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Material Corrosion Tests for Developing Cr Casing Steel at High Temperature Acid Conditions

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ABSTRACT

To develop a geothermal power plant risk assessment system for high-temperature acidic hot water, we carried out the material corrosion tests using a flow-through autoclave at GNS Science, New Zealand. A test piece, having a diameter of 8 mm and a length of 13 mm, was isolated with zirconia beads inside a pressure vessel 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 sulfuric acid was used. Three types of specimens, TN125Cr13U steel, TN110Cr13S steel, and 17Cr steel were used, and the tests were conducted at a flow rate of 10 L/ min for about 1, 3 and 8 days. 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. We also estimated corrosion rates from the metal concentrations in the experimental effluents. The results of the comparison between the corrosion rate obtained in the tests and the predicted values by the material corrosion prediction formula by Cr equivalent, are introduced.

1. INTRODUCTION

To estimate material corrosion rates under high temperature and acidic conditions, 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 funded by NEDO 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. At first, material corrosion tests, using several metal samples, were carried out using a flow-through autoclave. The first tests were carried out for 6 hours and the flow rate was varied from 5 mL/h to 200 mL/h (Yanagisawa et al., 2020). However, the first test had several problems, for example, short test duration and variable flow rate.

We changed the test conditions to a fixed flow rate of 10 mL/h giving a test duration of 72 hours (3 days). And all tests were carried out using sulfuric acid. In this paper, we show the results of these corrosion tests and comparison with a previously developed estimation formula of material corrosion rate using Cr equivalent of material, c.f., Yanagisawa et al., 2017, Yanagisawa et al. 2020.

2. SIMULATION OF CORROSION RATE USING CR EQUIVALENT

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 concept 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 experimental data. In a H_2SO_4 acidified system, the Cr equivalent was calculated as follows:

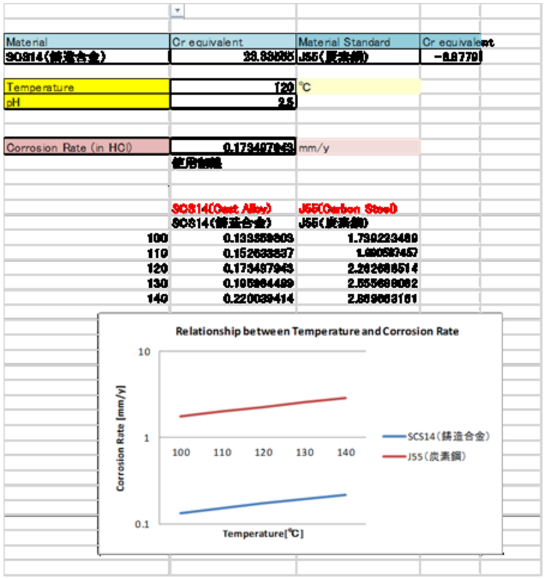
$$Creq = Cr - 16.76\,C + 0.63\,Si + 0.193\,Mn - 10.2\,P + 35.11\,S + 0.187\,Ni + 0.02\,Mo + 0.725\,Cu\ (wt\%). \qquad (1)$$

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

$$\log (C.R) = 6.467 - 1633\,(1/T) - 0.697\,(pH) - 0.093\,(Creq) \qquad (2)$$

An example of calculation results for Creq is shown in Table 1 based on the above equations. The calculations were made using a Microsoft excel spreadsheet. An example of this system is shown in Figure 1.

The corrosion rate is calculated by first selecting the material and supplying the Cr equivalent and second by inputting the temperature and pH. In this example, the estimated corrosion rate at 100 to 140ºC 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)	23.83555	J55(炭素鋼)	-0.8779

Temperature	120	°C
pH	2.5	

Corrosion Rate (in HCl)	0.173497943	mm/y
	[illegible]	

	SCS14(Cast Alloy) SCS14(鋳造合金)	J55(Carbon Steel) J55(炭素鋼)
100	0.133859603	1.739223489
110	0.152638837	1.990587457
120	0.173497943	2.262686514
130	0.195964489	2.555696082
140	0.220039414	2.869863161

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

Table 1: The key chemical element composition of tested materials and Cr equivalent.

Material	Cr Concentration	Mo concentration	Cr equivalent
TN95Cr13S	13 %	2.0 %	13.2
TN125Cr13U	13 %	3.0 %	13.5
17Cr	17 %	2.5 %	18.6

3. LABORATORY CORROSION TEST UNDER HIGH TEMPERATURE AND ACID CONDITION

To select materials that can be used in a high temperature, low pH, hydrothermal environment, we evaluated the corrosion resistance of three candidate materials. The corrosion test was conducted by using a hydrothermal flow simulator provided by GNS Science, New Zealand (Figure 2).

