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Development of Corrosion Risk Evaluation System in Acidic Geothermal System

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ABSTRACT

We have developed a tool "Geothermal power plant risk assessment system (acidic hot water version)" that can consider the optimal materials for power plant construction when the hot water for geothermal power generation is found to be acidic. If the geothermal resource is acidic hot water, the corrosion and damage to the power generation facilities are large, which is a factor in the decline in the utilization rate of geothermal power plants and the abandonment of development. By using this tool, it is possible to evaluate the corrosion rate and economic efficiency of each metal material, and select the optimum material, including corrosion resistance performance and cost. In addition, preliminary examination of each metal material can be easily performed from the test data and related papers on the corrosion of the target metal material. This is expected to promote the utilization of acidic hot water resources, improve the utilization rate of geothermal power plants, and increase installed capacity.

1. INTRODUCTION

To archive the carbon neutrality by 2050, we need develop the power generation by renewable energy. Japan has the third largest geothermal resources potential. However, the acid hot water (assumed to have a hydrogen ion index [pH] of 5 or less) caused the corrosion and erosion of the materials in well casings, surface piping, and power generation equipment. The corrosion and erosion is one of the reasons for the declining rate and the abandonment of development.

According to the project "Survey Research on Acidic Hot Water Countermeasure Technology" conducted by NEDO (New Energy and Industrial Technology Development Organization) in 1992, based on the questionnaire survey of geothermal development companies , 13% of the geothermal hot water in water convection type resources may be acidic hot water. Since Japan's geothermal resources are about 23,000MW (Muraoka et al., 2008), acid hydrothermal resources are about 3,000MW. This is about five times of the recent power generation in Japan, 621MW (ThinkGeoEnergy, 2023). Then, it is expected that technological development for the utilization of acidic hydrothermal resources will be important in promoting the use of geothermal resources in the future.

Then, NEDO started the project "Geothermal Power Generation Technology Research and Development" at FY2013. And we proposed the project about scaling and corrosion titled "Research and development of risk assessment and countermeasure methods for geothermal power plants" (scale/corrosion prediction and countermeasure management) at FY2014. This project was carried out until FY2017, and main theme was the designing system to measure material corrosion behavior in a short time and conducting material corrosion tests using looped test system in the cases of single-phase flow and two-phase flow in two geothermal areas that generate acidic hot water in Japan. And in the process, we verified the material corrosion prediction formula (Kurata et al., 1992). This prediction formula uses the temperature and pH of the fluid and the Cr equivalent (index of corrosion resistance) of the material used.

Based on this project, we carried out new project titled "Technological development for the utilization of unused geothermal energy (development of technology for utilizing unused acidic hot water in conventional geothermal resources)". In this project, the purpose is to evaluate material corrosion in geothermal fluids (up to about 350°C) and acidity (about pH 3 at room temperature). However, since this test was difficult in Japan, we conducted laboratory tests at GNS Science in New Zealand and field tests at Geysers in the United States. This test also verifies the above material corrosion prediction formula. In addition, we examined inhibitors that suppress corrosion in acidic hot water, collected information on material corrosion cases overseas, and conducted an economic evaluation considering the life of materials.

After these seven-year project, we conclude the predictions of material corrosion rates, economic evaluations, and a corrosion database have been developed to expand the use of acidic hot water for geothermal operators who will develop and operate geothermal power in the future. It was compiled in the form of a power plant risk assessment system (for acidic hot water). The system was informed to press and media on October 20, 2022, by NEDO, GERD, AIST, and Kyoto University. The contents are introduced on each organization's website and taken up in some newspaper.

In this paper, we described the results of several corrosion tests and the contents of corrosion risk evaluation system.

2.CORROSION TESTS DURING PROJECT

2.1 Corrosion rate estimation formula

From the results of New Sunshine project (from 1974 to 2002) of several material corrosion test by AIST-Tohoku (Kurata et al., 1995, Sanada et al., 1995), the corrosion rate depends on temperature, pH and the chemical composition of material. For index 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. The Cr equivalent and corrosion rate (C.R mm/year) are calculated as follows:

In the case of HCl acid condition,

$Cr_{eq} = Cr - 13.73\ C + 1.598\ Si - 0.433\ Mn + 27.28\ P - 51.12\ S + 0.237\ Ni + 0.712\ Mo - 1.060\ Cu$ (wt%)

