C)	Outlet Temperature (Degree C)	Test Material	Measured C.R (mm/y)
Test1	1	3.74–3.72	171.3–172.1	168.2–168.5	K-55	0.33
					TN80SS	0.43
					TN80Cr13	0.19
					TN110Cr13	0.032
Test2	4	3.85–3.89	168.4–169.1	160.5–160.6	K-55	0.102
					TN80SS	0.115
					TN80Cr13	0.046
					TN110Cr13	0.016
Test3	15	3.69–3.86	170.7–173.5	165.9–170.0	K-55	0.11
					TN80SS	0.08
					TN80Cr13	0.02
					TN110Cr13	0.005

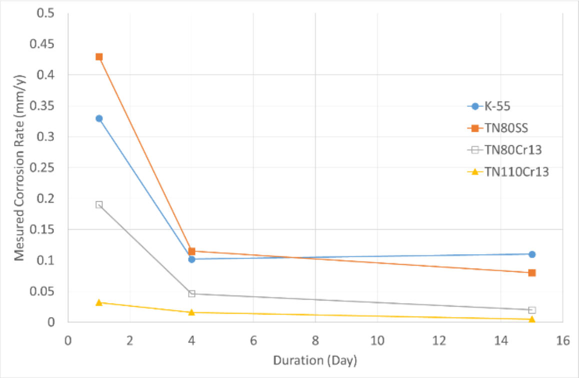


Figure 6: The change of average corrosion rate dependance on test duration.

The corrosion rate when pH was adjusted using H_2SO_4 and HCl solution are shown in Table 4. The corrosion rate of Carbon Steel at H_2SO_4 solution was about 3 times higher than for Test1 and the rate at HCl solution was about 10 times higher than for Test 1. The corrosion rates of K-55 and TN80SS with HCl solution were much higher than those obtained with H_2SO_4 solution. But the corrosion rate of TN80Cr13 (stainless steel) and TN110Cr13S (Stainless steel) with H_2SO_4 addition were similar tothose obtained with HCl addition.

Table 4: The results of corrosion rate of several materials on pH adjustment test.

	Duration (day)	pH	Inlet Tempreture (Degree C)	Outlet Temperature (Degree C)	Test Material	Measured C.R (mm/y)
Test5 (H2SO4)	0.9	3.00–3.58	172.2–173.2	171.9–173.1	K-55	1.19
					TN80SS	1.19
					TN80Cr13	5.41
					TN110Cr13	0.238
Test7 (HCl)	0.3	3.05–3.03	170.6–170.2	168.8–168.6	K-55	27.64
					TN80SS	58.41
					TN80Cr13	4.89
					TN110Cr13	0.134

4. COMPARE THE CORROSION RATE BETWEEN ESTIMATION USING DATA BASE AND ON-SITE TEST

Using the corrosion rate calculator of the excel file system shown in Figure 2, we estimated the corrosion rate of K-55 carbon steel, TN80SS, TN80Cr13 and TN110Cr13S under pH 3.8 at 170 degree C at 1, 4 and 15 days test in Table 5.

The corrosion rate of carbon steel shows from 0.1 to 0.3 mm/year, lower than estimated using previous data at 1.5 to 1.8 mm/year. The other steels show the same trend as carbon steel. One of the reason of low corrosion rate than estimation was thought to be the lower liquid/vapor ratio in the two-phase line. From the ratio of Measured Corrosion rate/Estimated corrosion rate, the ratio of liquid/vapor was estimated to be about 0.05 to 0.3.

Table 5: Comparison of the corrosion rate between estimation using data base and on-site testing.

