PROCEEDINGS, 45th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 10-12, 2020
SGP-TR-216

Corrosion Test of Casing Steel at High Temperature Acid Condition

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Keywords: Corrosion, Casing Steel, TN95Cr13S, TN125Cr13U, 17Cr, Acidic brine, Cylinder coupon, NEDO

ABSTRACT

The authors have been carrying out "development of technologies for utilizing unused acidic hot water in conventional geothermal resources" with the NEDO budget since FY2018. This is to develop a geothermal power plant risk assessment system for high-temperature acidic hot water that has not been used so far by evaluating the material corrosion characteristics of high-temperature acidic hot water at about 300 ° C and above pH3.

As one of the evaluation methods, a material corrosion test using a flow type autoclave of New Zealand GNS was conducted. A test piece having a diameter of 8 mm and a length of 13 mm was fixed with zirconia beads inside a flow-type autoclave having a length of about 15 cm. The test temperature was 250, 300, 350 ° C., the pH of the fluid was 3 at room temperature, and two types of tests, hydrochloric acid and sulfuric acid, were performed. Three types of specimens, TN125Cr13U steel, TN110Cr13S steel, and 17Cr steel, were used, and a test was conducted at a maximum flow rate of 200 L / min for about 5 hours.

The corrosion rate was calculated from the change in weight before and after the test obtained after removing the corrosion product present on the sample surface after the test. The results of the comparison between the corrosion rate obtained in the test and the predicted value by the material corrosion prediction formula by Cr equivalent are introduced.

1. INTRODUCTION

The corrosion and scale formation due to various chemical components are issues of concern for the operation of geothermal power plants. In particular, under acidic condition, the well casing made of carbon steel, the surface piping, and the power generation facility often suffer damage due to overall corrosion and erosion. For example, the carbon steel and low alloy steel, corrosion progresses in a high temperature environment of pH 4 or less. (Yanagisawa et al., 2016, Yanagisawa et al. 2017)

Selection of more corrosion resistant alloys must also address risk of Chloride SCC and Sulfide Stress Cracking. This work is concerned with corrosion rate determination as a function of temperature and pH for a selected set of geothermal fluid chemistry conditions. In order to estimate material corrosion rate under high temperature and acidic condition, we are carrying out "Technological Development towards Utilization of Unused Geothermal Energy (Development of Unused Acid Brine Utilization Technology in Conventional Geothermal Resources)" for utilization of unused geothermal energy by NEDO budget since FY2018. In this R&D project, we are developing a system that can derive optimal materials and countermeasure technologies when considering the use of acidic hydrothermal resources. Evaluation of the material corrosion rate has been progressed using a flow type autoclave and comparison with a previously developed estimation formula of material corrosion rate using Cr equivalent of material, see for example Yanagisawa et al., 2016, Yanagisawa et al. 2017.

2. ESTIMATION OF CORROSION RATE USING CR EQUIVALENT

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 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 corrosion resistance of Cr and elements other than Cr was deduced from the experimental data. In the HCl acidified system, the Cr equivalent was calculated as follows:

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

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

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

And in the H_2SO_4 acidified system, the Cr equivalent was calculated as follows:

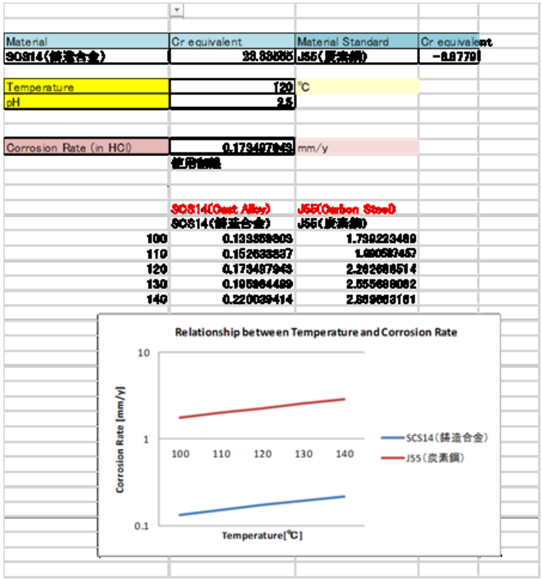
$$Creq = Cr - 16.76\,C + 0.63\,Si + 0.193Mn - 10.2P + 35.11S + 0.187\,Ni + 0.02Mo + 0.725Cu\ (wt\%). \qquad (1)$$

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

$$\log(C.R) = 6.467 - 1633\,(1/T) - 0.697(pH) - 0.093\,(Creq)$$

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 1.

