Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Corrosion Testing of Casing Steels in Acidic Two-Phase Production Fluid and the Field Testing at Yanaizu-Nishiyama Geothermal Field, Japan

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

[1] Advanced Industrial Science and Technology (AIST), Central 7, 1-1-1, Higashi,Tsukuba, Ibaraki 305-8567 Japan

[2]Geothermal Energy Research & Development Co., Ltd.(GERD), Shinkawa-1 Chome, Chuo-ku, Tokyo 104-0033, Japan

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

[4]Quest Integrity NZL Limited, PO Box 38096, Lower Hutt, New Zealand

Keywords: material corrosion rate, two-phase fluid, acidic fluid, pH, Cr equivalent, carbon steel

ABSTRACT

The material corrosion test in acidic fluid and two-phase condition was carried out at Yanaizu-Nishiyama geothermal field. The test was carried out using a 30 mm size test piece of carbon steel, low metal alloy and stainless steel settled in the small loop flow system. The test condition was pH 3.8, 165˚C and 4.5L/min flow rate condition. To estimate the corrosion rate in the two-phase line, an estimation formula including Cr equivalent of material was used (Kurata et al., 1992) as follows;

$\text{Log (C.R)} = 6.696 - 1930\ (1/T) - 0.622\ (\text{pH}) - 0.085\ (\text{Creq})$.

The estimated corrosion rate of carbon steel at pH 3.8 and 165˚C was calculated about 1.6 mm/year. On the other hand, the experimental field data was from 0.1 to 0.3 mm/year and lower than estimated rate. The corrosion rate of other steels had a similar trend as carbon steel. Autoclave test using hot water single phase on the same pH and temperature, the corrosion rate was a similar value as the estimated rate. Then, the reason for the lower corrosion rate at field test was considered as the lower water/vapor ratio in two-phase line and the precipitation of As and Sb metal, especially on carbon steel in lower pH conditions.

1. INTRODUCTION

After the nuclear power plant accident with the Great East Japan Earthquake of 2011, the additional renewal energy source development including geothermal energy was accelerated. To accelerate the geothermal development, the government decided to introduce Feed-in Tariff (FIT), permitted to survey the geothermal potential inside national park near volcanic area and restarted to support the research and development of geothermal energy via the Japan Oil, Gas and Metals National Corporation (JOGMEC) and the New Energy and Industrial Technology Development Organization (NEDO). Especially, NEDO started the project “Research and Development of Geothermal Power Generation Technology” in FY2013 to support the research and development for surface facilities, including binary system, scale and corrosion, environmental monitoring system, etc.

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

The reason for the proposal the project is as follows;

1) The survey of erosion and corrosion in the geothermal power plant system, including the surface facilities and borehole was carried out mainly at AIST-Tohoku branch from 1974 to 2002 supported by New Sunshine Project of METI. In this survey, several laboratory and field 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). However, after FY2002, the corrosion survey was interrupted due to no budget and the corrosion researcher retired. It was needed to rebuild the corrosion database from the report of New Sunshine Project and the estimation formula of corrosion rate using Cr equivalent of test materials.

2) Based on a questionnaire (NEDO, 1992) for geothermal development companies, the ratio of the number of wells with acid hydrothermal water of pH 5 or less was 13.3% in a developed geothermal area. The more potential area near volcanic region, the acidic fluid will increase due to volcanic gas. The development of countermeasure technology for utilizing acidic hydrothermal water resources is considered an essential technology for promoting geothermal resource utilization in the future.

3) Instead of the previous corrosion test system with large pipelines and long-term tests, it was proposed for the small loop corrosion test system (Osato et al., 2017, Yanagisawa et al., 2017). Using this system continuing measuring corrosion rate, the duration of corrosion tests will become shorter in smaller areas. It was attempted to use several geothermal fields in acidic fluid and estimation corrosion behavior in shorter time including two-phase flow conditions.

During this project, 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 tests, 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. The testing was 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.

This paper shows the results of corrosion rate under acidic and two-phase conditions and compares with the estimation corrosion rate using Cr equivalent. Discussing the difference of the corrosion rate between two-phase condition and single-phase condition in autoclave corrosion test.

