SCALE AND CORROSION OF A KALINA POWER GENERATION SYSTEM USING HOT SPRING WATER

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ABSTRACT

A power generation test of a Kalina system using hot spring water is progressing in Japan. In order to investigate this system, estimation of scaling and corrosion of a heat exchanger is being carried out at Otari and Matsunoyama hot spring field.

First, the scaling and corrosion test was carried out at the Otari test site. The fluid has high T-HCO_3, Cl and SO_4 concentration with pH 7 and a temperature of 70 ºC. In the hot spring water path, sulfide minerals were deposited on a Cu plate and iron reacted with CO_2. Aragonite, calcite and silica precipitated in the heat exchanger. However in the cooling water path, aragonite precipitated especially in the high temperature area due to super-saturation by heating.

For the second test, at Matsunoyama field, we estimated the possibility of scaling in the system by calculating the equilibrium of silicate minerals and carbonate minerals using Solveq-Chiller, developed by Reed (1982). The test well at Matsunoyama, Takanoyu#3, has a high Cl concentration of about 9,000 mg/l, about 3700 mg/l Na, 140mg/l K, 2,070 mg/l Ca, 0.6 mg/l Mg and 27.3 mg/l HCO_3. During the cooling process of hot spring fluid from 100 to 40 ºC, in the heat exchanger, quartz and calcite become supersaturated, but other minerals such as dolomite, amorphous silica, talc and tremolite are under-saturated. Thus we estimated that the scale problem will not be so serious because silica scaling (usually occurring as amorphous silica) is not expected as silica is under-saturated over 40 ºC at Takanoyu#3 and the super saturation of calcite decreases with decreasing temperature. One of the reasons for the low risk of scaling is the low HCO_3 and Mg concentrations at Takanoyu#3.

1. INTRODUCTION

Bathing in hot springs is one of the main direct uses of geothermal energy and is used by many people in many countries, especially in Japan

In Japan, there are about 28,000 hot springs (Onsen) and the range of temperature of hot springs is from 25 to over 100 ºC. In volcanic areas, for example Hokkaido, Tohoku-area, Kyushu Island etc., many high temperature hot springs exist. For about 15 % of the hot springs the temperatures are higher than 60 ºC and for about 4 % of hot springs are higher than 90 ºC.

The high temperature hot spring fluid is not hot enough for flash-plant power generation. But in this case, the initial temperature of the hot springs are too high for bathing (about 42 ºC). The hot spring owners are making various efforts to lower the temperature. For example, cooling in a long channel or by stirring using human power and by release of waste heat to the air.

To investigate the utilization of high temperature hot spring water (about 100 ºC), a project based on a 50 KW class Kalina cycle power generation system has been developed (Osato, 2005. , Muraoka et al., 2008).

The concept of this system is as shown in Figure 1. The small-scale Kalina cycle power generation system is built into the upper stream of the high-temperature hot springs, so that we could obtain electricity and adjust the bath temperature without any dilution. The minimum power generation temperature required by the Kalina cycle is 53 ºC which is adequate as input for bath use after the power generation stage. Also we can use heated cooling water for space heating etc.

One of the problems with this system is corrosion and scaling on the plates of the heat exchanger between the hot spring fluid and ammonia-water fluid in the Kalina cycle. This problem is similar to the corrosion and scaling that occurs in standard geothermal system. To investigate the problem we carried out heat exchanger tests at Otari hot spring well and estimated scaling at Matsaunoyama hot spring power generation test site.

