CORROSION RATE ESTIMATION OF Cr CASING STEELS AT HIGH TEMPERATURE ACID CONDITIONS

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ABSTRACT

To develop a geothermal power plant risk assessment system for high-temperature acidic hot fluid, 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. Measurement of the corrosion rate under the conditions from 150 to 350 ºC was carried out for the two chromium (Cr) type materials, Super 13Cr, and 17Cr. The test brine had a pH of 3.0 at room temperature and contained non-condensable gases (Total 3%, CO_2: 96%, H_2S: 4%) and chloride ion (10,000 ppm).

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 estimated corrosion rates from the dissolved metal concentrations in the experimental effluents, and we estimated corrosion rates using Cr equivalent, pH and temperature using models proposed by Kurata et al. (1992).

With brine and pH adjusted to 3.0 by addition of sulfuric acid at room temperature, the measured corrosion rate from weight change and dissolved metal concentration showed the highest value at 250 ºC and was higher than the testing at 350 ºC. The reason for this result was hypothesized to be the change of pH at higher temperature, for example, 3.38 at 250 ºC and 4.5 at 350 ºC based on geochemical simulator modelling. Comparing the results for the two alloys tested, the relative corrosion rate of Super 13Cr/17Cr was lower in the higher temperature exposure testing than the 1.6 ratio value that would be predicted based on Cr equivalent. Analysis results suggest that that the Super 13Cr performed better than predicted by the Cr equivalent because of the better formation of adherent and protective corrosion products on this alloy at the higher pH encountered at the higher temperature.

1. INTRODUCTION

To estimate material corrosion rates under high temperature and acidic conditions, we are carrying out research within the framework of “Technological Development Towards Utilization of Unused Geothermal Energy (Development of Unused Acid Brine Utilization Technology in Conventional Geothermal Resources)” for utilization of unused acid wells for 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. Material corrosion tests, using several metal samples, were carried out using a flow-through autoclave. The testing was done using a fixed flow rate of 10 mL/h with test durations of 24 hours (1 day), 72 hours (3 days) and 192 hours (8 days). All tests were carried out using sulfuric acid for pH adjustment. In this paper, we show the results of these corrosion tests and provide a 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 (Creq) was calculated as follows:

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

An example of calculation results for Creq is shown in Table 1 based on the above equations.

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

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

The materials used for the test coupons were Super 13Cr and 17Cr. Table 1 shows the Cr equivalent of several casing materials including the 17Cr and Super 13Cr processed and supplied by Tenaris NKKTubes for this testing. Table 1 shows the relative corrosion rate compared to 17Cr which has the highest Creq. The calculation was based on formula (2). The estimated corrosion rate of Super 13Cr is about 1.6 times that of 17Cr and the rate of carbon steel is about 10 times that of 17Cr.

Table 1: The Cr equivalent of typical casing material and tested material and the relative corrosion rate at Sulfide condition

Material	Cr equivalent	Relative Corrosion Rate
17Cr	18.6	1.0
Super 13Cr	13.5	1.6
13Cr	8.9	2.4
Low alloy	-3.1	7.4
Carbon Steel	-6.54	10.3

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 the two considered candidate materials by corrosion testing that was conducted by using a hydrothermal flow simulator provided by GNS Science, New Zealand (Figure 1).

This apparatus can conduct a corrosion test with a slow flow of hot brine that has been adjusted for pH, and having non-condensable gas (CO_2 and H_2S) 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 used for testing were 150 ^oC, 250 ^oC, 300^oC, and 350 ^oC, and the pressure was set to 20 MPaG (T(saturation) of 366 ^oC). The test duration was 72 hours (3 days) and 192 hours (8 days).

The materials used for the test coupons were Super 13Cr and 17Cr. These materials were processed and supplied by Tenaris NKKTubes.

After 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.