	Duration (day)	Test Material	Estimated C.R (mm/y)	Measured C.R (mm/y)
Test1	1	K-55	1.83	0.33
		TN80SS	1.18	0.43
		TN80Cr13	0.43	0.19
		TN110Cr13	0.27	0.032
Test2	4	K-55	1.59	0.102
		TN80SS	1.04	0.115
		TN80Cr13	0.37	0.046
		TN110Cr13	0.23	0.016
Test3	15	K-55	1.78	0.11
		TN80SS	1.15	0.08
		TN80Cr13	0.42	0.02
		TN110Cr13	0.26	0.005

Table 6 shows the estimated corrosion rate and measured corrosion rate at pH adjustment tests for pH 3 using H_2SO_4 and HCl additions. For the TN110Cr13 (Stainless Steel) the estimated corrosion rate was about 2 to 3 times higher than the measured corrosion rate. However the TN80Cr13 measured corrosion rate was about 9 times higher than the estimated corrosion rate. This result is opposite from the case of the TN110Cr13 where a lower corrosion rate result was obtained for both H_2SO_4 and HCl additions compared to estimated values.

The K-55 (carbon Steel) and TN80SS (Low Alloy Steel) had markedly different results for H_2SO_4 addition compared toHCl addition. In the case of H_2SO_4 addition, the estimated corrosion rates are slightly higher than the measured corrosion rates for both alloys. But in the case of HCl addition, the measured corrosion rate was more than 10 times higher than the estimated corrosion rate.

The additional acidity accelerated the metal corrosion rates for the Carbon and Low Alloy steels only when acidified by HCl. A similar result was seen for the TN80Cr13 (stainless steel) but not for the TN110Cr13 (stainless steel). The addition of HCl acidity to the bulk solution is believed to have accelerated the galvanic corrosion of the Carbon steel and low alloy steel and to a lesser extend the TN80Cr13 alloy.

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 pH 3.8 test (Test2 for 4 days) is shown in Figure 7. The figure shows a continuous adherent deposit layer broken on occasion with shallow localized corrosion pits. The figure suggests that the pH 3.8 fluids continuously deposited heavy metal and thereby controlled the corrosion rate by blocking the corrosive fluid from the metal surface. It is proposed that the lowering of pH by HCl and to a lesser extend H_2SO_4, accelerated the localized galvanic corrosion effect giving under deposit corrosion and higher corrosion rates. These effects are continuing to be investigated.

Table 6: Comparison of the corrosion rate between estimation using data base and on-site pH adjustment tests.

	Duration (day)	Test Material	Estimated C.R (mm/y)	Measured C.R (mm/y)
Test5 (H2SO4)	0.9	K-55	2.51	1.19
		TN80SS	1.62	1.19
		TN80Cr13	0.61	5.41
		TN110Cr13	0.37	0.238
Test7 (HCl)	0.3	K-55	2.79	27.64
		TN80SS	1.81	58.41
		TN80Cr13	0.66	4.89
		TN110Cr13	0.42	0.134

Figure 7: Metallurgical cross section (prepared at a 45° angle) of heavy metal deposited layer on carbon steel sample exposed at pH 3.8 after 4 days in Test2.

5. SUMMARY

The corrosion ratescalculated from weight change of coupons exposed to two-phase acidic fluids from well 33P were compared to a corrosion rate estimation system developed using previous corrosion data by AIST from 1980 to 2003 and temperature, pH and metal chemical composition.

The corrosion rate for produced pH 3.8 fluids for carbon steel were from 0.1 to 0.3 mm/year and lower than estimated using previous data which predicted 1.5 to 1.8 mm/year. The low alloy steel tested showed same trend as carbon steel. One of the reasons proposed for these differences was the low liquid/vapor ratio in the two-phase line and we have considered the influence of this ratio on each tested steel as a means of improving the prediction. And especially on carbon steel, the precipitation of As and Sb metal is found.

However pH adjustment too pH 3 using HCl showed a different trend. The corrosion rate of carbon steel increased to about 27 mm/year being 10 times higher than the estimated rate. The addition of HCl acid to the bulk solution was proposed to accelerate galvanic corrosion under deposited heavy metal scales rich in As and Sb.

ACKNOWLEDGEMENTS

We express our thanks to Oku-Aizu geothermal Co. Ltd. for the support of on-site corrosion test at Yanaidu-Nishiyama geothermal plant. And this research project is supported by New Energy and Industrial Technology Development Organization (NEDO).

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