$\log(C.R) = 6.696 - 1930\ (1/T) - 0.622\ (pH) - 0.085\ (Cr_{eq})$

And in the case of H_2SO_4 acid condition,

$Cr_{eq} = Cr - 16.76\ C + 0.63\ Si + 0.193\ Mn - 10.2\ P + 35.11\ S + 0.187\ Ni + 0.02\ Mo + 0.725\ Cu$ (wt%)

$\log(C.R) = 6.467 - 1633\ (1/T) - 0.697\ (pH) - 0.093\ (Cr_{eq})$

2.2 Hydrothermal fluid test in Japan

To evaluate corrosion rate, we designed the small loop test system as shown in Figure 1 and carried out the corrosion test using acid fluid at Kakkonda geothermal field. The pH and temperature of fluid are 3.5 and from 135 to 145 ℃ (Yanagisawa et al., 2016)

Figure 1: Corrosion test loop system at Kakkonda geothermal field

In this test, we try to measure the corrosion rate using the corrosion meter, LPR probe and cylinder coupon samples. And for cylinder coupon samples, we prepared four materials, K-55 (carbon steel), TN80SS (low alloy steel), TNCr13 and TNCr13S (stainless steel). Firstly, we measured the weight difference by flow test. But several scales such as amorphous silica and metal minerals precipitated on samples, we remove the scale by washing using several acid and NaOH and we measured the weight after DHACP and calculate the corrosion thickness and corrosion rate for each test. And we estimate the average corrosion rate as follows; K-55 is 1.61 mm/year, TN80SS is 1.61 mm/year, TNCr13 is 0.17mm/year and TNCr13S is 0.03mm/year under 145 ℃ and pH 3.6.

Using corrosion rate calculator we estimated the corrosion rate of K-55 carbon steel, TN80SS, TNCr13 and TNCr13S under pH 3.6 at 135 and 145 ℃ in Table 1. And in Table 1 show the average corrosion rate on-site test at Kakkaonda geothermal field. In the case of carbon steel K-55, the calculated corrosion rate is almost same as the average corrosion rate of on-site. Corrosion rate of TN80SS and TNCr13 show almost the same digit as on sites. Regarding TNCr13S shows one digit lower, which is requested to the further investigation.

So far, the equation of corrosion rate using Cr equivalent is useful for the estimation of the corrosion rate of carbon steel, K-55 in the case of one-day flow test at Kakkonda geothermal field.

Table 1: The list of corrosion rate of test materials at Kakkonda geothermal field.

Material	135℃	145℃	On-site
K-55	1.36	1.53	1.61
TN80SS	0.88	0.99	1.61
TNCr13	0.32	0.36	0.17
TN13CrS	0.21	0.23	0.03
			(mm/y)

And we carried out the pH adjustment test using the hot water line by injecting sulfuric acid or hydrochloric acid at Kakkonda geothermal field. The target pH was 4 and 3. The low pH tests were limited by the facilities available for neutralization and so the duration of pH control tests were 5 hours (Yanagisawa et al., 2019). The relative corrosion rate standardized as K-55 (Carbon Steel) is shown in Figure 2. The closed circle shows relative measured corrosion rate and the bar shows estimated corrosion rate. Almost similar relative rate shows between measured and estimated rate.