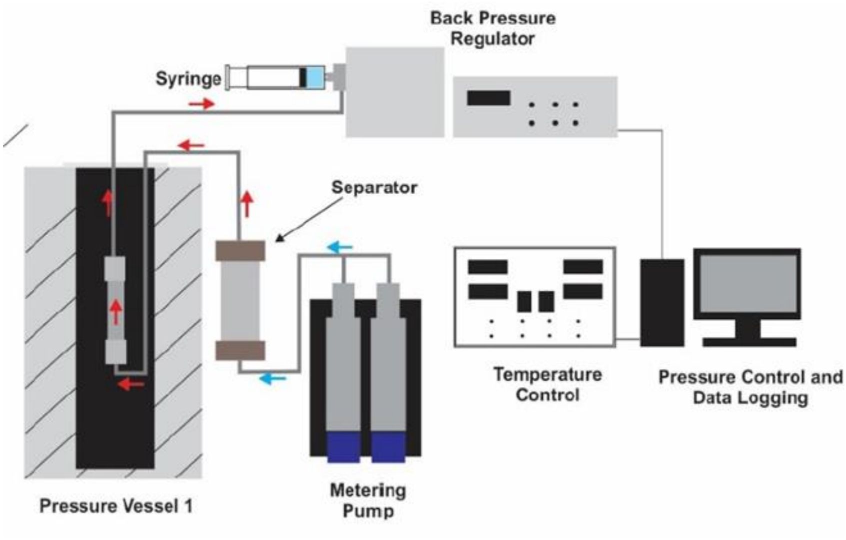

Figure 1: Hydrothermal flow simulator at Wairakei Research Centre, GNS Science, New Zealand.

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 by weight change. 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 change (loss) was determined 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. In this estimation, the pH at temperature was estimated using the geochemical equilibrium solver, Solveq-Chim (Reed, 2014). Figure 2 shows the result for the calculated pH from room temperature to 375ºC, for a solution containing non-condensable gases (Total 3%, CO2: 96%, H2S: 4%), chloride ion (10,000 ppm) and pH 3 at room temperature. The pH is similar from the start at room temperature conditions up to 100 ºC and gradually rises with further increases in temperature. Above 300 ºC, the pH rapidly raises with increasing temperature. The calculated pH was 3.38 at 250 ºC, 3.66 at 300 ºC, and 4.5 at 350 ºC.

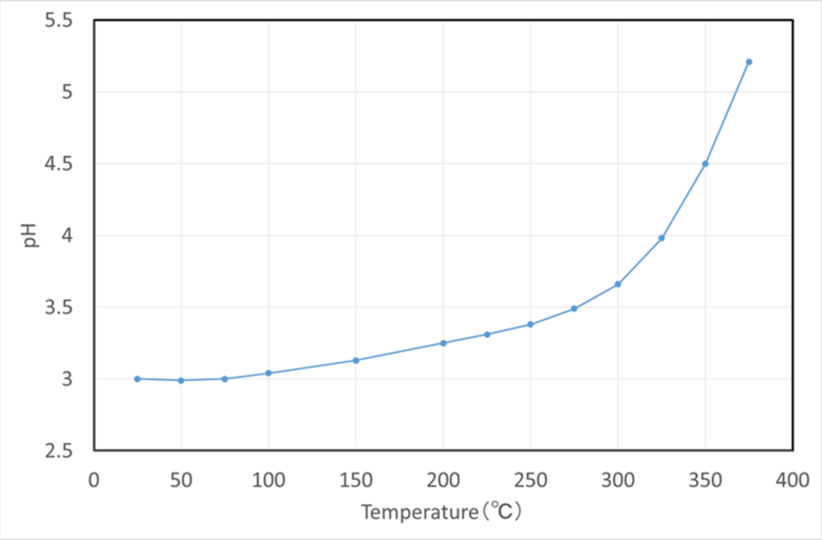

Figure 2: Calculated at temperature pH with H_2SO_4 added at room temperature to give pH of 3.0.

4.RESULTS AND DISCUSSION

4.1 The corrosion rate change depends on material and temperature

During testing, the fluid Fe content was analyzed every 24 hours. During the test, the Fe production rate was relatively constant and total dissolved Fe increased linearly as illustrated in Figure 3 for the 17Cr alloy at 350 °C. The concentration of dissolved Fe was more than 95% of all metals analyzed including Ni, Cr etc. The material corrosion rates obtained by this method were subsequently constant for the individual tests based on the linearly increasing dissolved Fe concentrations.