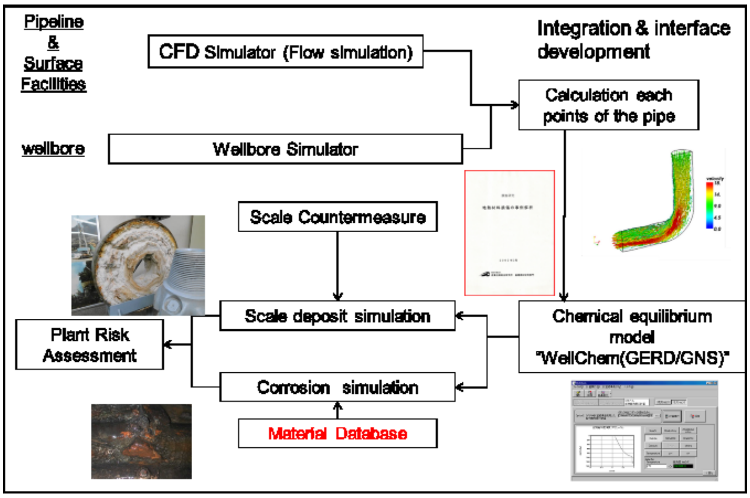


Figure 1: The concept of the project of Plant risk assessment.

2. ESTIMATION OF CORROSION RATE USING CR EQUIVALENT

From 1974 to 2002, the 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 depends 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).

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

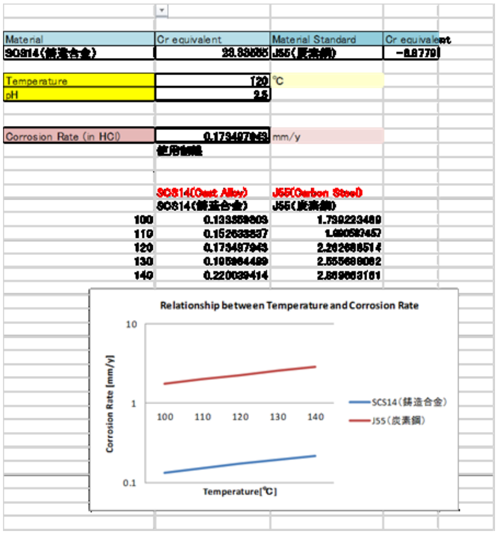
$$Creq = Cr - 13.73\ C + 1.598\ Si - 0.433\ Mn + 27.28\ P - 51.12\ S + 0.237\ Ni + 0.712\ Mo - 1.060\ Cu\ (wt\%). \quad (1)$$

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, the calculations were done 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 inputting the temperature and pH. 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.



Material	Cr equivalent	Material Standard	Cr equivalent
SCS14(鋳造合金)	23.33655	J55(炭素鋼)	-0.8779

Temperature 120 °C

pH 2.5

Corrosion Rate (in HCl) 0.173497943 mm/y

使用鋼種

	SCS14(Cast Alloy) SCS14(鋳造合金)	J55(Carbon Steel) J55(炭素鋼)
100	0.133359603	1.739223489
110	0.152633537	1.990587457
120	0.173497943	2.262686514
130	0.195964489	2.555698082
140	0.220039414	2.869663161

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

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

3. CORROSION TEST PROCEDURE

3.1 On-site corrosion test of two-phase condition

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 30MW capacity.

At Yanaizu-Nishiyama geothermal field, the test loop system was connected to a two-phase line connected directly to the one of production well, as shown in Figure 3. The test started on February 7 2017. The condition of two-phase flow was as follows; wellhead temperature was 170°C, vapor flow was 21.4 ton/h, liquid flow was 15.5 ton/h, vapor/liquid ratio was 0.58, pH was 3.8 (at room temperature), and Cl concentration was 9,650 mg/l. The detail of geochemistry is shown in Table 2.

Table 2: The geochemical composition of test fluid, pH was measured at room temperature.

pH	SiO2	Na	Cl	Ca	K	SO4	Fe	As	Sb
3.8	570	5060	9650	493	1030	40	5	9.9	0.4
									(mg/l)

In this test system, it was attempted 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 meters height. The temperature, pressure and flow rate of test loop was controlled by the open ratio of valves at the entrance and exit of the test loop.