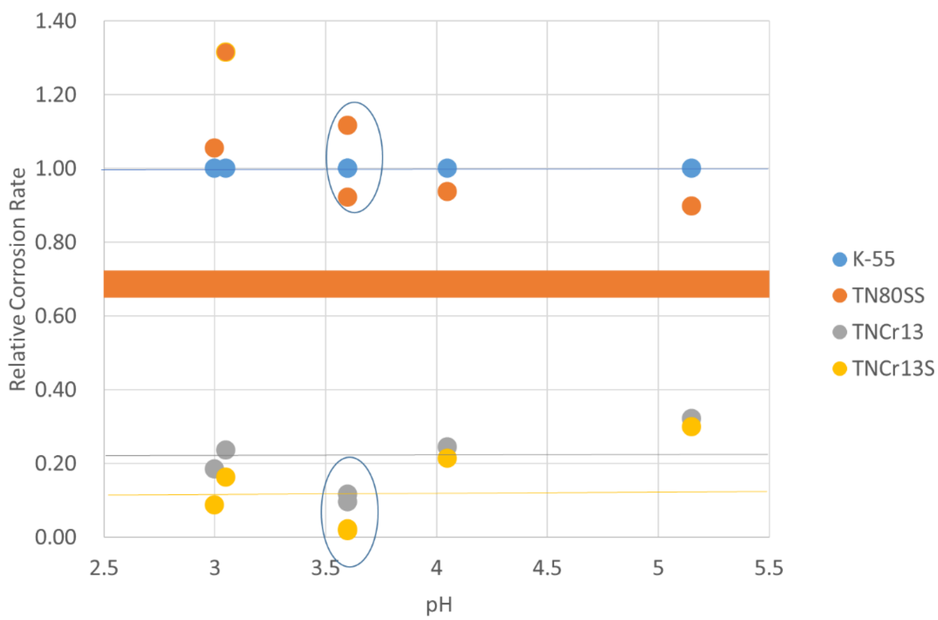

Figure 2: Corrosion test loop system at Kakkonda geothermal field

2.3 High temperature acid fluid test in laboratory

To select materials that can be used in a high temperature, low pH, hydrothermal environment, we evaluated the corrosion resistance of the two candidate materials、TN13CrS and 17Cr, higher CR equivalent than materials used in Kakkonda test, was conducted by using a hydrothermal flow simulator provided by GNS Science, New Zealand (Figure 3).

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, 250, 300, and 350 °C.

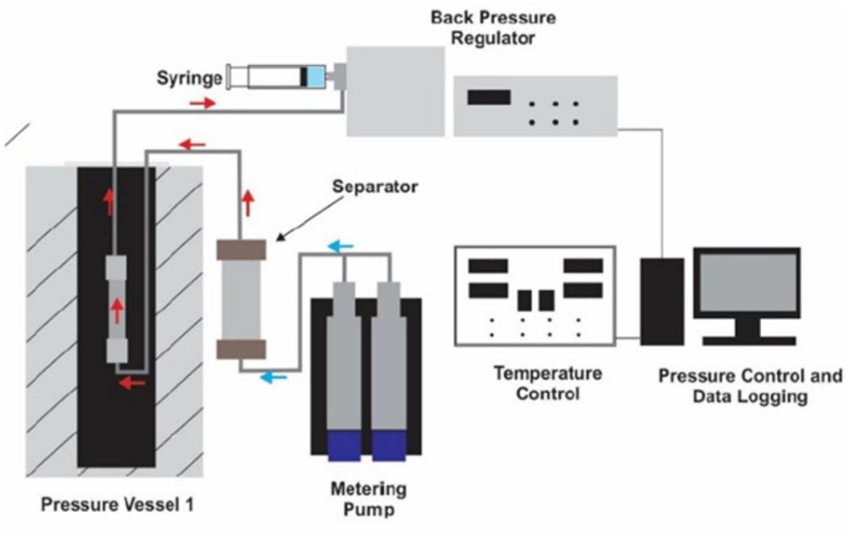

Figure 3: Hydrothermal flow simulator at Wairakei Research Centre, GNS Science, New Zealand.

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.

2) We measured the material change directly due to corrosion by weight change. 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). The pH is similar from the start at room temperature conditions up to 100 ℃ and gradually rises with further increases in temperature. Above 300 ℃, the pH rapidly raises with increasing temperature. The calculated pH was 3.38 at 250 ℃, 3.66 at 300 ℃, and 4.5 at 350 ℃.

Figure 4 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 ℃. Figure 4(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 ℃. Deviation between modelled rate and measured rate (weight/solution) was the highest at 150℃. Figure 4(b) shows the measured corrosion rate using weight change was higher than the rate using metal concentration of solution at 250 ℃ in the case of TN13CrS. The rate using weight change was lower than that using solution concentration at 150 ℃. The measured corrosion rate was highest at 250 ℃, whereas the highest modelled corrosion rate was at 300 ℃. TNCr13S shows the same tendency as Table 1 again.