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



Material	Cr equivalent	Material Standard	Cr equivalent
SCS14(鋳造合金)	28.83	J55(炭素鋼)	-0.8779

Temperature 120 °C

pH 2.5

Corrosion Rate (in HCl) 0.1734979 mm/y

	SCS14(Cast Alloy) SCS14(鋳造合金)	J55(Carbon Steel) J55(炭素鋼)
100	0.133859803	1.739223489
110	0.152633837	1.990587457
120	0.173497943	2.262688514
130	0.196964489	2.555698082
140	0.220039414	2.859863181

Figure 1: sample of the corrosion rate calculation system using Microsoft excel file

Table 1: The chemical composition of materials and Cr equivalent

Material	Cr Content	Mo Content	Cr equivalent(H_2SO_4)	Cr equivalent(HCl)
TN95Cr13S	13%	2.0%	13.2	15.5
TN125Cr13U	13%	3.0%	13.5	16.2
17Cr	17%	2.5%	18.6	21.4

3. LABORATORY CORROSION TEST UNDER HIGH TEMPERATURE AND LOW PH CONDITION

In order to select materials that can be used in a high temperature, low pH hydrothermal environment, we evaluated the corrosion resistance of each material. The corrosion test was conducted by using a Hydrothermal flow simulator owned by GNS Science of New Zealand (Figure 2). It can also be used for a material corrosion test.

This apparatus is capable of conducting a corrosion test in a state where hot water flows after adjusting pH, temperature, and non-condensable gas to conditions suitable for the purpose. Corrosion testing can be performed in an environment where metal specimens are always exposed to fresh hot water. For this reason, it is possible to conduct corrosion testing which closely approximates the corrosion chemistry of an actual casing or piping under low flow conditions.

3.1 Experimental apparatus for corrosion test

The apparatus can simulate water-rock interaction in a geothermal reservoir, using an input fluid prepared for the pH, temperature, and non-condensable gas conditions desired. Corrosion tests can be conducted in an environment where metal specimens are always exposed to fresh brine. It is possible to conduct the corrosion testing under conditions that closely approximate the actual corrosion chemistry for casings and pipes.

Prepared test materials for the work were in the form of a cylindrical coupons of OD 8 mm x 13 mm. Single coupons were set so as not to directly touch the pressure vessel made of titanium by inserting OD 2 mm Zirconia beads. Test brine was prepared in a 1 L separator. The flow rate was set between 5 mL/h and 200 mL/h, and the test brine was passed through the pressure vessel at a constant flow rate. The temperature in the pressure vessel was controlled by the heater and the pressure was controlled by the back-pressure regulator. The temperature was set to 250 deg. C, 300 deg. C, and 350 deg. C, and the pressure was set to 20 MPa. In addition, the test brine after reacting with a metal coupon can be collected by a syringe located at the outlet of the pressure vessel after the pressure letdown valve, and analysis of pH and dissolved chemical components could be conducted.