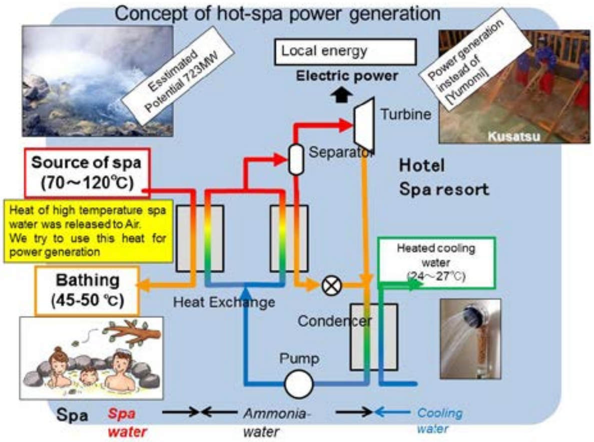

Figure 1: The concept of power generation using hot spring fluid

2. SCALING AND CORROSION TEST AT THE OTARI SITE

2.1 Test system and fluid chemistry

The Otari test site is north of the Nagano prefecture, as shown in Figure 2. In Otari, 3 wells were drilled and we used OT-2 well for the scaling and corrosion test.

The test system is shown in Figure 3. This system was connected at the wellhead of OT-2 and first hot spring fluid was supplied to the corrosion test vessel. This vessel is about 50 cm long and 18 cm diameter. In the vessel, five metal plates were inserted to test for corrosion. The size of the test plate is 3 cm x 5 cm and it is about 40 g in weight. Two SUS304, two copper and one iron plate were used.

After the corrosion test, the hot spring fluid was supplied for a scaling test using the heat exchanger. We used a two-plate type heat exchanger made by Hisaka Co. Ltd. This heat exchanger has twelve plates and the plate size is 15 cm x 30 cm and 1 mm thickness. We stored cooling water in a 2 m^3 tank and circulated it to the heat exchanger by using a pump. We used cooled hot spring fluid for the cooling water.

This corrosion and scaling test was carried out over about 20 days from 20 January to 8 February 2008. During the test, the temperature of hot spring fluid increased from 51.2 ºC to 69.2 ºC and the flow rate increased from 10 L/min to 18 L/min as shown in Table 1. The temperature of cooling water increased from 20.1 ºC to 35.2 ºC but the flow rate decreased from 20 L/min to 13 L/min.

The chemistry of the hot spring fluid from OT-2 is shown in Table 2. We analyzed the pH and EC on-site using a pH and EC meter (modelHoriba D-53). We sampled hot spring fluid at the inlet and outlet of the heat exchanger at end of the test. HCO_3 concentration was measured using titration with H_2SO_4. SiO_2 was analyzed by ICP method. Na, K, Mg, Ca, Cl, F and SO_4 concentrations were analyzed by ion chromatography. In Table 2, the units of chemical composition (from Na to SiO2) are mg/l.

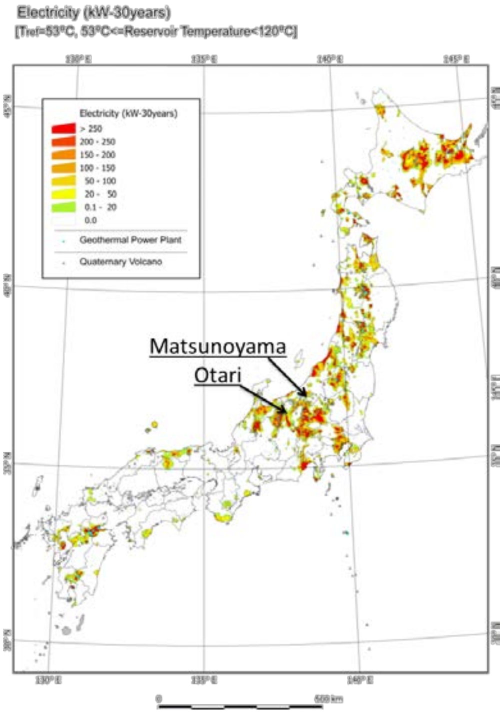

Figure 2: Map of potential hot spring power generation and test sites.