This apparatus can conduct a corrosion test in a state where hot brine 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 brine. 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

Prepared test materials were in the form of cylindrical coupons of OD 8 mm x 13 mm length. Single coupons were set so as not to directly touch the titanium pressure vessel by surrounding them within OD 2 mm zirconia beads. Test brine was prepared in a 1 L separator. 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.

The flow rate was set to 10 mL/h, and the test brine was passed through the pressure vessel at the desired flow rate. The temperature in the pressure vessel was controlled by an oven and the pressure was controlled by a back pressure regulator. The temperatures were 150 ^{o}C, 250^{o}C, 300^{o}C, and 350^{o}C, and the pressure was set to 20 MPaG (T(saturation) of 366 ^{o}C). The test duration was normally 72 hours (3 days).

The materials used for the test coupons were TN95Cr13S (13CrS), TN125Cr13U (13CrU), and 17Cr. These materials were processed and supplied by Tenaris NKKTubes. The ratio of Cr to Mo in each material was as shown in Table 1.

During the reaction with the metal coupon, the test brine was collected by a syringe located at the outlet of the back pressure regulator. These brine samples were analysed for pH and dissolved chemical components.

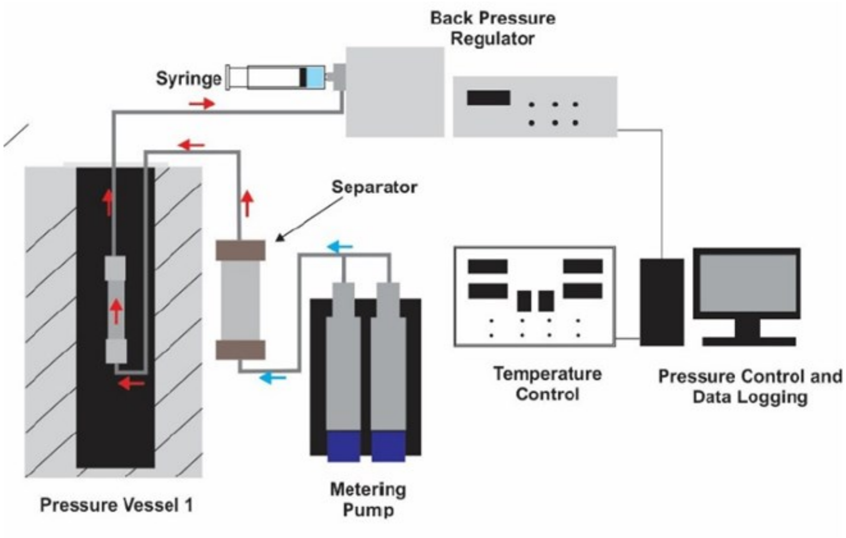


Figure 2 Hydrothermal flow simulator at Wairakei Research Centre, GNS Science, New Zealand.

3.2 Estimates of the material corrosion rate

After the corrosion tests, analysis of the exposed materials was completed as follows.

1) The dissolved concentration of metal elements such as Fe, Cr, Ni, Mo, Mn and Cu were analyzed by GNS Science. The total dissolved metal content was calculated using solution volume and the metal concentrations. From calculated total dissolved metal content, we calculated the material corrosion rate using material surface area and duration time.

2) We measured the material change directly due to corrosion. After each series of tests, the controlled removal of the corrosion product, such as oxide iron (Fe_3O_4) was carried out at Advanced Industrial Science and Technology (AIST) and the final weight loss was determined. Di-hydrogen ammonium citrate was used to dissolve the corrosion products. The dissolution was carried out at 70^oC with cathodic protection using a carbon rod for the anode. After corrosion products were removed, the weight was measured and material corrosion rate calculated.

3) We compared the estimated corrosion rate using solution concentrations and expressed as measured material loss with the modelled corrosion rate using the calculation formula including temperature, pH and Cr equivalent.

4. RESULTS AND DISCUSSION

4.1 Dissolution of material

During testing of the 17Cr alloy, the fluid Fe content was analyzed every 24 hours. During the test, the Fe concentration was relatively constant and total dissolved Fe increased linearly (Fig. 3). The concentration of dissolved Fe was more than 95% of all metals analysed including Ni, Cr etc. The material corrosion rate is approximately constant.