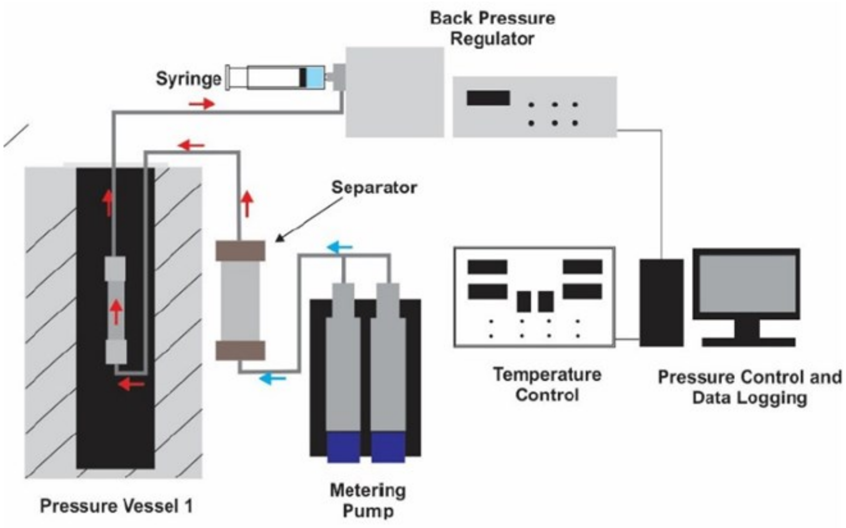


Figure 2 Hydrothermal flow simulator at Wairakei Research Centre, GNS Science.

3.2 Conditions of Corrosion Experiments

The materials of the test coupon were TN95Cr13S (13CrS), TN125Cr13U (13CrU), and 17Cr. These materials were processed and supplied by TenarisNKKTubes. The mixing ratio of Cr and Mo in each material was as shown in Table 1.

Measurement of corrosion rate under the conditions of 250 deg. C, 300 deg. C, and 350 deg. C was carried out for the three materials TN95Cr13S, TN125Cr13U, and 17Cr. The test brine had a pH of 3.0 and contained non-condensable gas (Total 3%, CO_2: 96%, H_2S: 4%) and chloride ion (10,000 ppm). The pH was adjusted with sulfuric acid and hydrochloric acid. The flow rate of the test brine was adjusted stepwise to 10 mL/h, 50 mL/h, 100 mL/h, and 200 mL/h, and an exposure test of a total of 6 hours was conducted.

After the corrosion test, controlled removal of the corrosion product was carried out at Advanced Industrial Science and Technology (AIST), and the final weight loss was measured. Di-hydrogen ammonium citrate was used to dissolve the corrosion products. The dissolution was carried out at 70 deg. C with cathodic protection using a carbon rod for the anode.

3.3 Results of Corrosion Tests

The results of converting measured weight loss of test material into corrosion rate after one year are summarized in Figures 3 and 4. Figure 3 shows the test results in sulfuric acid. In case of sulfuric acid, the corrosion rates appeared to be higher at lower temperature especially in the case of TN125Cr13U. The corrosion rate at 250 ºC was 1.55 mm/year and the rate at 350 ºC was 0.75 mm/year

In the case of TN95Cr13S, the highest corrosion rate, 0.83mm/year, was seen at 300 ºC and was 0.51mm/year at 350 ºC. In contrast, the corrosion rate of 17Cr showed the lowest rate at 300 ºC about 0.42mm/year and the highest rate at 350 ºC. The change in corrosion rate with temperature was not always monotonic, compare the corrosion rate decrease of TN125Cr13U from 250 ºC at 1.55 mm/year, to about 1 mm/year at higher temperatures with the corrosion rate changes for TN95Cr13S and 17Cr which showed differing trends in Figure 3.

Figure 4 shows the result in hydrochloric acid. In the case of TN95Cr13S, the corrosion rate deceased with increasing temperature. The corrosion rate at 250 ºC was 1.62 mm/year and the rate at 350 ºC was 0.94 mm/year. In contrast, the corrosion rate of 17Cr increased with temperature. The corrosion rate at 250 ºC was 0.09 mm/year and the rate at 350 ºC was 1.36 mm/year. In the case of TN125Cr13U, the highest corrosion rate was seen at 1.20mm/year, at 300 ºC and decreased to 0.77mm/year at 350 ºC.

In hydrochloric acid, the corrosion rate often exceeded 1 mm/year and was higher than with sulfuric acid.

3.4 Comparison with estimation formula using Cr equivalent

Based on the formula of material corrosion rate using temperature, pH and Cr equivalent, the corrosion rate tends to increase with temperature and with lower pH whereas in this testing work the corrosion rate did not always increase with temperature.

In order to resolve the differing trend seen in the testing the pH in higher temperature was simulated using geochemical calculator, Solveq-Chim (Reed, 2014). Figure 5 shows the result for the simulated pH from room temperature to 375 ºC for case of this test, containing non-condensable gas (Total 3%, CO_2: 96%, H_2S: 4%) and chloride ion (10,000 ppm) and pH 3 at room temperature. The pH is almost same from room temperature to 100 ºC and gradually increases with temperature. And pH rapidly increases at higher temperatures. The pH shows 3.38 at 250 ºC, 3.66 at 300 ºC and 4.5 at 350 ºC.