Figure 4 shows the corrosion rate measured by dissolved metal concentration and the change with duration time. Figure 4 (a) shows the corrosion rate of 17Cr in the case of 3 and 8 days of testing at 250 ºC and 1, 3 and 8 days of testing at 350 ºC. Figure 4(b) shows the corrosion rate of Super 13Cr in the case of 3 and 8 days of testing at 250 ºC and 350 ºC. In this Super 13Cr case, the corrosion rate obtained by dissolved iron concentration analysis slightly decreased with test duration.

Figure 5 shows the corrosion rate measured by weight change after removal of corrosion products and the change with exposure time. Figure 5 (a) shows the corrosion rate of 17Cr in the case of 3 and 8 days of testing at 250ºC and 1, 3 and 8 days of testing at 350 ºC. Figure 5(b) shows the corrosion rate of Super 13Cr in the case of 3and 8 days of testing at 250 ºC and 350ºC. In the case of 17Cr, the corrosion rate slightly decreased with test duration, as was the case for dissolved metal concentration (compare Figure 5 (a) with Figure 4 (a)). However, in the case of Super13Cr, at 250 ºC testing, the corrosion rate increased with test duration unlike the case of 350 °C and the dissolved metal concentration.

One of the reasons of this phenomenon was the seemingly different formation of iron sulfides and iron oxides as well as iron-chromium oxides on the Super 13Cr coupons at 250 ºC compared to 350 ºC as shown in Figure 6. The iron of corrosion products at 250 ºC had a porous appearance while those at 350 ºC show a uniform adherent layer that may have limited the corrosion and less corrosion was indicated by the weight change and less iron would be included in the dissolved solution analysis.

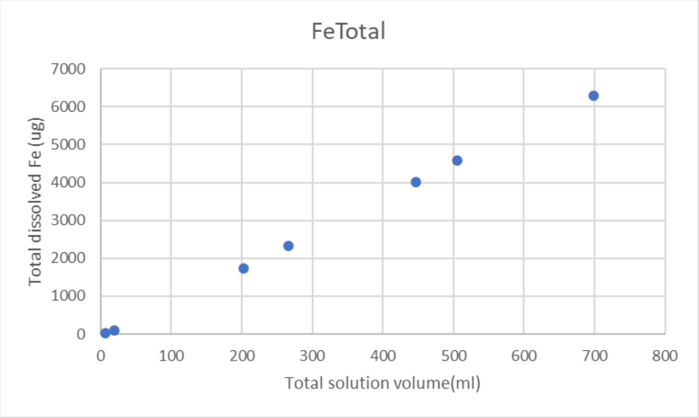

Figure 3: The relation between total dissolved Fe and total solution volume for 17Cr alloy at 350 ºC.

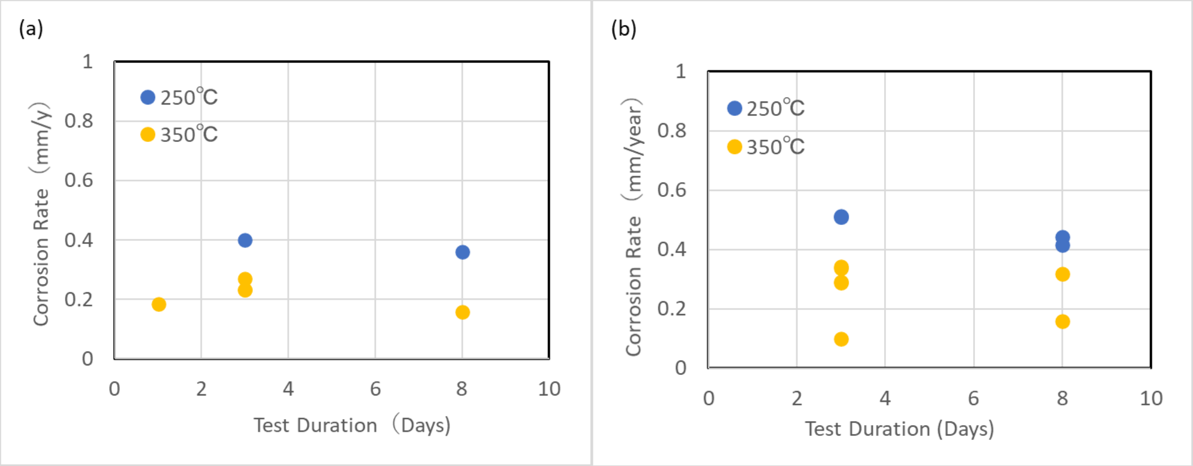

Figure 4: The corrosion rate measured by dissolved metal concentration versus the test duration. (a) 17Cr, (b) Super 13Cr