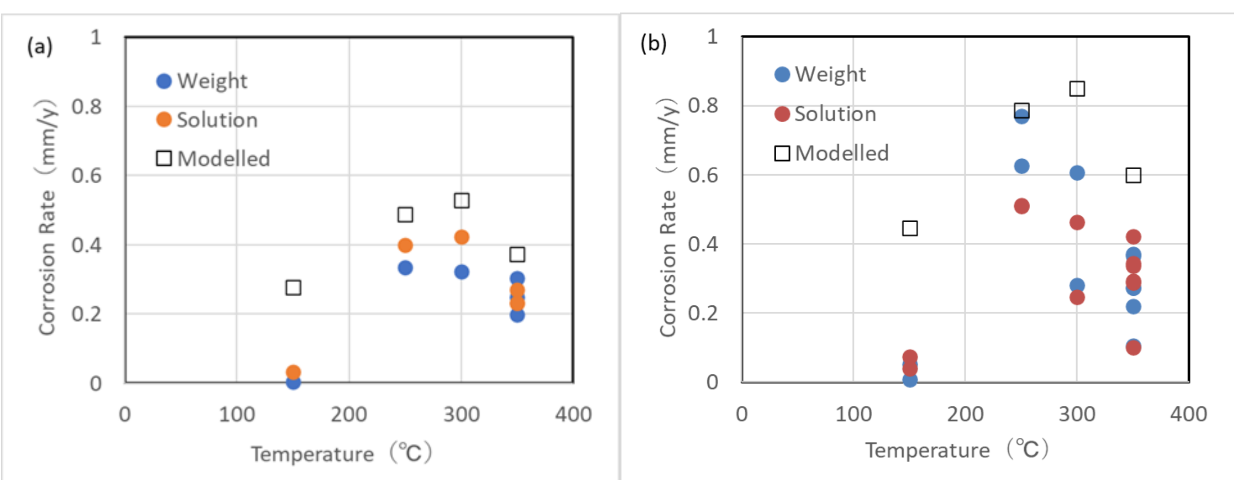

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Figure 4: Measured corrosion rate using weight change and dissolved metal concentration and modelled corrosion rate using Cr equivalent after 3 days of testing from 150 to 350 °C with addition of H_2SO_4, (a) 17Cr, (b) TN13Cr

3. CONTENTS OF ASSESSMENT SYSTEM

The geothermal power plant risk assessment system (for acidic hot water) has the following five functions (see Figure 5).

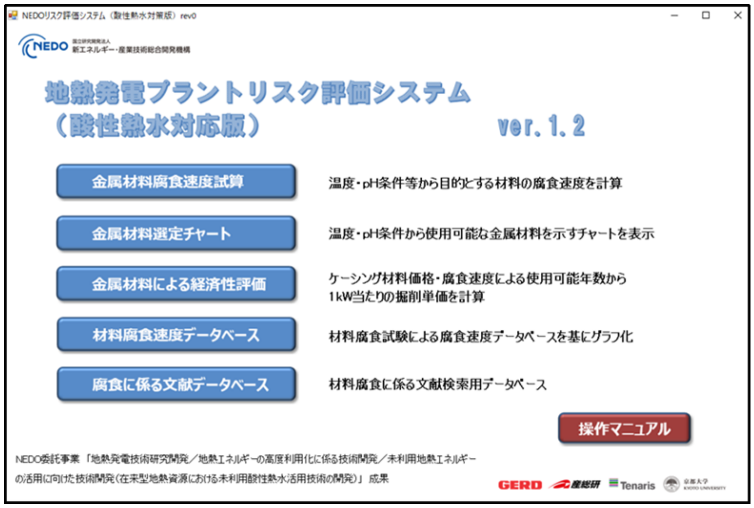


Figure 5: "Geothermal power plant risk assessment system (acidic hot water version)" basic screen.

3.1 Material corrosion rate estimation sheet

The material corrosion rate estimation sheet is shown as Figure 6. By inputting hydrothermal analysis data on the ground surface, such as the temperature and pH of the hot water, you can estimate the corrosion rate (mm/y) of selected material using the corrosion rate estimation formular introduced with the concept of Cr equivalent (Kurata et al., 1992).

