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Laboratory Corrosion Testing of Casing Steels in Acidic Brine and the Field Testing at Kakkonda Geothermal Field

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ABSTRACT

Casing steels of geothermal wells are exposed to high temperature brine and brine of especially low pH, which are capable of causing serious corrosion. The object of this work was to identify cost-effective casing materials under several acidic geothermal brine conditions.

Prior to the laboratory test program, separated brine fluids from a production well of the Kakkonda geothermal field were used for corrosion testing of candidate casing materials for acid well applications. The casing materials were exposed in as-produced mildly acidic fluids, and selected alloys were also tested in further acidified brine fluid. The corrosion test was conducted by a newly developed corrosion test loop which includes an Electrical Resistance probe (ER probe), Linear Polarization Resistance probes (LPR probe), and coupon exposure test rods to monitor the corrosion and scaling data. These works identified pH limits for utilization of the readily corroded casing materials. ER and LPR probe measure more realistic corrosion rates, reflecting the effect of a protective film in a short time. It will be one of methods for monitoring the actual conditions of materials and to make a maintenance plan for a plant. The obtained results provide cost effective casing materials options for utilization of mildly acidic geothermal well fluids.

We have conducted laboratory corrosion tests using a hydrothermal apparatus that can conduct corrosion tests under continuously flowing conditions at the Wairakei Research Centre, GNS Science. The objective of the experiment was to determine the extent and characteristics of corrosion of several casing materials after being exposed to fluid at elevated temperatures between 250-350 °C and low pH. We have conducted initial experiments using this apparatus and take corrosion rate data for about 6 hours exposure time. We will have a plan to conduct the experiments for more long exposure time. The corrosion data will be important to select a suitable material using a material selection chart.

This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

1. INTRODUCTION

As it has been desirable to introduce renewable energy since the Great East Japan Earthquake of 2011, geothermal power generation that can be used as a baseload power source has attracted much attention in Japan. Geothermal power generation uses resources such as brine and steam (geothermal fluid) in a reservoir. Therefore, corrosion and scale formation due to various chemical components contained in hot water greatly affect operation of the geothermal power plant. In fact, according to a questionnaire survey of domestic geothermal power producers, corrosion, erosion, and scale formation have accounted for 75% of damage observed in geothermal facilities (geothermal wells, transmission piping, power generation facilities). In order to improve the utilization rate of a geothermal power plant, it is necessary to reduce these operational risks by predicting these risks and taking appropriate measures at the design stage and in maintenance planning of the power plant.

Geothermal fluid has a major impact on the operation of geothermal power plants. In particular, when the hot water is acidic, the well casing, the surface piping, and the power generation facilities that are typically made of carbon steel often suffer damage due to overall corrosion and erosion. In carbon steel and low alloy steel, corrosion progresses in a high temperature environment of pH 4 or less. In austenitic stainless steels and duplex stainless steels, it is known that chloride stress corrosion cracking (Cl SCC) is more likely to occur at shutdowns when both chloride and hydrogen sulfide are present. In non-aerated hydrogen sulfide containing geothermal environments, pitting corrosion, crevice corrosion and sulfide stress cracking (SSC) may occur, for example, in martensitic stainless steel. As described above, when using acidic hot water, it is necessary to select an appropriate metal material depending on the hydrothermal conditions, the components of the non-condensable gas, temperature, pH, and other contaminants. According to a questionnaire (NEDO, 1992) for geothermal development companies implemented in fiscal 1992, the percentage of the number of wells with acid hydrothermal water of pH 5 or less was 13.3%. Moreover, the distribution of acidic hot water resources in Japan is of the order 30%. Geothermal wells are typically drilled for production purposes, but it is impossible to predict near-neutral fluids in places where acid hot water appears frequently. Assuming that the resource potential of high-temperature hydrothermal convection resources (>150 °C) is 23,470 MW (Muraoka, 2008), which is the latest evaluation value, 7,041 MW, corresponding to 30% of the total, are potentially acidic hydrothermal resources. In addition, 30% of 980 MW, which is the target of new power plant construction in 2030, corresponds to a worst-case scenario where 294 MW is from acidic fluids. In other words, the development of countermeasure technology for utilizing acidic hydrothermal water resources is considered an important technology for promoting geothermal resource utilization in the future.

We have developed a "Risk Assessment System for Geothermal Power Plants" by "Geothermal power generation technology research and development / Innovative technology development conducive to expansion of introduction of geothermal power / R&D of risk assessment and countermeasure method of geothermal power plant (scale/corrosion forecast countermeasure management)" from FY 2014 to FY 2017. It is composed of corrosion rate prediction calculations based on Cr equivalent, corrosion rate prediction calculations based on regression of experimental results, field testing data, and literature data. We also referred to research data of material corrosion experiment, which is studied by the Sunshine Project Research, started in 1980, by the Government Industrial Research Institute, Tohoku (presently: Tohoku Center of National Institute of Advanced Industrial Science and Technology (AIST)). Hereinafter, the research data is referred to as the "Sunshine Project Data" (The Government Industrial Research Institute, Tohoku, (1985)).

Since FY2018 we have been 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. In this R&D project, we will develop a system that can specify optimal materials and countermeasure technologies when considering the use of acidic hydrothermal resources.

2. DEVELOPMENT OF CORROSION MONITORING SYSTEM

An important consideration is to select suitable materials that are acceptable for the geothermal brine in order to maintain and manage the geothermal power plant. Especially, when using acid brine, it is necessary to select appropriate materials that correspond to the corrosion risk. When fluid properties change after operation, it is important for maintenance and management of the power plant to find out the information appropriately and to respond accordingly. The corrosion monitoring technology is aimed at evaluating the corrosion resistance performance of metallic materials in selected brines in a short time, and at achieving this with a compact system.