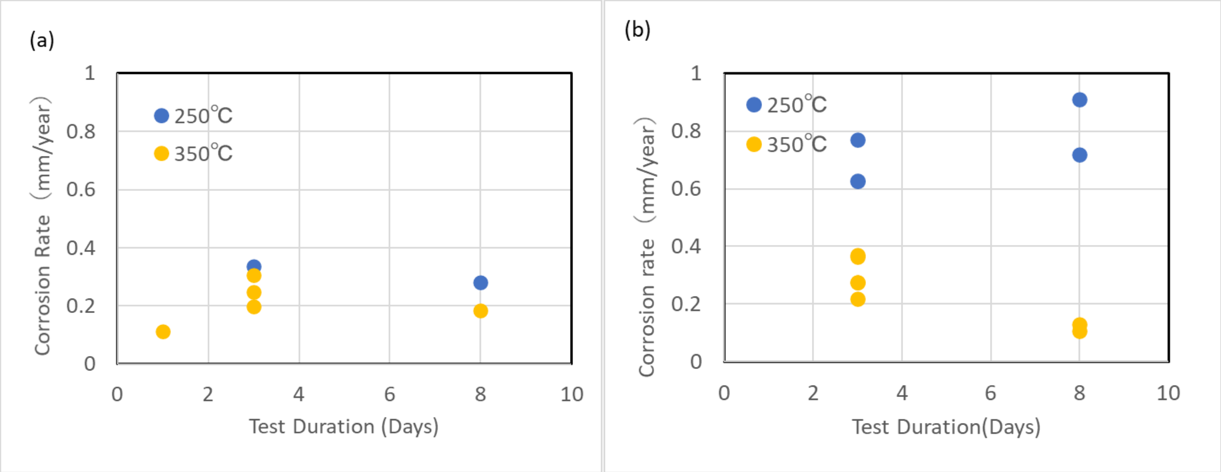

Figure 5: The corrosion rate measured by weight change versus the test duration. (a) 17Cr, (b) Super 13Cr