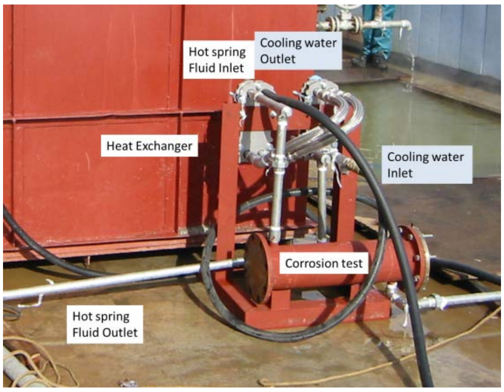

Figure 3: Corrosion and scaling test using OT-2 hot spring fluid.

Table 1: Temperature and flow rate of hot spring fluid and cooling water

		Start test	End test
Hot Spring Fluid	Inlet	51.2℃	68.9℃
	Outlet	28.4℃	51.8℃
	Flow	10L/min	18L/min
Cooling Water	Inlet	20.1℃	35.2℃
	Outlet	31.9℃	39.6℃
	Flow	20L/min	13L/min

Table 2: Geochemistry (mg/l) at the inlet and outlet of the heat exchanger for OT-2 hot spring fluid at the end of the test

	Temp	pH	EC	Na	K	Mg
Inlet	69.2	7.1	8.2	1906	30	11
Outlet	51.8	6.9	7.9	1849	29	11
	Ca	F	HCO3	Cl	SO4	SiO2
Inlet	84	0.55	2167	1487	559	112
Outlet	85	0.56	2182	1450	545	95

2.2 Material corrosion

After the 20 day test, we measured the weight change of each test plate and identified the corrosion materials by X-ray powder diffraction. The weight changes of the test plates are shown in Table 3. The weight change of SUS304 is about 0.02g resulting from a small precipitation of iron oxide. The weight change of the copper plates depends on their loaction in corrosion test vessel.

Figure 4 shows the copper and iron test plates after corrosion test. The copper plate is covered in black sulfide minerals. The surface of the iron plate changed to black and red deposited materials. From X-ray powder diffraction, $FeCO_3$ is the main deposit on the iron plate.

The sulfide minerals, bornite (Cu_5FeS_4) and chalcopyrite ($CuFeS_2$), precipitated on copper plate. This means the copper reacted with sulfur in the hot spring fluid and made sulfide minerals. If the sulfide minerals were removed from the copper plate, the weight of the plate decreased. Copper has a high heat conductivity but is susceptible to corrosion by hot spring fluid. The weight of the iron plate decreased by about 11.12g, one fourth of the original weight of the plate. On the iron plate, iron carbonate ($FeCO_3$) precipitated due to the reaction of iron with the carbonate ions in the hot spring fluid.

The stainless plate, SUS304 did not suffer corrosion by the fluid. Thus, the stainless plate is suitable for the Hot Spring power generation system.

Table 3: Weight change of the test plate after the corrosion test

	Weight Change
SUS304(Inlet)	0.015(g)
SUS304(Outet)	0.018(g)
Cu plate(Inlet)	1.212(g)
Cu plate(Outlet)	(−)0.168(g)
Iron plate	(−)11.120(g)

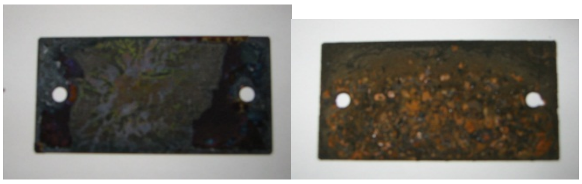

Figure 4: Photographs of corrosion on the Cu plate and the iron plate.

2.3 Scaling in the heat exchanger

During the 20 day test, scale precipitated on the plates of the heat exchanger. Figure 5 shows a photo of the hot spring fluid side of the heat exchanger. About 0.4g of scale precipitated on one plate. The main components of the scale are amorphous silica, calcite, aragonite and iron oxide.