Three tests were carried out at different duration. These tests durations were one day, 4days and 15 days.

After on-site testing, the weight difference of cylinder coupon samples at TEST Point3 was determined after the removal of all deposits and corrosion products. Scales including amorphous silica and heavy metals such as Sb and As require differing cleaning methods, and so before cleaning the scales present, they were chemically analyzed.

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 analyzed test sample. The absence of S from SEM-EDS data suggests the coating material includes something like Fe_3Sb_2 and Fe_3As_2. 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 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.

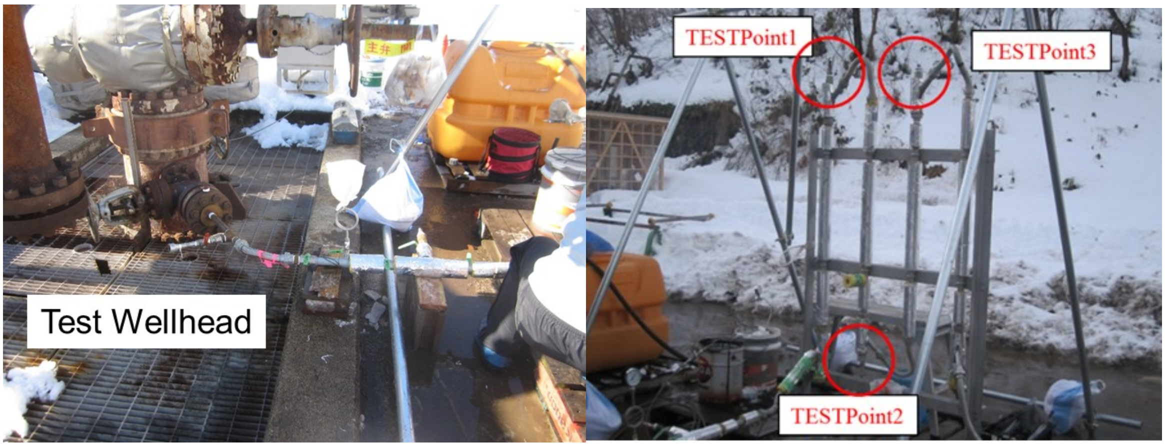


Figure 3: Corrosion test loop system at Yanaizu-Nishiyama geothermal field

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

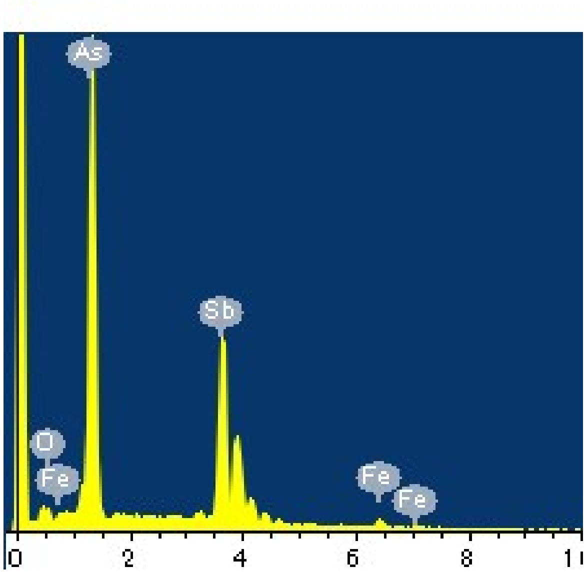


Figure 5: The spectrum of SEM-EDS. As and Sb exists on Carbon Steel (K-55) Cylinder coupon sample before NaOH and DiHAC Cleaning

3.2 Laboratory corrosion test of single-phase condition

To estimate the influence of flow condition, we conducted a laboratory test where the conditions of temperature and pH were equal to the test at the Yanaizu-Nishiyama geothermal field. Also, since the geothermal environment contains heavy metal elements such as As and Sb. The experiment was also conducted to examine the influence.

The test duration was 1 day, 3 days and 7 days under 170°C, pH 3.8 and Cl concentration was 10,000 mg/l. Two materials were used for this test. The Cr equivalent of test materials was same as TN80SS (-1.7) and TN80Cr13 (10.0).