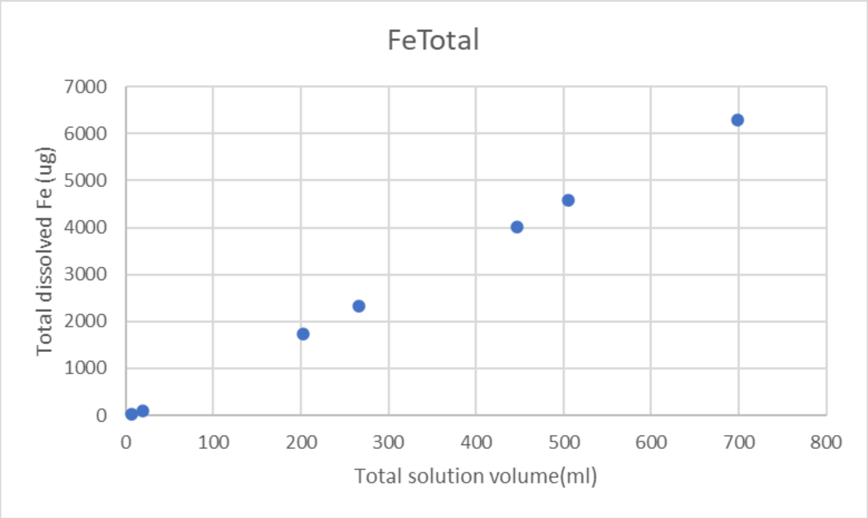


Figure 3 The relation between total dissolved Fe and total solution volume for 17Cr alloy at 350ºC.

4.2 Measured corrosion rate

Figure 4 shows the measured corrosion rate of 17Cr steel from 150 to 350 ˚C estimated from the total dissolved metal. At 150 ˚C, the corrosion rate was 0.033mm/y. The corrosion rate increased until 0.423mm/y at 300℃. However, at 350ºC, the corrosion rate decreases to 0.23mm/y in experiments. The tests were carried out several times and consistent results obtained.

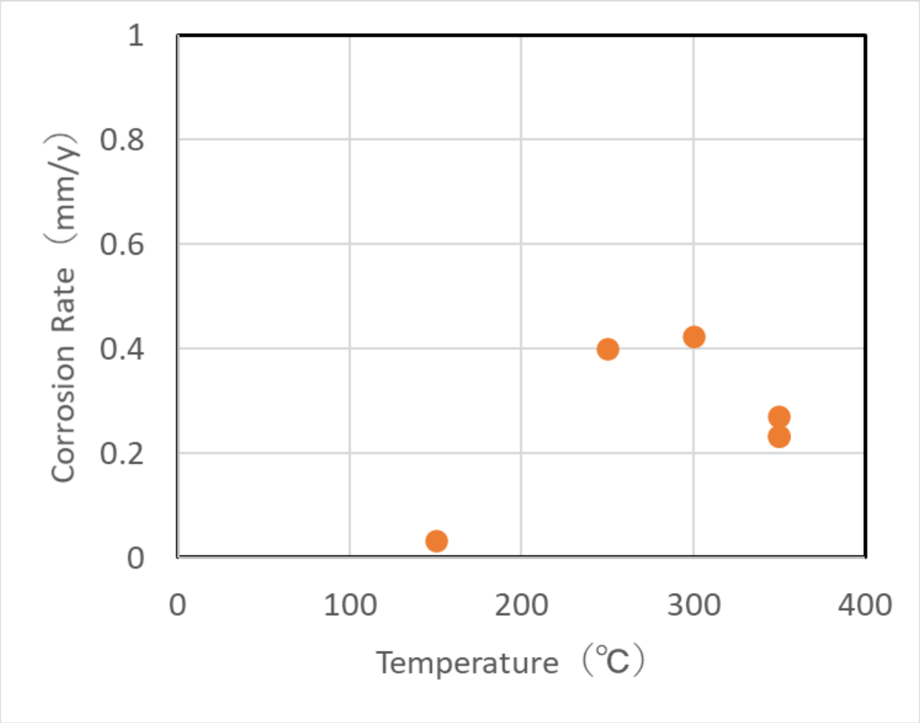


Figure 4 Measured corrosion rate of 17Cr by solution analysis from 150 to 350ºC with H_2SO_4

Figure 5 shows the corrosion rate based on directly measured weight change of exposed material. The results shown is for 17Cr steel and temperature is from 150 to 350˚C. The trend of corrosion rates was similar to that in Figure 4. However, the highest corrosion rate at

250℃ was 0.033mm/y lower than rate based on collected solution chemistry. This means that the measured corrosion rate based on metal concentrations in solution corresponded well with those measured be weight change.