2.1 Development of Risk Assessment System for Geothermal Power Plants

We will develop a system that integrates corrosion/scale and other prediction technologies/countermeasures databases, and actual field monitoring methods, with the aim to reduce damage that may occur in geothermal equipment. The risk assessment system of the geothermal power plant is a system to estimate the corrosion rate of metallic materials from the chemical properties of geothermal fluid, using a Cr-equivalent formula developed on the basis of Excel, and the regression formula of Sunshine Project Data. The material selection flowchart can be used for selection of a metal material suitable for use in a geothermal power plant by reference to the geochemical properties of the brine. The basic process is based on the flow chart by Sanada et al. (2000). Figure 1 shows the conceptual flow of a geothermal power plant risk assessment system and the targeted development from this NEDO project.

We developed a flow-type corrosion test system to conduct corrosion tests using actual geothermal fluid in order to select metal materials. This equipment has, for example, been installed as a bypass route for the target well piping. Use of on-line electrical resistance and electrochemical methods enables evaluation of the corrosion rate for various metal materials in a relatively short time. By using this test system, accurate corrosion rate data can be obtained in a short time to support material selection and maintenance decision-making.

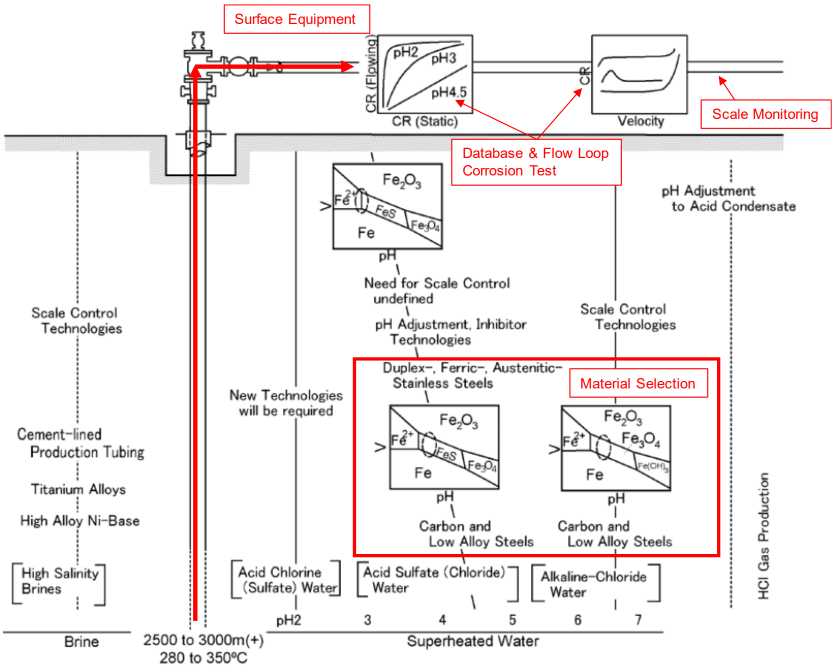

Figure 1: Conceptual flow diagram of a geothermal power plant risk assessment system (adapted from Sanada et al., 2000).

2.2 Corrosion monitoring system

The corrosion monitoring system was developed as a flow-type corrosion test system that can be installed as a bypass route in piping, or at a wellhead. The system was described by Osato et al. (2015) and by Yanagisawa et al. (2015). The apparatus is equipped with four Y-shaped measurement points for installing corrosion rate measurement probes and thermometers. By making the measuring point Y-shaped, each measuring instrument can be installed parallel to the flow, and the flow is less likely to be disturbed as compared with right-angle piping and other monitor access systems. A Computational Fluid Dynamics (CFD) model for the Y-shaped measuring points has been described by Lichti et al. (2020). Readily installed probes, an Electric Resistance probe (ER probe) for continuously measuring the amount of corrosion, and a Linear Polarization Resistance probe (LPR probe) capable of continuously measuring an instantaneous value of the corrosion rate were used (Table 1). We also set multiple metal coupons that were manufactured in a cylinder shape. They were attached to a metal rod which was insulated by Teflon coating. The coupons were separated electrically by placing a Teflon O-ring between adjacent coupons. The specifications of each probe are shown below.

Table 1: Description of measurement probes.

	Electric Resistance Probe (ER Probe)	Linear Polarization Resistance Probe (LPR Probe)	Coupon (Cylindrical type)
Manufacture	COSASCO	Probe: COSASCO Electrode: Tenaris NKKTubes	TenarisNKKTubes
Model	Model 2500HT	Model 7012	-
Max Temperature (deg.C)	540 deg.C	150 deg.C	-
Max. Pressure (MPa)	27.6 MPa	3.4 MPa	-
Material	Carbon Steel	K55 (Carbon Steel), TN80SS (1Cr), TN80Cr13 (13Cr), TN110Cr13S (13CrS)	K55 (Carbon Steel), TN80SS (1Cr), TN80Cr13 (13Cr), TN110Cr13S (13CrS)
Type	Cylinder Type D, T-20, Span 10	2 Electrodes	O.D.: 8 mm I.D.: 5.2 mm Length: 29 mm

3. DEMONSTRATION TESTS AT KAKKONDA GEOTHERMAL FIELD

Field testing at Kakkonda was proposed, as there is considerable energy availability from intermediate depth wells in this field. However, these wells tend to produce acidic brines (Kasai et al., 2000). In addition, acid wells, such as well A, have been successfully used for production for many years and it was desired to understand the reasons for this good performance. The steam is passed to the power station while the brine is sent to reinjection by gravity feed to a well located downhill from the production well pad. Fluid from the brine pipeline was made available for testing in the corrosion test loop from a bottom of pipe sampling valve.