The test piece was a 20 mm × 30 mm strip test piece with a thickness of 5 mm, and the entire surface was polished with # 800 emery paper, degreased with an organic solvent, and the weight before the test was measured to test. The test piece was placed in a Teflon mesh bag and hung on a Teflon coated suspending jig in order to support crevices as much as possible in order to prevent crevice corrosion. The test solution was 6 liters, and the test piece was placed in the liquid phase.

After the gas replacement with nitrogen gas in the preliminary degassing container for more than two hours, the test pieces were set in the autoclave. Next, the test solution was introduced from the preliminary degassing container into the autoclave and the gas substitution by nitrogen gas and added the H_2S gas until the partial pressure 0.02 MPa. The pH equilibrium adjusted with acetic acid to keep at 3.8. After 170 °C test, the corrosion products were removed and the corrosion rate was calculated.

4. RESULTS

4.1 On-site corrosion test of two-phase condition

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

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

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 reasons for the low corrosion rate than estimation was thought to be the lower liquid/vapor ratio in the two-phase line. The ratio of measured corrosion rate/estimated corrosion rate was calculated to be about 0.02 to 0.4 in Table 3.

Table 3. The results of the corrosion rate of several materials on the test, 1,4 and 15 days, and comparison of the corrosion rate between estimation using database and on-site testing.

	Duration (day)	pH	Inlet Tempreture (Degree C)	Outlet Temperature (Degree C)	Test Material	Measured C.R (mm/y)	Estimated C.R (mm/y)	Ratio of M/E
Test1	1	3.74-3.72	171.3-172.1	168.2-168.5	K-55	0.33	1.83	0.18
					TN80SS	0.43	1.18	0.36
					TN80Cr13	0.19	0.43	0.44
					TN110Cr13S	0.032	0.27	0.12
Test2	4	3.85-3.89	168.4-169.1	160.5-160.6	K-55	0.102	1.59	0.06
					TN80SS	0.115	1.04	0.11
					TN80Cr13	0.046	0.37	0.12
					TN110Cr13S	0.016	0.23	0.07
Test3	15	3.69-3.86	170.7-173.5	165.9-170.0	K-55	0.11	1.78	0.06
					TN80SS	0.08	1.15	0.07
					TN80Cr13	0.02	0.42	0.05
					TN110Cr13S	0.005	0.26	0.02

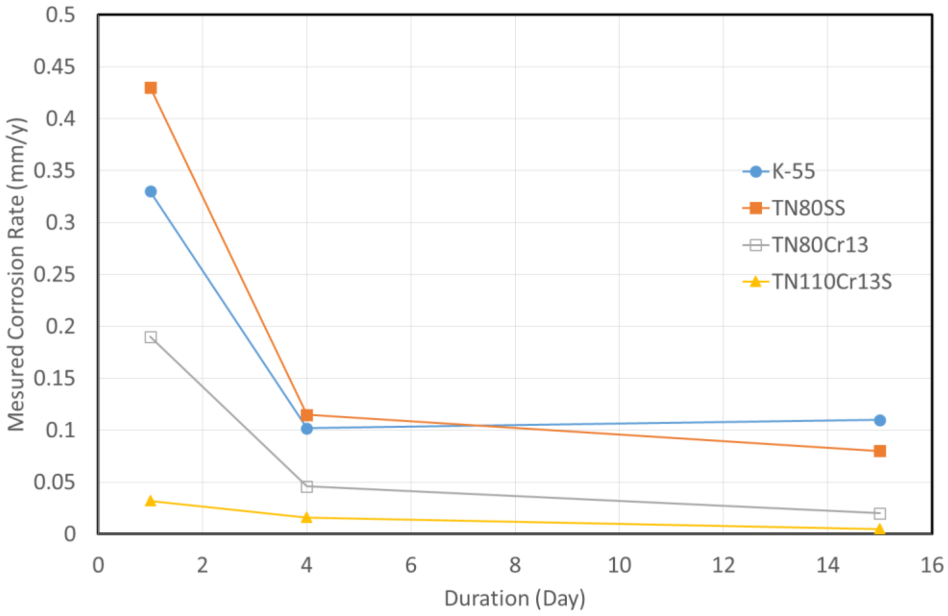


Figure 6: The change in average corrosion rate dependence on test duration.