Then, we calculated the corrosion rate using the simulated pH at 250, 300, 350 ºC. In this case, the corrosion rate was highest at 300 ºC. Figure 6 shows a comparison of the estimated corrosion rate using simulated pH and measured corrosion rate of TN95Cr13S at H_2SO_4 condition. Note that the estimated carrion rates correspond to the measured rates for the range from 0.5 to 1 mm/year. A similar trend has been observed for the case of TN125Cr13U with HCl acid. While the remaining alloys still show some variation between measured rate and estimated rate. One of the reasons for the observed variation of material corrosion rate in the present corrosion test was due to the short exposure time of about 6 hours. The results must be interpreted as being from a short-term corrosion rate test. Long-term exposure tests are planned in the future, in which we plan to evaluate the change in corrosion rate due to formation of the protective corrosion product films.

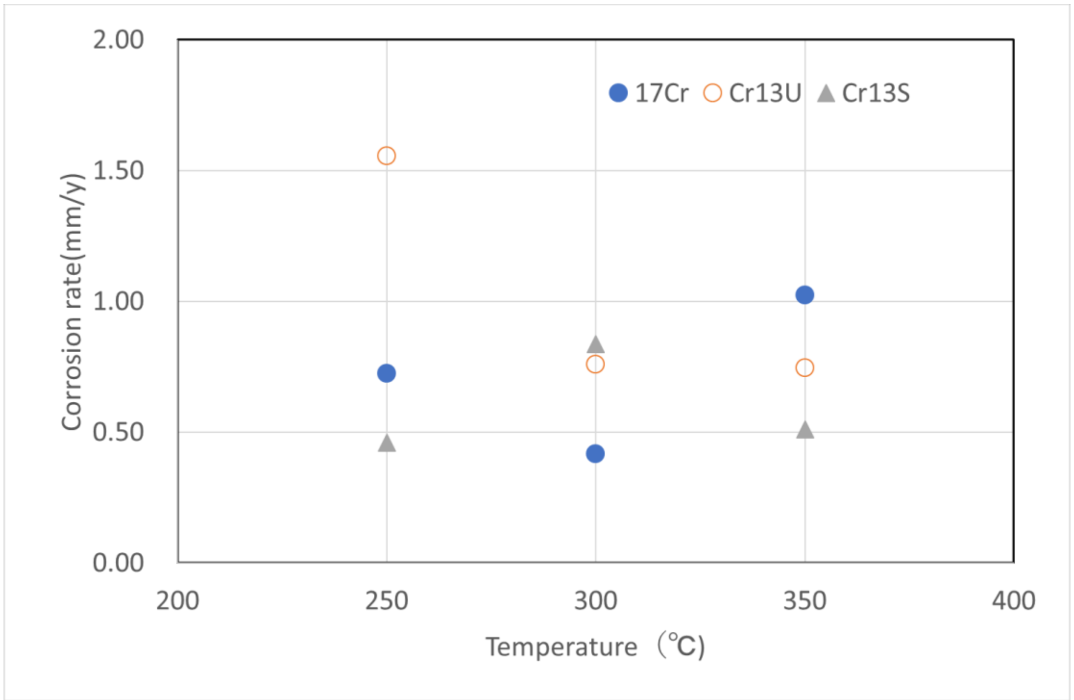


Figure 3 Measured corrosion rate of TN95Cr13S, TN125Cr13U, and 17Cr from 250 to 350 deg. C at H_2SO_4 condition