Well A was operated at a pressure of 2.59 MPa and a temperature of 223ºC during the testing. The steam and brine flow rates were 22 t/h and 31 t/h, respectively, under the separation condition of 152ºC and 0.4 $\mathrm{MPa_g}$. The pressure of the brine pipeline was a critical control parameter for the operation of the separator and power station. Therefore, the opening of the supply valve feeding the corrosion test loop was required to be critically controlled, and power station operators had to be notified regarding changes so that adjustments to control could be made.

3.1 Site set-up for the corrosion test loop

The corrosion test loop arrangement used on site is illustrated in Figure 2. During commissioning of the corrosion test loop, a pressure of 0.2 MPa and temperature of 132.6 ºC were established with a flow rate of 456 kg/h of brine, giving a velocity of 0.25 m/s in the corrosion test loop. Small variations in mass flow could be achieved through changes in the corrosion test loop temperature and pressure. Control of flashing in the corrosion test loop was achieved mainly through control of the exit control valve set points.

Any variation in mass flow could be approximated by examination of the discharge flush that was sent to a nearby open tank. The corrosion test loop arrangement for flow control proved to be quite stable and could be left overnight with little variation in resultant conditions the following morning.

3.2 On-site chemistry monitoring and on-line corrosion monitoring

On-site chemistry monitoring was achieved by sampling of the brine through a cooling coil and measurement of pH and conductivity. Horizontal positioning of the sampling point was critical to avoid formation of a steam pocket and dilution of the acid brine with steam condensate. Periodic measurements were conducted to confirm stable chemical conditions. On-line corrosion monitoring of the ER probes was done immediately on start-up after reaching operating temperature and repeated shortly after with a 15- to 30-minute measurement interval for the duration of the test. Monitoring of LPR probes is known to result in some potential shift to the working electrode, and some rest time is required before a repeat measurement can be conducted. LPR probes were measured immediately on exposure and reaching temperature, and on a 30- to 45-minute repeated cycle for the duration of the test.

Measurements of corrosion potential of the LPR electrodes were conducted with reference to a prepared silver/silver sulfide reference electrode (Crowe and Tromans, 1986). The room temperature rest potentials of the silver/silver sulfide reference electrode, as measured before and after the tests, were inconsistent, suggesting some drift in the electrode properties while on-line. Although the measurements were continuous and appeared to be consistent from test to test, the quantification of the corrosion potential is not without question. Flow tests were completed only when changes were made to conditions of testing (P and T). On completion of each test, the exposed samples were immediately removed from the corrosion test loop as soon as the pressure was reduced, and the liquid stream was allowed to discharge. The samples were not further washed but allowed to dry on nearby "hot" piping where photographic records were prepared, and a visual examination was completed. The probes, electrodes, and coupons were then allowed to cool before being packed with desiccant for transport in sealed plastic containers.

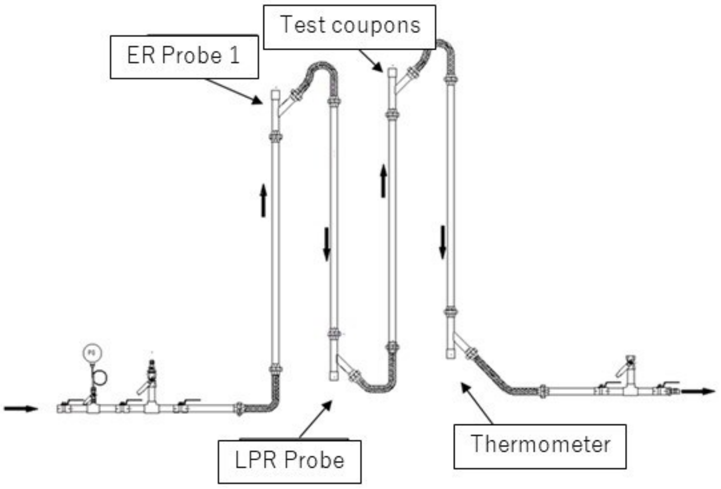

Figure 2: Flow-through type portable corrosion test equipment.

3.3 Site testing program and analysis of results

The results of the on-line monitoring were evaluated during the testing period to identify trends in the data. These on-site analysis results were used to establish timing for completion of the individual tests and for re-confirmation of the proposed next test conditions. Each test result was further evaluated in the evening following the testing, and in a meeting held to re-confirm the testing program for the next day. The testing program included two longer term tests that ran overnight. These extended tests were successful in terms of control of exposure conditions using the manually set valves. No significant upsets were observed. Early morning measurements following an extended period of exposure confirmed trends observed the previous day after only a few hours. The ER probe results gave additional confidence that the short-term testing results were valid. The confirmation of the LPR trends was considered most significant, as the measurements after the long period without polarization also followed initial projections.

3.4 Laboratory analysis program

Exposed materials, once moved to the laboratory, were again subjected to visual examination prior to selective cleaning and inspection of corroded surfaces, and some samples were used for selected analysis of un-cleaned samples for identification of formed scale and corrosion products. Exposed LPR electrodes and coupons were re-weighed to four significant figures prior to and after cleaning for comparison with the original weights. Cleaning solutions used included 20% NaOH solution with cathodic protection for removal of deposited silica scale and di-hydrogen ammonium citrate solution with cathodic protection for removal of iron-based corrosion products. In combination, these two solutions are known to be capable of removing other deposits and scale commonly formed in geothermal fluids. The mechanisms of removal are believed to be a combination of scale dissolution and metal complexing. Cathodic protection was applied via a carbon anode. Each sample was individually cleaned. Cleaning was always followed by washing and warm air drying, and for samples that were to be weighed, storage under desiccant and cooling prior to re-weighing.

Following cleaning, the surfaces of the cleaned samples were examined under a binocular microscope for evidence of localized pitting corrosion. The five deepest pits were marked for pit depth measurement using an optical microscope with a calibrated stage. The deepest five pits (fewer if less were found), and mean and maximum pit depths were then tabulated. Selected duplicate samples were kept for surface scale and corrosion product analysis by one or more rounds of SEM-EDX analysis.