Figure 6 shows a photo of the cooling water side of the heat exchanger. Scaling depends on temperature and much of the precipitation occurs at the high temperature regions at the inlet for the hot spring fluid and the outlet for the cooling water. The range of weights of scale is from 1 g to 10g per plate depending on the flow rate and temperature of the plate. Due to scaling, the flow rate of cooling water decreased from 20 L/min to 13 L/min. The main composition of the scale is calcite and aragonite. This scaling is due to the lower solubility of calcium carbonate, as show in Figure 7. Especially this is a problem as we used cooled hot spring fluid, high in Ca and HCO_3, , as shown in Table 2. This is the reason for the large amount of scale precipitation. Thus technology for preventing scaling is needed not only for the hot spring water path but also for the cooling water path.

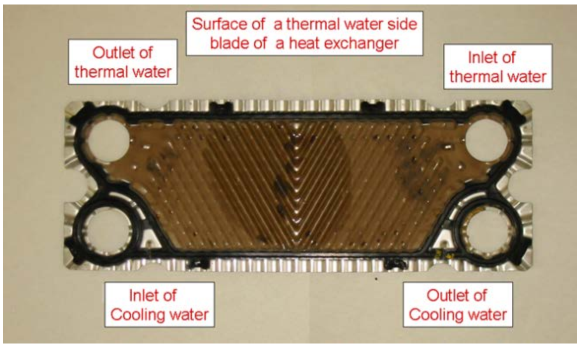

Figure 5: Scale on the hot spring fluid side of the heat exchanger

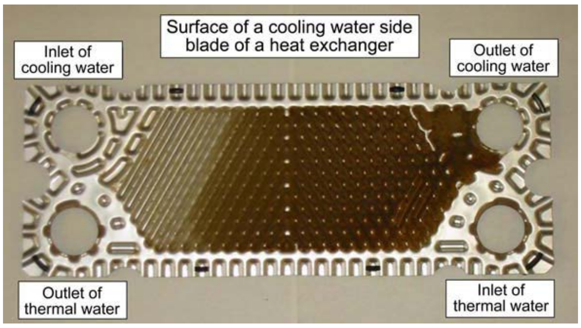

Figure 6: Scale on the cooling water side of the heat exchanger

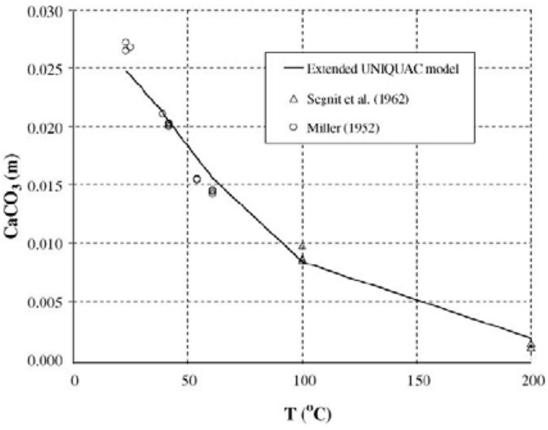

Figure 7: Solubility curve for calcite

3. HOT SPRING POWER GENERATION TEST AT MATSUNOYAMA

3.1 Matsunoyama project

After the material test at the Otari site, the Ministry of the Environment (MOE) of Japan started to support a hot spring power generation project from fiscal year 2010 (FY2010).

In this project, a power generation test of a 50kW class Kalina cycle system using about 100 °C hot spring water was carried out at Matsunoyama hot spring field in Tokamachi City, in the central part of Niigata prefecture about 200km NNW from Tokyo, as shown in Figure 2 (Yanagisawa et al., 2011)..

At Matsunoyama, a new hot spring well, Takanoyu#3, was drilled to about 1,200 meters depth in 2007. At the first production test, the fluid temperature was about 97 ºC and flow rate was about 630 l/min. This production rate is the largest in Matsunoyama hot spring resort.