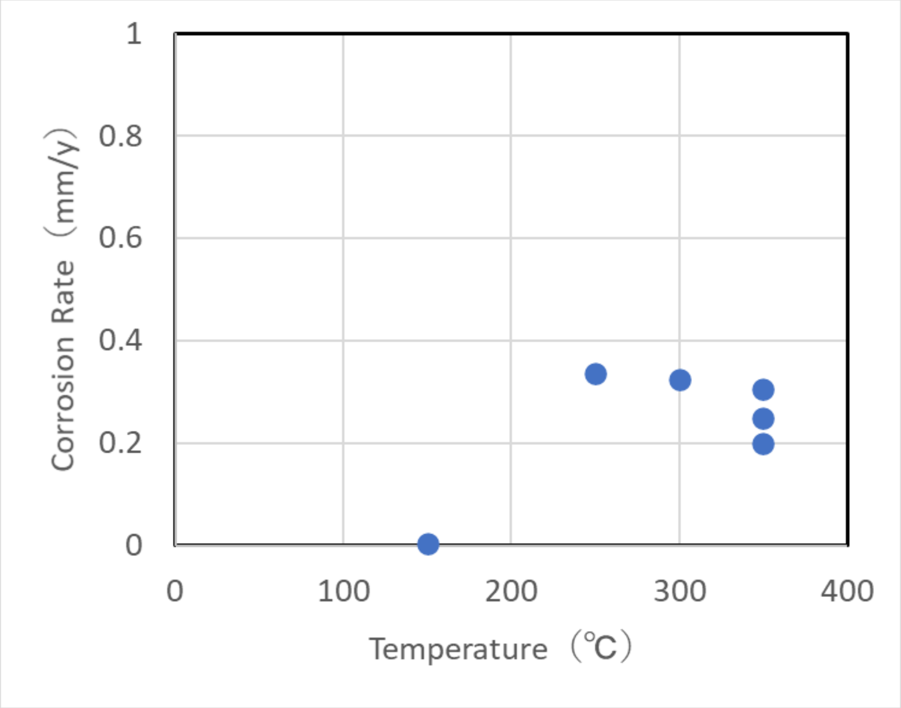


Figure 5 Measured corrosion rate of 17Cr by weight change of material from 150 to 350ºC at pH 3 by addition of H_2SO_4.

4.2 Comparison with estimation formula using Cr equivalent

According to the material corrosion rate formula by temperature, pH and Cr equivalent, the rate should increase with temperature and with lower pH. In our testing the corrosion rate did not consistently increase with temperature.

To resolve the differing trends seen, the pH at temperature was estimated using the geochemical equilibrium solver, Solveq-Chim (Reed, 2014). Figure 6 shows the result for the calculated pH from room temperature to 375ºC, for a solution containing non-condensable gases (Total 3%, CO_2: 96%, H_2S: 4%), chloride ion (10,000 ppm) and pH 3 at room temperature. The pH is similar from room temperature to 100ºC and gradually rises with further increases in temperature. Above 300ºC, the pH rapidly raises with increasing temperature. The calculated pH was 3.38 at 250ºC, 3.66 at 300ºC, and 4.5 at 350ºC.

We calculated the corrosion rate using the estimated pH at 250, 300, and 350ºC. These results are shown in Figure 7 as open squares. In this case, the modelled corrosion rate gave a value about 0.53 mm/y at 300ºC. The trend of corrosion rate change was again similar as the measured corrosion rate using metal concentrations. However, the measured corrosion rate was lower than the modelled rate, especially, at 150 ℃ (the measure corrosion rate was 0.004mm/y but the modelled rate was 0.03mm/y).

Other tested materials, TN95Cr13S and TN125Cr13U showed a similar trends to 17Cr alloy, that is, the measured corrosion rate based on metal concentrations and material weight loss showed highest value at 250℃. On the other hand, the modeled corrosion rate was highest at 300℃. The corrosion rate at 350℃ was again lower than at 250 and 300℃.

At the given flow rate the 3 day tests gave corrosion rates that are temperature-dependent and show similar trends as the calculated rate based on pH change.