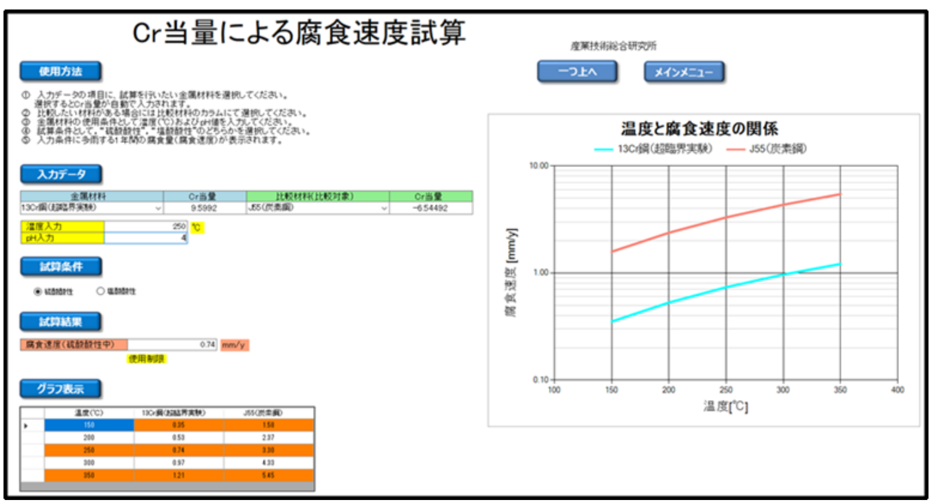
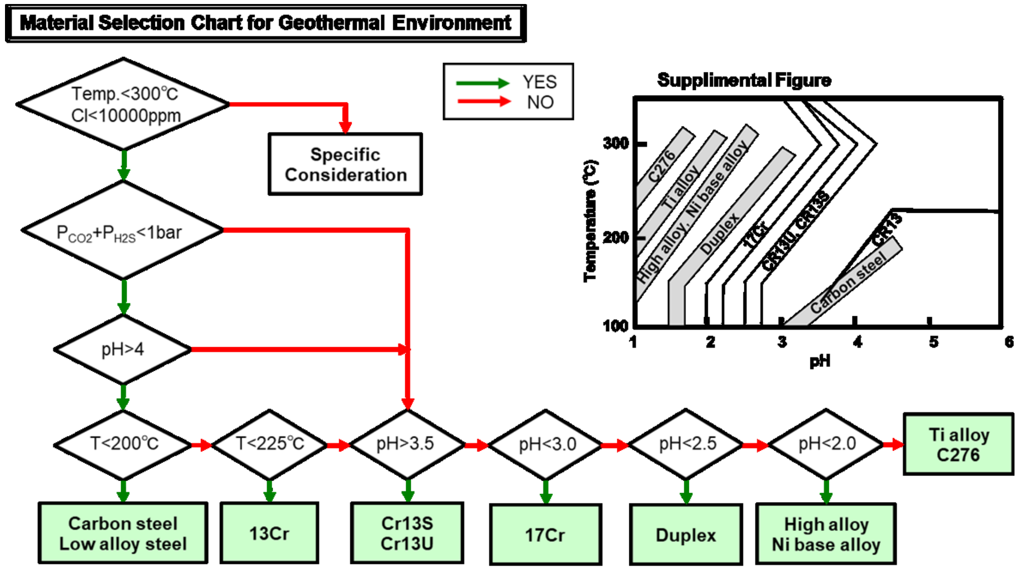


Figure 6: Corrosion rate calculation screen using Cr equivalent.

3.2 "Metal material selection chart" showing usable metal materials

The applicable materials are simply displayed on the chart based on the temperature and pH of hot water actually measured or predicted on the ground surface. As shown in Figure 7, the material selection diagram showing the applicable range of each material for temperature and pH, and a material selection flowchart for selecting materials based on pH, temperature, and H_2S/CO_2 partial pressure. In this system has two sheets, 1) supplemental figure and 2) material selection chart based on Figure 7.

The material selection chart is applicable under 300 ℃ and higher temperature zone is specific consideration based on high temperature corrosion test at GNS Science as previous chapter.



[SSC]

Temperature	Grade
All temperature	Sour service material
T>66℃	C95
T>79℃	P110
T>107℃	Q125

in accordance with NACE

Figure 7: Concept of the material selection for flowchart screen.

3.3 "Economic evaluation using metal materials" that calculates the drilling unit cost per 1 kW

The development company need the economic evaluation to select the best casing material for production well.

In this sheet, firstly we need to input pH and temperature of production fluid, steam production (ton/h) and this decreasing ratio (%) per year. And we need to input the casing thickness and limitation ratio (%) of casing thickness loss by corrosion. Figure 8 shows the case study of economic evaluation.

Firstly, the corrosion rate is calculated from pH, temperature of fluid and Cr equivalent. And the lifetime of casing (year) is calculated from corrosion rate and limitation thickness loss by corrosion. Then, we can calculate total production steam during lifetime of casing. Secondary, total drilling cost is calculated. In this case, drilling cost without casing material is estimated about 400MJPY. And casing material cost is 77MJPY multiply relative cost of material. The standard of relative cost is based the cost of J55, carbon steel. Then, we can calculate the drilling cost per 1 kW from previous results.