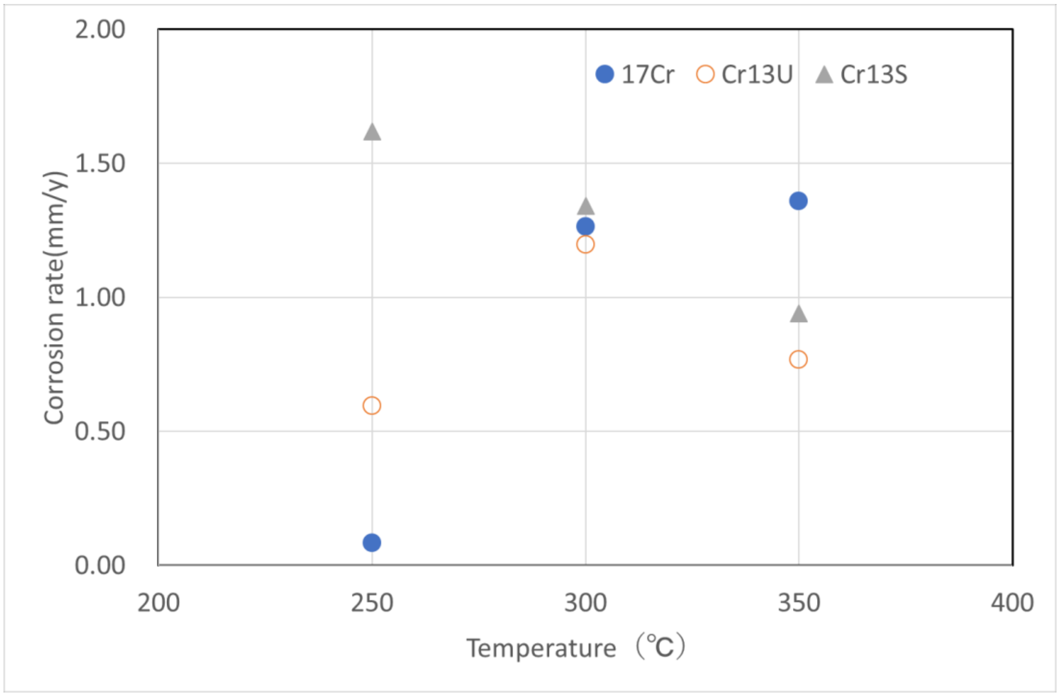


Figure 4 Measured corrosion rate of TN95Cr13S, TN125Cr13U, and 17Cr from 250 to 350 deg. C at HCl condition

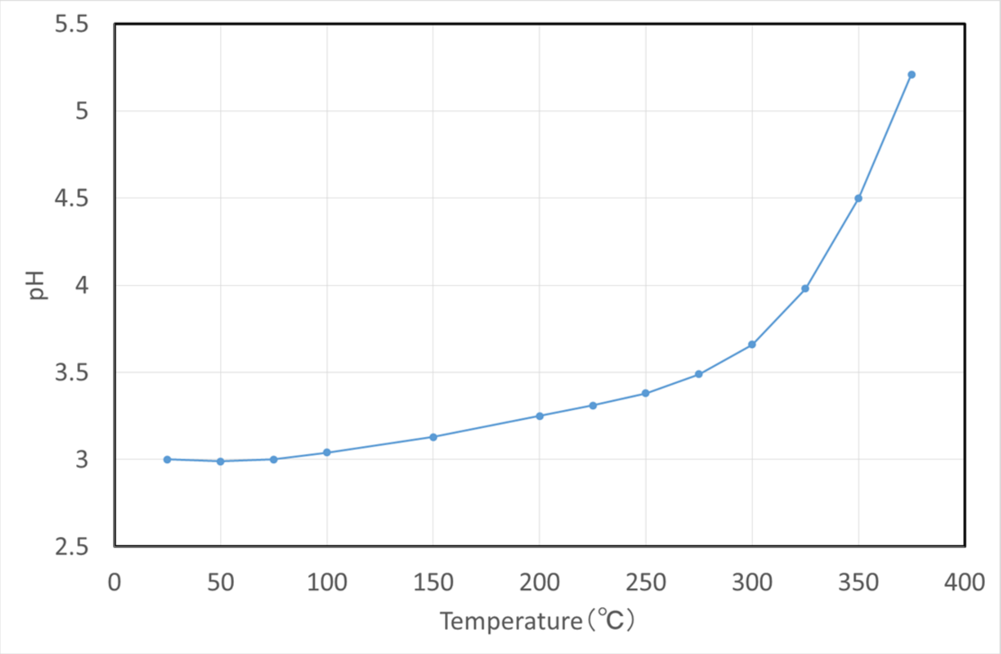


Figure 5 Simulated pH with temperature change for H_2SO_4 condition.