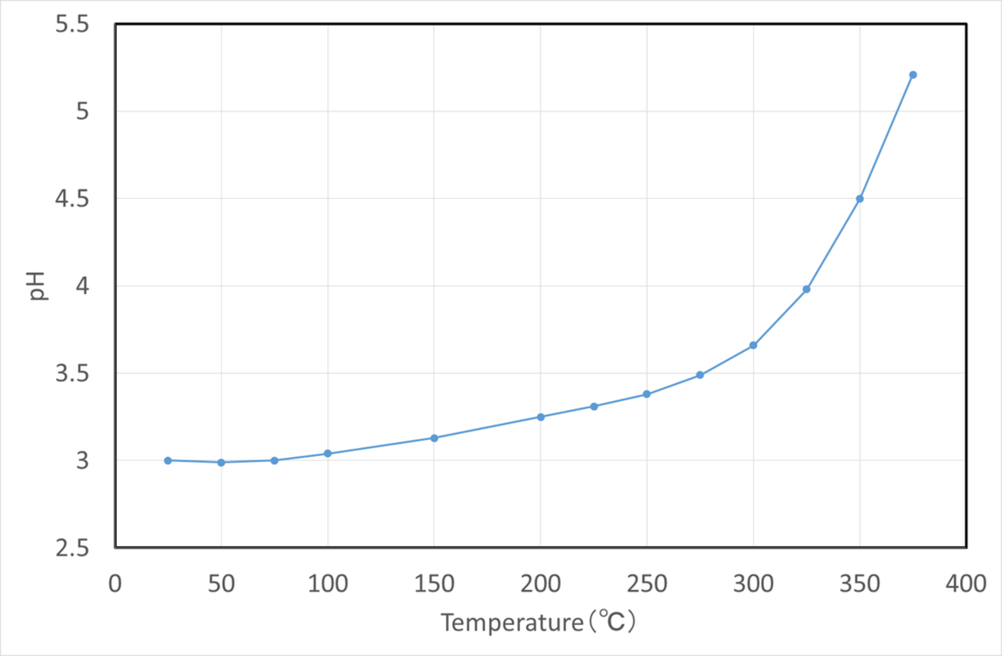


Figure 6 Calculated at temperature pH with H_2SO_4.

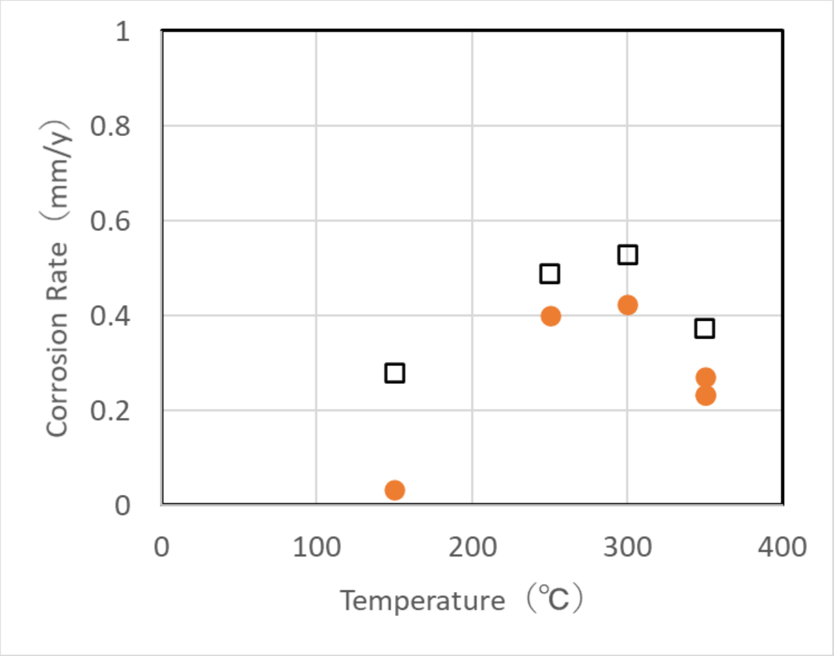


Figure 7 The measured and calculated (open squares) corrosion rate of 17Cr with H_2SO_4 using Cr equivalent formula and calculated pH at test temperature

6. CONCLUSION

It is important to select materials that have acceptable corrosion rates for geothermal brine to maintain and manage a geothermal power plant. It is especially important, when using acid brine, to select appropriate materials that correspond to the corrosion risk. To select materials that can be used in a high temperature, low pH, hydrothermal environment, we have conducted laboratory corrosion tests using a hydrothermal flow simulator provided by GNS Science. Measurement of the corrosion rate under the conditions from 150 to 350ºC was carried out for the three materials TN95Cr13S, TN125Cr13U, and 17Cr. The test brine had a pH of 3.0 and contained non-condensable gases (Total 3%, CO_2: 96%, H_2S: 4%) and chloride ion (10,000 ppm).

With brine and pH adjusted to 3.0 by addition of sulfuric acid, the corrosion rate of 17Cr shows 0.4 mm/y at 300℃ which is close to the modelled corrosion rate of 0.5 mm/y. Both measured and calculated corrosion rates are highest at 300℃. The lower calculated corrosion at higher temperature is explained by the pH increase of the brine.

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