4. TEST RESULTS OF DEMONSTRATION TESTS

The corrosion test of the geothermal well was conducted using the developed Flow-Through Type Portable Corrosion Test Equipment. The corrosion rate obtained by the test was evaluated. The evaluation was carried out by comparison with the Sunshine Project Data.

4.1 Corrosion rate measurement by each method in demonstration test

In the demonstration test, corrosion rate measurement was conducted using single-phase injection brine. Since the electrical resistance probe (ER probe) is made of carbon steel, it is compared with K-55 cylindrical coupons and J-55 data of the Sunshine Project Data. The linear polarization resistance probe (LPR probe) and the cylinder type test piece were prepared from K-55, TN80SS (1Cr), TN80Cr13 (13Cr), and TN110Cr13S (13CrS).

4.2 Evaluation result of corrosion rate in the condition of single-phase

The following data are summarized as the evaluation results of the corrosion rate, including the ER probe and LPR probe data, which produces continuous corrosion data, and the cylindrical coupon data, which produces corrosion rate by weight loss data. In the case of the ER and LPR probes that produce continuous corrosion rate data, it is possible to find a decrease in the amount of corrosion due to the formation of a protective film on a metal surface. For this reason, it is possible to estimate the amount of corrosion after one year. In the coupon method, the amount of corrosion rate after one year is obtained by linear approximation, because the number of data are limited. On the other hand, the continuous measurement method makes it possible to estimate by parabolic approximation with consideration of the formation of a protective film. Since the corrosion rate estimated by the coupon method is a linear approximation, it is a conservative evaluation from the viewpoint of equipment management. On the other hand, the evaluation value in the continuous measurement method may be used to estimate the replacement time of equipment more accurately. This information will be useful for maintenance of the geothermal plant.

A comparison of corrosion rate data by each measurement method is summarized in Figure 3. It also includes Sunshine Project Data that are analyzed by laboratory testing, as reference data. It describes ranges of the corrosion rate data for K55, 1Cr and 13Cr at the conditions of pH 3.0 acidified with H_2SO_4 and HCl, and a temperature of 150 °C. The field experiments are conducted using single-phase brine of pH 3.6. The exposure time is a maximum of about 23.8 hours. We compared the corrosion rate, which is estimated by the continuous method, coupon method and Sunshine Project Data. In case of the continuous measurement method (ER and LPR probe), the corrosion rate after one year was estimated by parabolic approximation.

The corrosion rates of K-55, TN80SS and TN80Cr13 are nearly consistent with the coupon method of the Sunshine Project Data. The corrosion rate of TN110Cr13S is lower than Sunshine Project Data. The estimated corrosion rate of K-55 by ER probe is about 0.19 mm/year. The corrosion rate is one order of magnitude lower than the estimated corrosion rate by coupon method (1.61 mm/year) and Sunshine Project Data (1.0-2.3 mm/year). In the case of the LPR probe, the number of measurements is limited, and the TN80SS data fluctuated. The estimated corrosion rate, based on the data, are 0.34 mm/year for K-55, 0.69 mm/year for TN80SS, 0.069 mm/year for TN80Cr13. We could not measure the corrosion rate for TN110Cr13S because no corrosion occurred. The corrosion rate without the TN80SS data are one order of magnitude lower than the estimated corrosion rate by the coupon method (1.61 mm/year for K-55 and TN80SS, 0.17 mm/year for TN80Cr13) and the Sunshine Project Data (1.0-2.3 mm/year for K-55, 0.4-1.0 mm/year for 1Cr (TN80SS), and 0.18-0.48 mm/year for 13Cr (TN80Cr13)).

These results suggest that the actual life of metal material can be longer than the value predicted by the coupon method. In the case of the coupon method, it is also possible to monitor changes of corrosion rate by using multiple coupons. But it takes a significant amount of time to collect a sufficient quantity of data. In the case of continuous measurements, the experiment results revealed that it is feasible to determine a corrosion rate in an experiment lasting a few days. These data are considered to be valuable for creating a maintenance plan for a plant, because they may allow operators to know the service life of a facility that is closer to actuality.