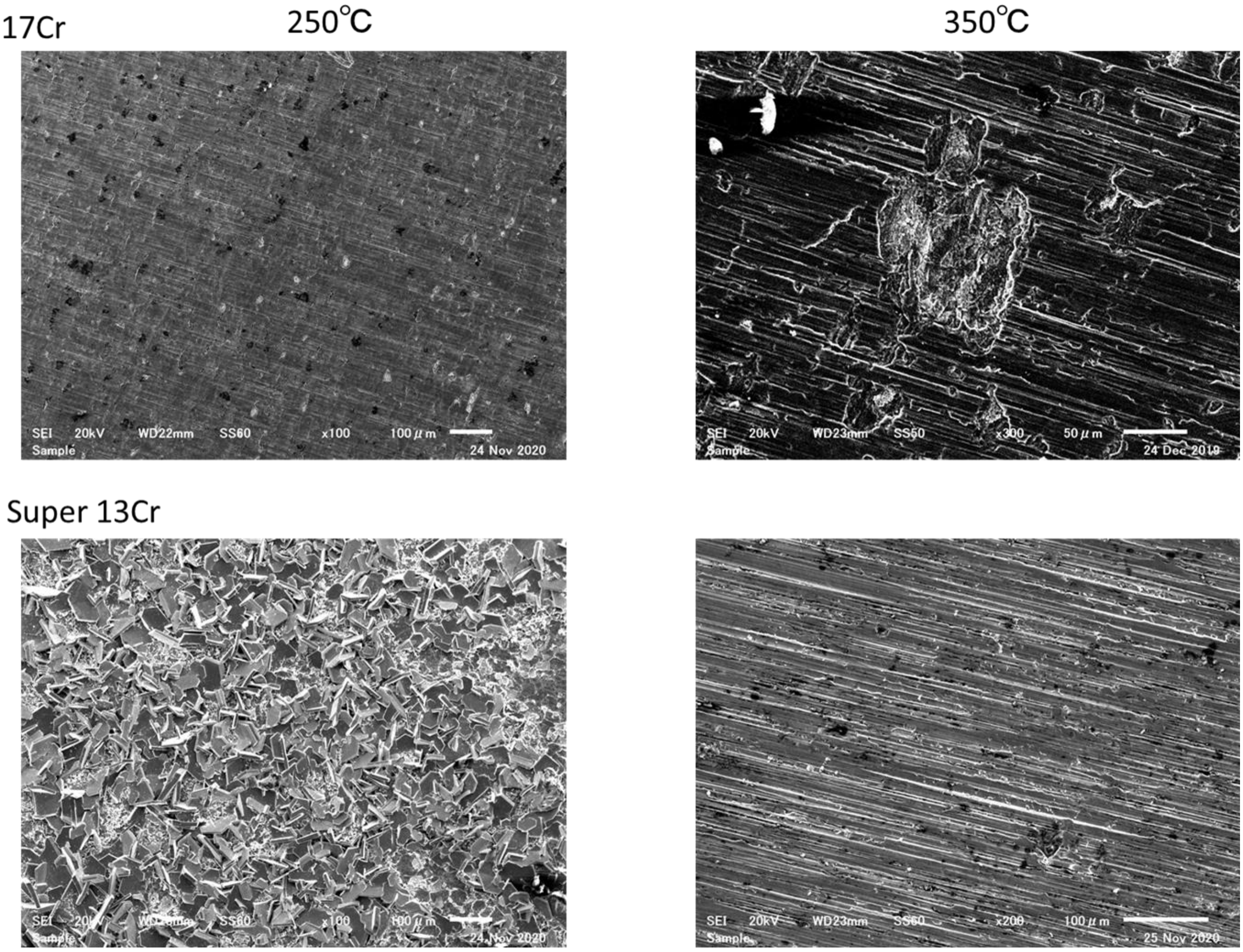

Figure 6: SEM images of corrosion products formed on 17Cr and Super 13Cr at 250 and 350 °C

4.2 Comparison with estimation formula using Cr equivalent

Figure 7 shows the measured corrosion rate using weight change and dissolved metal concentration in solution and modelled corrosion rate using Cr equivalent after 3 days of testing from 150 to 350 °C.

Figure 7(a) shows the measured corrosion rate using metal concentration was slightly higher than the rate using weight change in the case of 17Cr. The measured corrosion rates using metal concentration and the modelled rates were highest at 300 °C. The ratio of measured corrosion rate and modelled rate was highest at 150 °C.

Figure 7(b) shows the measured corrosion rate using weight change was higher than the rate using metal concentration of solution at 250 ºC in the case of Super 13Cr. The rate using weight change was lower than that using solution concentration at 150 ºC. The measured corrosion rate was highest at 250 ºC, whereas the highest modelled corrosion rate was at 300 ºC.