In the case of pH higher, the corrosion rate is low and the J55 carbon steel is most economic (low cost). But in the case at pH=4.5 and 250 degree C as shown in Figure 4, the corrosion rate became higher, and the Cr-Mo steel is lowest cost than carbon steel. The most economic material changes depend on the pH and temperature.

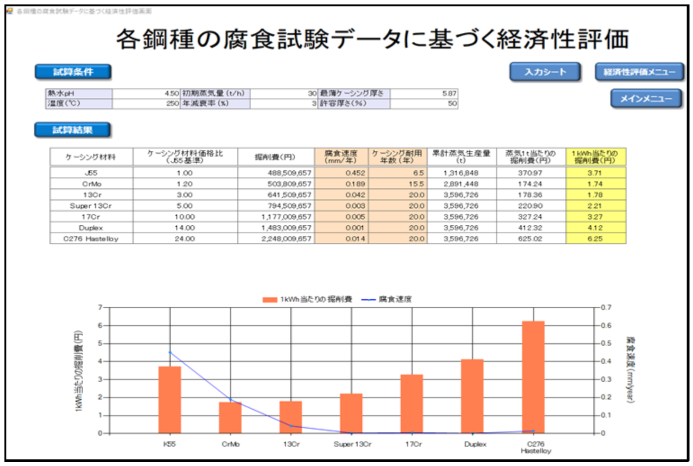


Figure 8: Economic evaluation trial calculation result screen.

3.4 "Material Corrosion Rate Database" graphed based on material corrosion tests

From the corrosion test data in the Sunshine Project Report "Research on the development of geothermal materials, FY1985"(AIST-Tohoku, 1986) conducted at the AIST-Tohoku database and the pH and temperature dependence is displayed.

3.5 Corrosion Literature Database for literature search

This search sheet of published literature on geothermal corrosion (approximately 300 publications) by keyword, author name, corrosion test conditions (temperature, pH, metal setting) include to this system.

4. DIRECTION OF SYSTEM UTILIZATION

In the past, when geothermal resource developers found acidic hot water, they tend to give up development and use of wells in the area. However, by using this system, it is possible to calculate the lifetime and cost of materials used in geothermal facilities and predict their applicability. This system has made it easier to obtain predictive information on the corrosion behavior of materials in acidic hot water, which has been difficult to collect information due to the difficulty of experiments.

By conducting actual corrosion tests on-site based on these prediction results, it is possible to efficiently select the optimum material in terms of corrosion resistance performance and cost. As a result, utilization of acidic hot water resources will advance, and an increase in the utilization rate and installed capacity of geothermal power plants can be expected.

We will distribute the "Geothermal Power Plant Risk Assessment System (for acidic hot water)" and the operation manual for this system and GERD will maintain this system. And this system will revise with high temperature and acid test progressing.

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REFERENCES

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).

Muraoka, H., Sakaguchi, K., Komazawa, M. and Sasaki, S.: Assessment of hydrothermal resource potential in Japan 2008. Abstract of annual meeting of the geothermal research society of Japan, B01 (2008)

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).

ThinkGeoEnergy: ThinkGeoEnergy's Top 10 Geothermal Countries 2022 – Power Generation Capacity (MW), https://www.thinkgeoenergy.com/thinkgeoenergys-top-10-geothermal-countries-2022-power-generation-capacity-mw/(2023)

Reed, M.H., Spycher N.F. and Palandri, J.: SOLVEQ-XPT: A Computing Aqueous-Mineral-Gas Equilibria. Version 2.22. Department of Geological Sciences, University of Oregon, 42 pp. (2014)

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., Sato, M., Kasai, K, Osato, K. and Sakura, K.: The material corrosion test on pH adjustment condition by acid at geothermal field in Japan, Proc. 41st New Zealand Geothermal Workshop, Auckland, New Zealand. (2019)

Yanagisawa, N., Sato, M., Osato, K., Yamamoto, Y., Lichti, K., Mountain, B. and Sajkowski, L.: Corrosion Rate Estimation of Cr Casing Steels at High Temperature Acid Conditions, Proc. 43rd New Zealand Geothermal Workshop, Wellington, New Zealand. (2021)