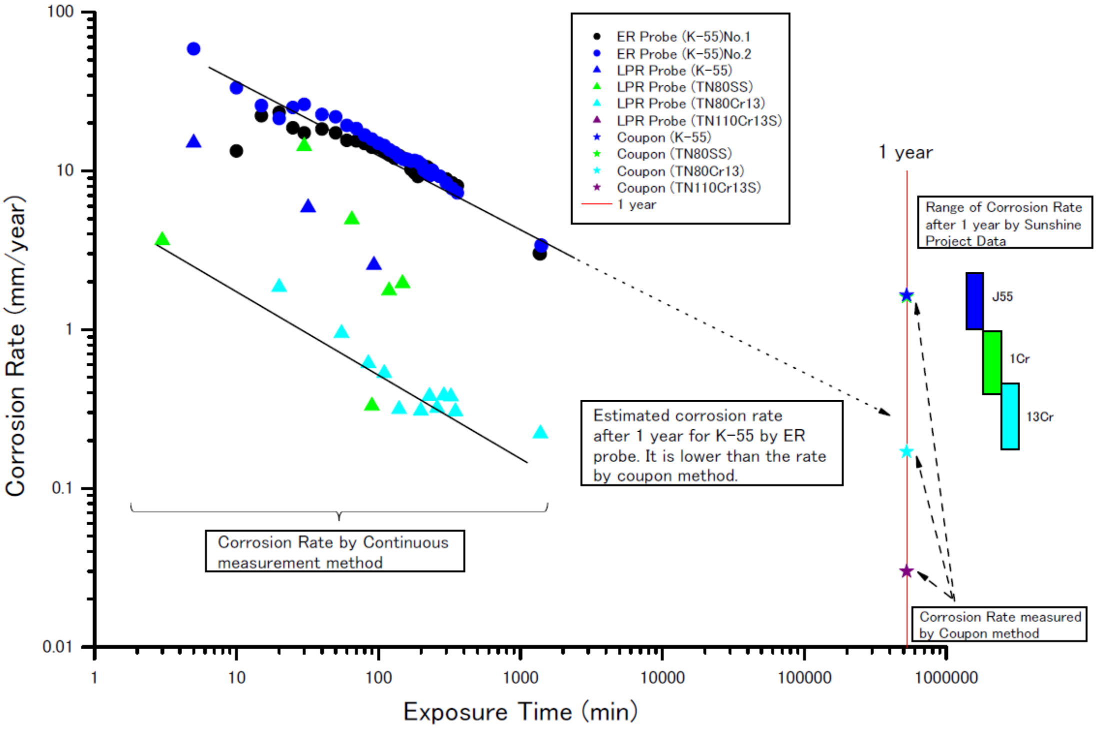

Figure 3: Corrosion rate data by each measurement method compared with Sunshine Project Data.

5. LABORATORY CORROSION TEST UNDER HIGH TEMPERATURE AND LOW PH CONDITIONS

In order to select materials that can be used in a high temperature, low pH hydrothermal environment, we evaluated the performance of 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 4). 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 corrosive environment of an actual casing or piping.

5.1 Experimental apparatus for corrosion test

In the corrosion test, we used a Hydrothermal flow simulator owned by GNS Science of New Zealand. This apparatus can simulate water-rock interaction in a geothermal reservoir, and can adjust pH, temperature, and non-condensable gas conditions for this purpose. 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 chemistry of actual corrosive environment for casings and pipes.

Prepared test materials include a cylindrical coupon of OD 8 mm x 13 mm. The coupon was set so as not to directly touch the pressure vessel made of titanium by inserting OD 2 mm Zirconia beads. We have set just one coupon in the pressure vessel. Initially, we planned to set multiple coupons, but the test plan was changed because the downstream coupons were affected by the corrosion of the upstream coupons. 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 a heater and the pressure was controlled by a back-pressure regulator. The temperature was set to 250 °C, 300 °C, and 350 °C, and the pressure was set to 20 MPa. In addition, the test brine after reacting with a metal coupon can be collected by syringe from an outlet of the pressure vessel, and analysis of pH and a chemical component can be conducted.

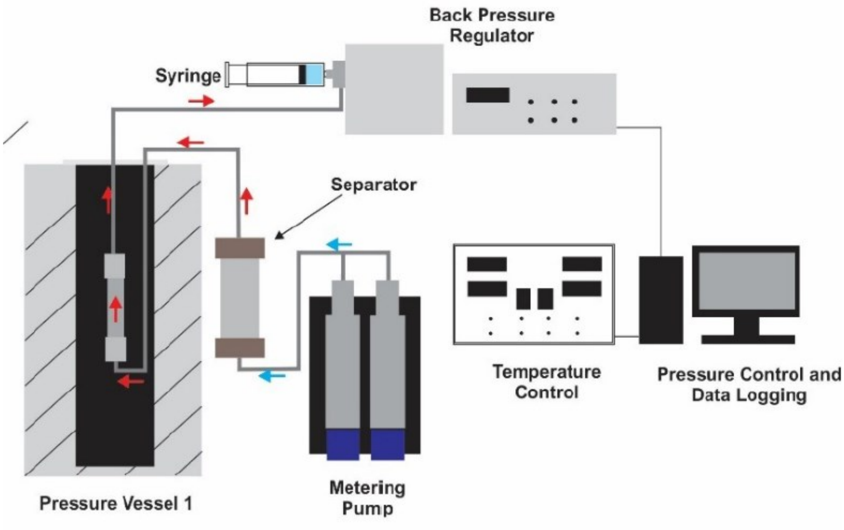

Figure 4: Hydrothermal flow simulator at Wairakei Research Centre, GNS Science.

5.2 Conditions of Corrosion Experiments

The materials of the test coupons were TN95Cr13S, TN125Cr13U, and 17Cr. These materials were processed and supplied by TenarisNKKTubes. The mixing ratio of Cr and Mo in each material is shown in Table 2. The test brine used in this test was adjusted to pH 3.0 with sulfuric and hydrochloric acid, and mixed with 3 vol.% non-condensable gas (96% CO_2, 4% H_2S).

Table 2: Cr and Mo content in each material.

Material	Cr Content	Mo Content
TN95Cr13S	13%	2.0%
TN125Cr13U	13%	3.0%
17Cr	17%	2.5%

5.3 Results of Blank Test

Blank tests were conducted under two conditions. Condition 1 was carried out without putting anything in the pressure vessel that was made of titanium, and Condition 2 was carried out with the zirconia beads packed in the pressure vessel. For the zirconia beads of Condition 2, we tried to use new zirconia beads and used zirconia beads that had been cleaned by multiple use. The experiment conditions were carried out at a temperature of 300 °C, using test brine with pH 3.0, Cl^- 10,000 ppm, and containing NCG. The test results are shown in Figure 5. As a general trend, the pH of the outlet brine was raised due to the presence of the zirconia beads. The extent of the pH increase depended on the flow rate, rising to 3.0-3.5 at 10 mL/h and to 3.0 to 3.25 at 50 mL/h. In addition, it was found that the pH increased slightly even with the pressure vessel alone under the condition of a flow rate of 10 mL/h. The analysis result of the Mg concentration in the outlet brine after passing through the pressure vessel is shown in Figure 6. As a result, the concentration of Mg in the outlet brine shows the same concentration in the case of using new zirconia beads and in the case of using repeatedly washed zirconia beads. Magnesium oxide is added to improve the corrosion resistance performance of the zirconia beads (Table 3). The pH of the outlet brine was slightly increased by reaction with the magnesium oxide. Since the amount of hot test water was limited by the separator volume (1 L), it was necessary to set a low flow rate to carry out the corrosion test for as long as possible. In this result, when the flow rate was set to 50 mL/h, the pH at the outlet brine was about 3.25. This indicates that the rate of pH increase can be controlled to 10% or less. Also, the test coupon was set on the inlet side of the pressure vessel. This means that the test brine adjusted to pH 3.0 will contact a metal coupon at almost the same time as entering the pressure vessel. It was considered that it is possible to conduct the corrosion test within pH 3.0-3.3 (a 10% variation).