After this test, the production rate from Takanoyu#3 was about 230 l/min and about 100 l/min fluid was not used for bathing and released to the river directly due to over production for the hotels. Thus, Takanoyu#3 was selected as the test well for the hot spring generation project.

The power plant system was installed at Takanayu#3 in December of 2011. The power generation system consists of a one meter long heat exchanger for hot spring fluid and the ammonia/water mixture, a separator to separate ammonia gas from water, an ammonia tank and a pumping system. The system size is about 5 cubic meters as shown in Figure 8 (Welch et al., 2011).

Figure 8: The Kalina power generation system using hot spring fluid at Matsunoyama

3.2 Geochemistry of Matsunoyama

After October 2010, we started monitoring the flow rate, temperature and geochemistry of Takanoyu#3, the generation test well, and the Kagaminoyu, Yusaka and Koshinnoyu wells as neighbours of Takanoyu#3.

Table 4 shows the fluid composition of the Matsunoyama wells with high Cl concentration of about 9,000 mg/l in all wells measured at November 2010. Takanoyu#3 has about 3,700 mg/l Na, 140mg/l K, 2,070 mg/l Ca and 27.3 mg/l HCO_3 and this composition did not change from the start of production at September 2007.

Table 4: Geochemistry of the hot spring well Takanoyu#3 and surrounding wells (mg/l)

	Na	K	Cl	Ca
Takanoyu#3	3700.0	140.3	9400	2070.0
Yusaka	3708.0	103.3	9252	1980.0
Kagaminoyu	3392.0	83.4	8764	1882.0
Kousinnoyu	5680.0	30.7	8661	205.0

(mg/l□

	HCO3	Mg	Si	SO□
Takanoyu#3	27.3	0.6	66.7	85.5
Yusaka	23.0	7.7	36.7	80.0
Kagaminiyu	19.3	15.7	20.1	81.1
Kousinnoyu	316.6	44.1	11.5	2.6

(mg/l)

3.3 Estimation of scaling at Takanoyu#3

We estimated the possibility of scaling in the heat exchange system at Takanoyu#3 by calculating equilibrium of silicate and carbonate minerals using Solveq-Chiller (developed by Reed (1982)). The diagram of mineral equilibrium is shown in Figure 9.

During cooling of the hot spring fluid from 100 to 40 ºC, in the heat exchanger, quartz (SiO_2) and calcite ($CaCO_3$) are supersaturated, but other minerals such as dolomite ($MgCaCO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$), tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and amorphous silica (SiO_2) are undersaturated.

From Figure 9, we deduced that the scale problem may not be serious because silica scaling usually occurs as amorphous silica which is under saturated at temperatures of over 40ºC at Matsunoya#3 and the degree of supersaturation of calcite decreases with decreasing temperature. Thus to prevent scaling, we have to take care to prevent boling and pH change in the heat exchanger.

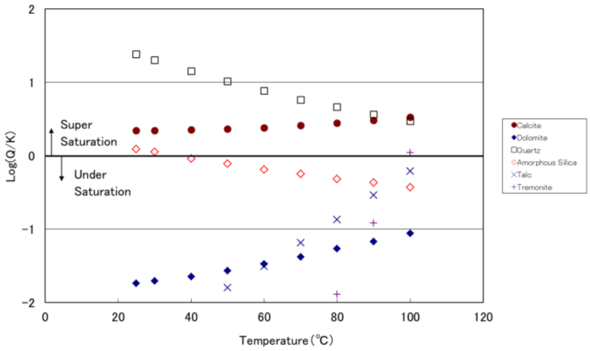

Figure 9: Estimation of equilibrium of scale minerals for Takanoyu#3

3.4 Comparison of scaling possibility with other wells

As described above, the scaling risk is estimated to be low for Takanoyu#3. But at Otari, calcite and silica precipitated on plates in the heat exchanger. Thus, we decided to calculate the equilibrium of minerals using the Otari composition data given in Table 2. The results of this nanalysis are shown in Figure 10.