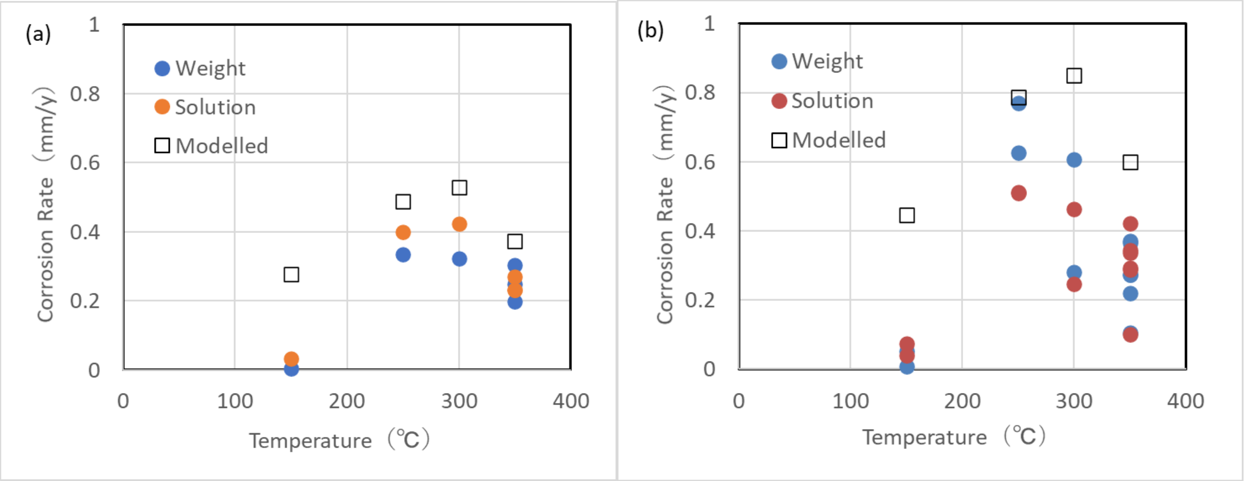

Figure 7: Measured corrosion rate using weight change and dissolved metal concentration and modelled corrosion rate using Cr equivalent after 3 days of testing from 150 to 350 ºC with addition of H_2SO_4, (a) 17Cr, (b) Super 13Cr

4.3 Ratio of corrosion rate between 17Cr and Super 13Cr

Figure 8 shows the ratio of corrosion rate of Super 13Cr/17Cr of measured rate using solution and weight change after 8 days of testing from 250 to 350ºC. Based on the modelled corrosion rate, the ratio of Super 13Cr/17Cr was 1.6 as shown in Table1.

The ratio was higher by about 3 times in the case of weight change at 250 ºC. In all other cases the ratio was lower than 1.6. The ratio estimated by metal concentration in solution was between 1 and 1.6 and slightly increased with temperature. The ratio estimated by weight change decreased with temperature, and was lower than 1 at 350 ºC. The corrosion products on Super 3Cr have been proposed as the main reason for this change of the ratio.

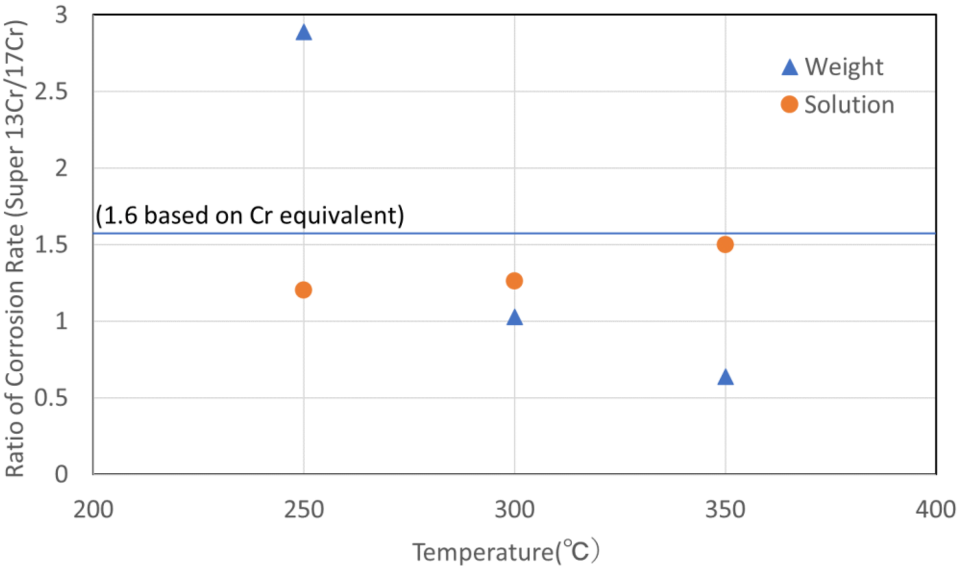

Figure 8 The ratio of corrosion rate of Super13Cr/17Cr of measured rate using solution and weight change after 8 days of testing from 250 to 350 ºC.

6. CONCLUSIONS

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 is encountered, to select appropriate materials that minimise 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 350 ºC was carried out for the two materials Super 13Cr, and 17Cr. The test brine had a pH of 3.0 at room temperature 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 measured corrosion rate from weight change and dissolved metal concentration shows the highest value at 250 ºC compared to the testing at lower and higher temperatures (up to 350 ºC). The reason of this result has been hypothesized to be a change in corrosion product protective properties resulting from a change of pH at higher temperature (from 3.38 at 250 ºC to 4.5 at 350 ºC) based on geochemical simulator. The ratio of corrosion rate, Super 13Cr/17Cr was lower than the 1.6 estimated value based on Cr equivalent because of these changes.

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