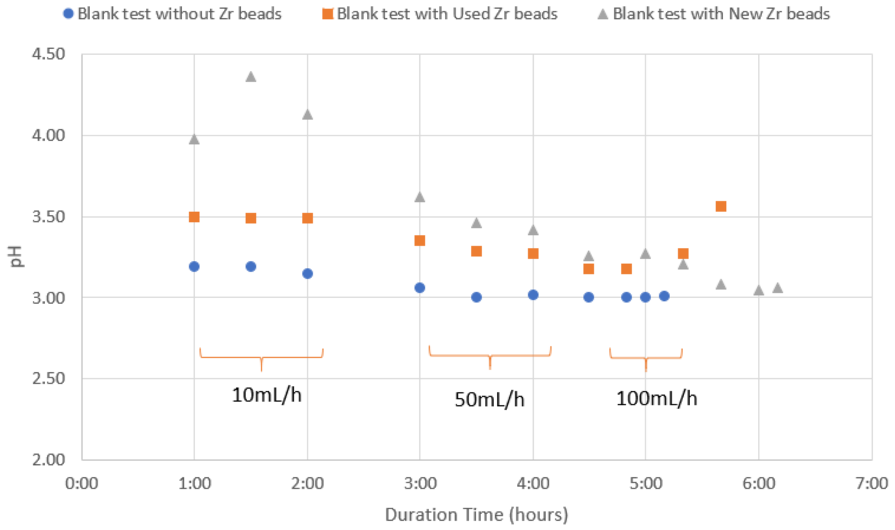

Figure 5: Results of Blank test (pH in outlet brine).

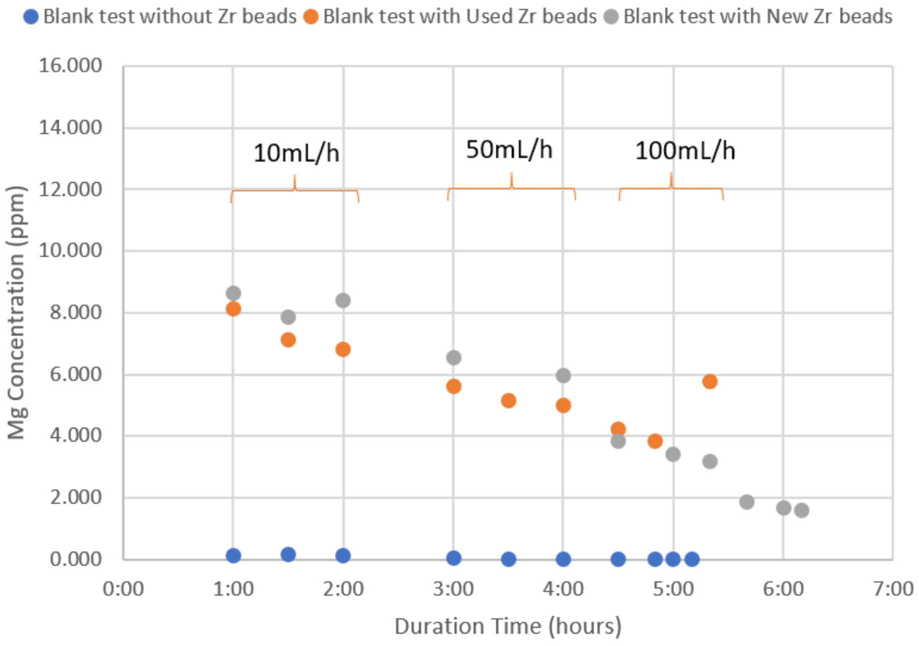

Figure 6: Results of Blank test (Mg concentration in outlet brine).

Table 3: Quantitative analysis of Zr beads.

Compound	Mass %
ZrO_2	95.92
MgO	2.35
Al_2O_3	1.39
CaO	0.09
FeO	0.25

5.3 Results of Corrosion Tests

Measurement of corrosion rates under the conditions of 250 °C, 300 °C, and 350 °C was carried out for the three materials TN95Cr13S, TN125Cr13U, and 17Cr. The test brine had a pH of 3.0 and contained 3% non-condensable gas (96% CO_2, 4% H_2S) and 10,000 ppm 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, dissolution 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 (Braithwaite and Lichti, 1980). The dissolution was carried out at 70 °C with cathodic protection using a carbon rod for the anode. Final weight measurement was performed, because no weight loss was observed after about 20 minutes of dissolution (Figure 7).