4.2 Laboratory corrosion test of single-phase condition

Table 4 shows the measured corrosion rate after the autoclave test and the estimated corrosion rate using Cr equivalent of each sample and the ratio of measured corrosion rate/estimated corrosion rate. According to table 3, the average corrosion rate decreases with the test time, and the value of the prediction equation agrees with the value of around 3 days for low alloy metals and around 7 days for stainless steel with 13% Cr. The decrease in the average corrosion rate with the test time tends to be similar to that of the two-phase flow test, and the average corrosion rate after several days shows a value close to the predicted value.

Table 4. The results of the corrosion rate of several materials on the test, 1,3 and 7 days, and comparison of the corrosion rate between estimation using database and autoclave single-phase testing.

	Duration (day)	pH	Inlet Tempreture (Degree C)	Test Material	Measured C.R (mm/y)	Estimated C.R (mm/y)	Ratio of M/E
Test1	1	3.8	170	TN80SS	2.32	1.12	2.07
				TN80Cr13	1.07	0.4	2.68
Test2	3	3.8	170	TN80SS	1.01	1.12	0.90
				TN80Cr13	0.57	0.4	1.43
Test3	7	3.8	170	TN80SS	0.57	1.12	0.51
				TN80Cr13	0.37	0.4	0.93

5. DISCUSSION

Figure 7 shows the relationship between the duration time and the measured corrosion rate of low metal alloy (TN80SS) and stainless alloy (TN80Cr13) at a two-phase flow test at Yanaizu-Nishiyama and hot water single-phase autoclave test.

In this log-log graph, the linear relationship between the duration time and corrosion rate shows in the case of the autoclave test. However, in the case of two-phase field test, the corrosion rate of 15 days shows slightly higher than estimated from the linear relationship between 1 day and 4 days test. The reason is considered by As and Sb precipitation and these heavy metals accelerated galvanic corrosion due to the reaction with iron.

The corrosion rate of two-phase test is about one-fifth of that of the autoclave test. This shows the vapor/liquid ratio influence the corrosion rate under two-phase condition. In this case, the vapor phase does not act the material corrosion. Then we estimated the volume ratio of vapor phase in two-phase fluid, Void ratio. The weight vapor/liquid ratio was 0.58 at this Yanaizu-Nishiyama test. According to the result of Egen et al. (1957), the weight ratio converts to the Void ratio, and the result is about 0.9. This means the liquid volume ratio is about 0.1 and the estimated corrosion rate will be one-tenth of hot water single-phase condition.

The idea is corresponding to the two corrosion tests and estimation formula using Cr equivalent especially 4 days field test.

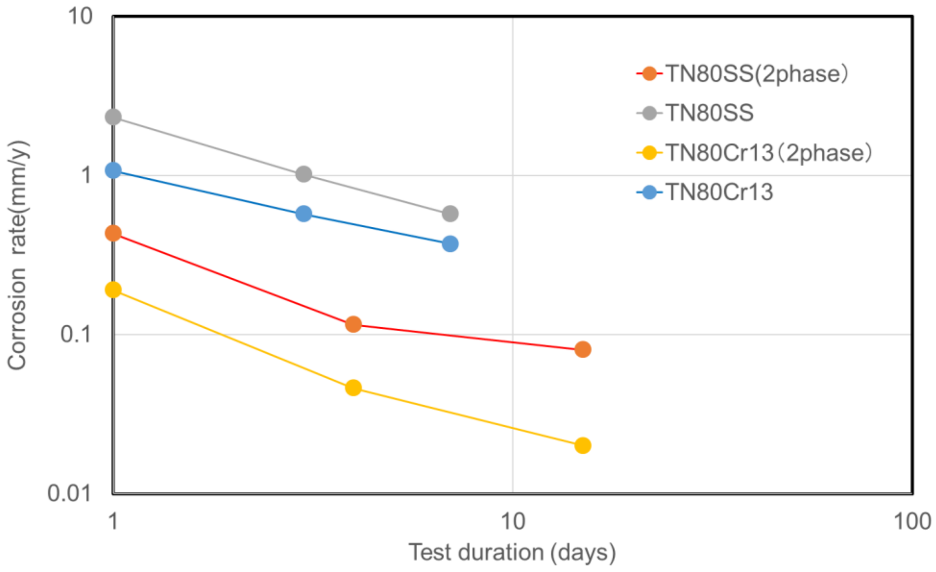


Figure 6: The change in average corrosion rate dependence on test duration.