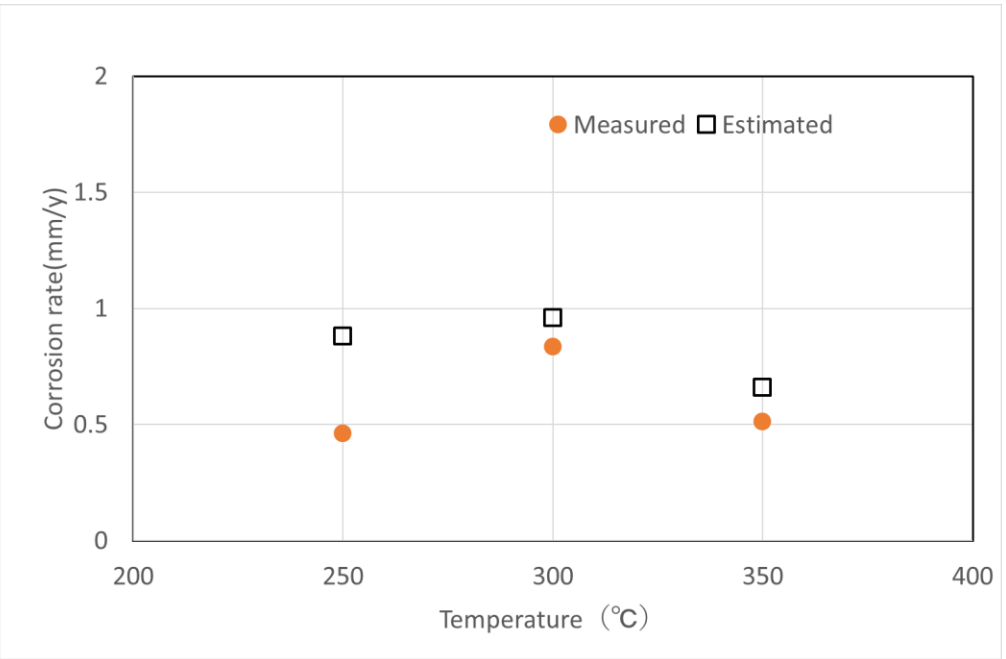


Figure 6 The corrosion rate of TN95Cr13S at H_2SO_4 condition; compare between measured rate and estimated rate using Cr equivalent formula and simulated pH at test temperature

6. CONCLUSION

It is important to select materials that have acceptable corrosion rate for geothermal brine in order to maintain and manage a geothermal power plant. Especially, when using acid brine, it is necessary to select appropriate materials that correspond to the corrosion risk.

In order to select materials that can be used in a high temperature, low pH hydrothermal environment, we have conducted a laboratory corrosion test using a Hydrothermal flow simulator owned by GNS Science. Measurement of the corrosion rate under the conditions of 250 ºC, 300 ºC, and 350 ºC was carried out for the three materials TN95Cr13S, TN125Cr13U, and 17Cr. The test brine had a pH of 3.0 and contained non-condensable gas (Total 3%, CO_2: 96%, H_2S: 4%) and chloride ion (10,000 ppm).

In the case of sulfuric acid, although the corrosion rate of TN125Cr13U at 250 ºC indicated 1.4 mm/year, was lower at the higher temperature conditions tested at 1 mm/year or less. When comparing the corrosion rates among the alloys tested, the same tendency was not found in all cases. The corrosion rate of 17Cr at 300 ºC was 0.384 mm/year, lower than at lower and higher temperatures. In the case of hydrochloric acid, the corrosion rate was higher than with H_2SO_4 and often exceeded 1 mm/year.

In order to compare the corrosion rate results obtained with previously developed models for corrosion rate estimate, we simulated pH change using Solveq-Chim with temperature. Considering the simulated pH, the estimated corrosion rate was highest at 300 ºC. In this experiment, the measured rate of TN95Cr13S at H2SO4 condition and TN125Cr13U at HCl condition corresponded, within a degree of accuracy, to the estimated corrosion rate.

ACKNOWLEDGMENT

This R&D project was performed as part of research project “Research and Development of Geothermal Power Generation Technology”, funded by the New Energy and Industrial Technology Development Organization (NEDO).

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