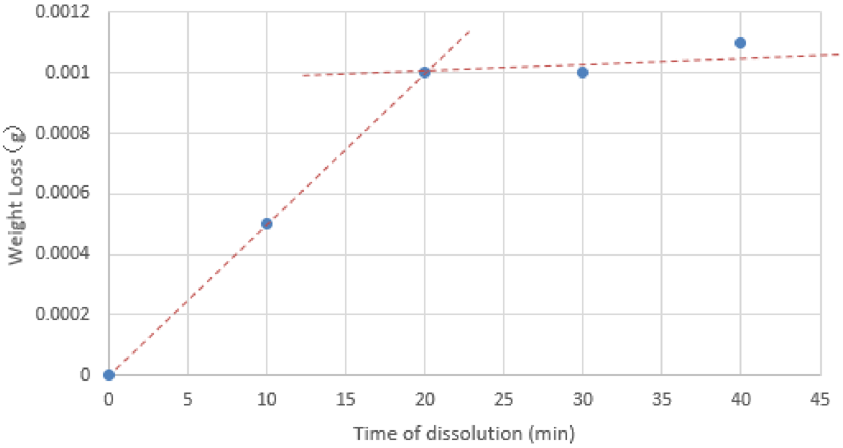

Figure 7: Weight loss versus time of dissolution.

The results of converting weight loss into corrosion rate after one year are summarized in Figure 8 and Figure 9. Figure 8 shows the test results in sulfuric acid, and Figure 9 shows the test results in hydrochloric acid. In the case of sulfuric acid, although the corrosion rate of TN125Cr13U at 250 °C indicates 1.4 mm/year, the corrosion rate of other conditions was 1 mm/year or less. When comparing the corrosion rates among the metals, the same tendency was not found in these results. However, the corrosion rate of 17Cr at 300 °C was 0.384 mm/year. In case of hydrochloric acid, the corrosion rate often exceeded 1 mm/year. The corrosion rate with hydrochloric acid was relatively high compared to that of sulfuric acid. The corrosion rate decreased significantly from TN95Cr13S to 17Cr at 250 °C. The same tendency is not seen at 300 °C and 350 °C, and a corrosion rate exceeding 1 mm/year was observed for 17Cr.

The pitting observation results are shown in Table 4, which summarizes the number and depth of observed pitting. Remarkably, pitting was low in this test series. There was 0-1 pit in each test, and very deep pitting was not observed. The present corrosion test had a short exposure time of about 6 hours, so it was likely that the corrosion rate was higher than the expected long-term performance of each metal. The result should be considered a short-term corrosion rate. 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 film.

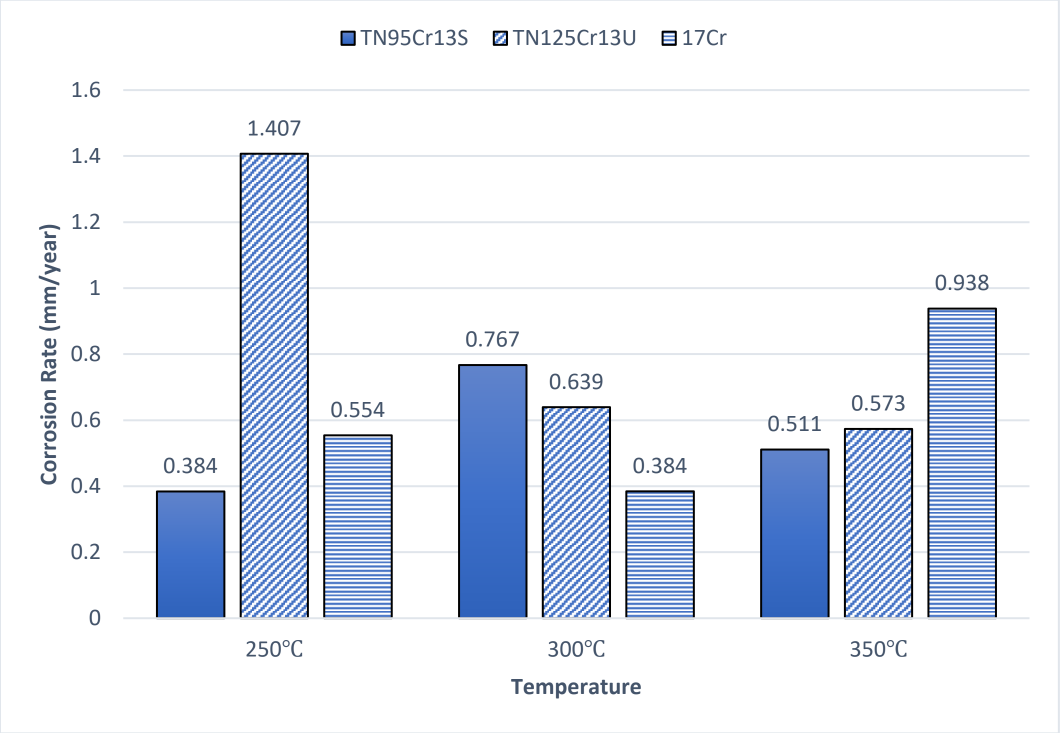

Figure 8: Corrosion rate calculated by weight loss (acidified to pH 3 with H_2SO_4, after 6 hours).