6. SUMMARY

The material corrosion test in acidic fluid and two-phase condition was carried out at Yanaizu-Nishiyama geothermal field. The estimated corrosion rate of carbon steel using Cr equivalent at pH 3.8 and 165°C was calculated about 1.6 mm/year. On the other hand, the experimental field data was from 0.1 to 0.3 mm/year and lower than estimated rate.

On the other hand, at the autoclave test using hot water single phase on the same pH and temperature, the corrosion rate was a similar value as the estimated rate. Then, the reason for the lower corrosion rate at field test was considered as the lower water/vapor ratio in two-phase line.

ACKNOWLEDGMENTS

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

REFERENCES

Egen, R.A., Dingee, D.A. and Chastain J. W.: Vapor Formation and Behavior in Boiling Heat Transfer. Bettelle Memorial Inst., Rept. No. 1163, (1957).

Kurata, Y., Sanada, N., Ikeuchi, J. and Okahara, Y.: Corrosion Database System for Geothermal Materials. Reports of the Government Industrial Research Institute, Tohoku (in Japanese), 25, pp.7-14 (1992).

Kurata, Y., Sanada, N., Nanjo, H. and Ikeuchi, J.: Casing Pipe Materials for Deep Geothermal Wells. Geothermal Resources Council Transactions, 19, pp.105-109 (1995).

Lichti, K.A., Ko, M., Kennedy, J.: Heavy Metal Galvanic Corrosion of Carbon Steel in Geothermal Brines, NACE Corrosion/2016, paper C2016-7554 (2016).

NEDO: Survey and Research for countermeasure technology about Acid Brine, (in Japanese) (1992)

Osato, K., Sato, M., Kasai, K., Omae, M., Yanagisawa, N., Sakura, K. and Lichti, K. A.: Development of New Field Testing Tools for Geothermal Power Plant Risk Assessment of Corrosion and Scaling, 39th New Zealand Geothermal Workshop, Auckland, New Zealand. (2017)

Sanada, N., Kurata, Y., Nanjo, H. and Ikeuchi, J.: Material Damage in High Velocity Acidic Fluids, Geothermal Resources Council Transactions, 19, pp.359-363(1995).

Sanada, N., Kurata, Y. and Lichti, K: Valuation and Development of Deep Geothermal Resources--Materials Subtask Update of IEA Research Collaboration Program, Geothermal Resources Council Transactions, 21, pp.317-324 (1997).

Sanada, N., Kurata, Y., Nanjo, H., Kim, H., Ikeuchi, J. and Lichti, K: IEA Deep Geothermal Resources Subtask C: Materials, Progress with a Database for Materials Performance in Deep and Acidic Geothermal Wells, Proc. Word Geothermal Congress 2000 Kyushu – Tohoku, Japan., pp.2411-2416 (2000),

Yanagisawa, N., Masuda, Y., Sakura, K. and Osato, K.: The review of the material corrosion under geothermal condition in Japan, Proc.41st Workshop on Geothermal Reservoir Engineering, Stanford University. (2016)

Yanagisawa, N., Masuda, Y., Osato, K., Sato, M., Kasai, k., Sakura, k. and Fukui, T. : The estimation of the material corrosion based on previous data and compare with on-site test at geothermal field, Proc. 38th New Zealand Geothermal Workshop, Auckland, New Zealand. (2016)

Yanagisawa, N., Masuda, Y., Osato, K., Sato, M., Kasai, k., Sakura, k. and Fukui, T. : The Material Corrosion Test Using Small Loop System at Geothermal Power Plant in Japan, Proc.42nd Workshop on Geothermal Reservoir Engineering, Stanford University. (2017)

Yanagisawa, N., Masuda, Y, Osato, K., Sato, M., Kasai, K., Sakura, K., Fukui, T, Akahori, M., and Lichti, K.: The Material Corrosion Test Using Loop System Under Acidic Condition at Geothermal Field in Japan, in Proceedings 39th New Zealand Geothermal Workshop, 22 - 24 November 2017, Rotorua, New Zealand.