IAs shown in Figure 10, magnesium silicates, and tremolite are super-saturated above 50ºC. Dolomite is super-saturated and log(Q/K) is more than 2 for temperatures above 50ºC. The log(Q/K) of these Mg-based minerals at Otari is higher than at Takanoyu#3 due to the high Mg concentration, 11mg/l. The log(Q/K) of calcite at Otari varies from 1 to 1.5 for temperatures between 60 and 100 ºC. This log(Q/K) is higher than that for Takanoyu#3 (from 0.3 to 0.5) due to the high concentration of HCO_3 at2162mg/l. Thus, the fluid from Otari has a higher likelihood of scaling than that from Takanoyu#3.

In the Matunoyama region, the concentrations of Ca, HCO_3 and Mg have a wide range even though the concentrations of Na and Cl are almost constant. For example, at Kousinnoyu, the Mg concentration is 44.1 mg/l which is about 70 times the value for Takanoyu#3 of 0.6mg/l. Similarly the HCO_3 concentration is 316mg/l which is about 10 times the value for Takanoyu#3. The log(Q/K) valuesfor minerals in the fluid at Kousinnoyu are shown in Figure 11. Several minerals including Mg and HCO_3 show high log(Q/K) values, similar to those for Otari.

The reason for a low risk of scaling at Takanoyu#3 is the concentrations of HCO_3 and Mg . Thus, the scaling risk will increase in high regions with high levels of HCO_3 and Mg.

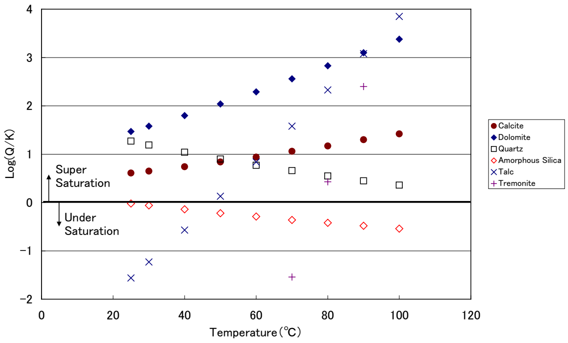

Figure 10: Estimation of equilibrium of scale minerals of Otari

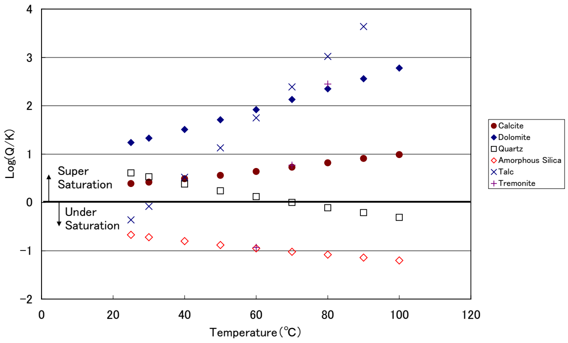

Figure 11: Estimation of equilibrium of scale minerals at Kousinnoyu in the Matsunoyama field

4. CONCLUSION

To investigate a power generation system using hot spring water, an estimation of scale and corrosion was carried out. The main results are as follows;

1) In the hot spring fluid, a copper plate reacted with sulfur, an iron plate reacted with CO_2 and a SUS304 plate was unaffected.

2) Aragonite, calcite and silica precipitated in the hot spring fluid path of the heat exchanger. However in cooling water path, aragonite precipitated, especially in the higher temperature area due to super-saturation by heating.

3) The scale problem at Takanoyu#3 in the Matsunoyama region will not be serious because silica scaling usually occurs as amorphous silica which is under-saturated, and the degree of super saturation of calcite decrease as the temperature decreases. The reason for the low risk of scaling is the low concentrations of HCO_3 and Mg at Takanoyu#3.

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