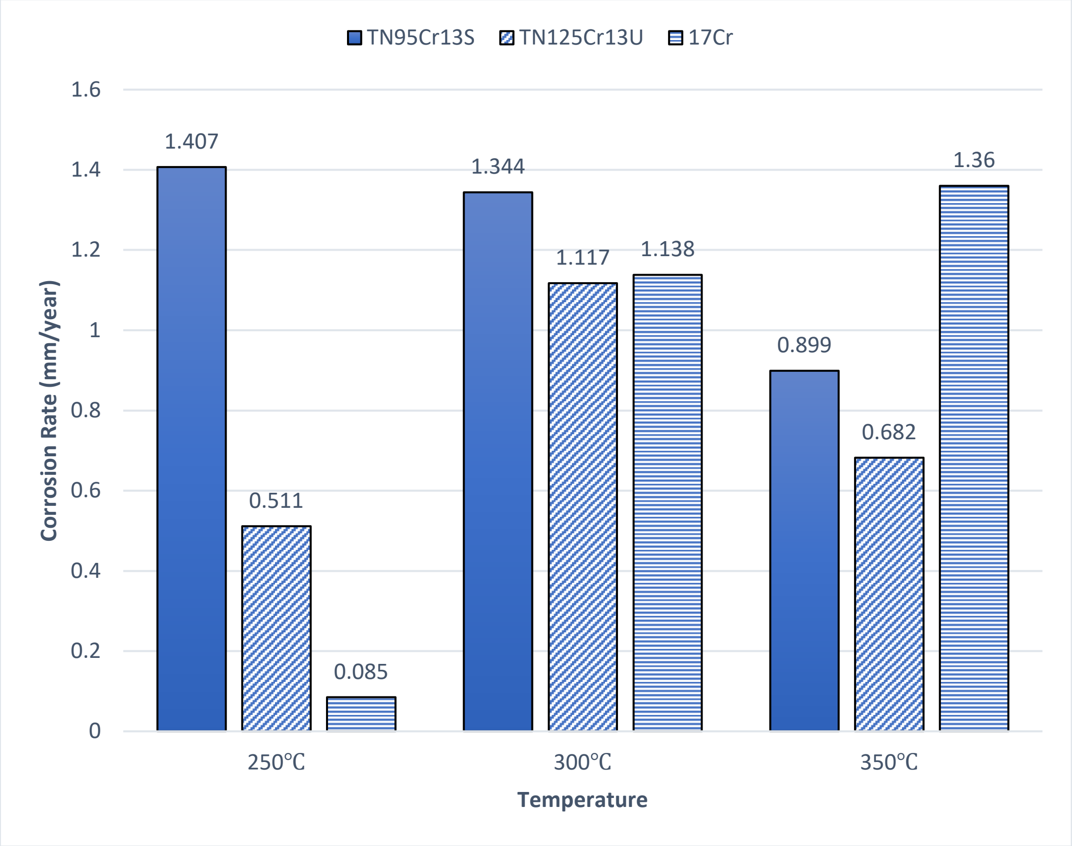

Figure 9: Corrosion rate calculated by weight loss (acidified to pH3 with HCl, after 6 hours).

Table 4: Results of pitting analysis and corrosion rate by mass loss.

Material	Temp.	Acid	Pitting	Depth (μm)	Length (μm)	Corrosion Rate (mm/year)
17Cr	250	H_2SO_4	1	17	–	0.554
		HCl	1	7	287	0.085
	300	H_2SO_4	1	–	–	0.384
		HCl	0	–	–	1.138
	350	H_2SO_4	0	–	–	0.938
		HCl	–	–	–	1.360
TN125Cr13U	250	H_2SO_4	0	–	–	1.407
		HCl	1	–	–	0.511
	300	H_2SO_4	1	–	–	0.639
		HCl	1	–	–	1.117
	350	H_2SO_4	1	–	–	0.573
		HCl	<1	–	–	0.682
TN95Cr13S	250	H_2SO_4	1	–	–	0.384
		HCl	1	–	–	1.407
	300	H_2SO_4	1	10	257	0.767
		HCl	–	–	–	1.344
	350	H_2SO_4	1	14	–	0.511
		HCl	0	–	–	0.899

6. CONCLUSION

It is important to select suitable materials that are acceptable 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 this project, we clarified that the developed Flow-Through Type Portable Corrosion Test Equipment can be used for monitoring corrosion rates using required materials in actual geothermal brine. The continuous measurement method (ER probe and LPR probe) will measure more realistic corrosion rates, reflecting the effect of a protective film in a short time. It will be one of methods for monitoring actual condition of material and to make maintenance plan for a plant. We have been proceeding Laboratory corrosion experiments under high temperature and low pH conditions for existing (TN95Cr13S) and newly materials (TN125Cr13U, 17Cr) for geothermal. The corrosion data will be important to select a suitable material using material selection chart. We will have a plan to conduct the experiments under more long duration time. The following is a summary of the results of corrosion testing.

i. We have developed “Flow-Through Type Portable Corrosion Test Equipment” that can be installed as a bypass route in piping, or at a wellhead. The apparatus is equipped with four Y-shaped measurement points for installing corrosion rate measurement probes and thermometers. It monitors real-time corrosion rates using an Electric Resistance probe (ER probe) and a Linear Polarization Resistance probe (LPR probe). It is also possible to set multiple cylindrical coupons in it and compare the corrosion rates with ER and LPR probe data.

ii. The corrosion rates measured by ER and LPR probes are one order of magnitude lower than the estimated corrosion rate by coupon method and Sunshine Project Data. It suggests that the actual life of metal material can be longer than the value predicted by the coupon method.

iii. In the case of the continuous measurement method, it is possible to monitor the changes of corrosion rates to duration time. It becomes possible to estimate a more probable corrosion rate (corrosion amount) after one year using the data. This information will be valuable for creating a maintenance plan of the plant facility.

iv. 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 °C, 300 °C, and 350 °C was carried out for three candidate casing materials: TN95Cr13S, TN125Cr13U, and 17Cr. The test brine had a pH of 3.0 and contained 3 vol% non-condensable gas (96% CO_2, 4% H_2S) and chloride ion (10,000 ppm).

v. In the case of pH adjustment by sulfuric acid, although the corrosion rate of TN125Cr13U at 250 °C was about 1.4 mm/year, the corrosion rates at 300 °C and 350 °C were 1 mm/year or less. When comparing the corrosion rates based on the temperature condition, the corrosion rate is not increased by the temperature. In the case of pH adjustment by hydrochloric acid, the corrosion rate often exceeded 1 mm/year. The corrosion rate with hydrochloric acid tended to be relatively high compared to that with sulfuric acid.

vi. The present corrosion test has a short exposure time of about 6 hours, so it is likely that the corrosion rate is higher than the expected long-term performance of each metal. The result should be considered a short-term corrosion rate. 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 film.

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