Proceedings of the 10th Asian Geothermal Symposium, 22-24 September 2013

SCALE AND CORROSION OF BINARY SYSTEM USING HOT SPRING WATER

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ABSTRACT

Recently, several small binary systems are installed at high temperature hot spring field. For example, the production test using small Kalina system is carried out at Matsunoyma hot spring field. And the power generation using small binary system using hydrofluorocarbon is installed at several hot springs in Kyushu Island. One of the problems with this system is corrosion and scaling on the plates of the heat exchanger in the binary system. This problem is similar to the corrosion and scaling that occurs in standard geothermal system. In order to investigate this system, estimation of scaling and corrosion of a heat exchanger is being carried out at several hot spring fields.

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, 200mg/l K, 2,100 mg/l Ca, 0.4 mg/l Mg and 36 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.

Keywords: hot spring power generation, scale, corrosion, geochemistry, Japan, Otari, Matsunoyama.

1. INTRODUCTION

In Japan, several hot springs owners and power generation companies have recently expressed interest in small binary power system using hot spring fluids (Muraoka et al., 2008) as shown in Figure 1.

After the recent nuclear power plant accident (caused by earthquake/tsunami), the Feed-in Tariff (FIT) for small geothermal power plant was set up at 42 JPY/kW which is sufficient to support the development of small binary system using fluids from the hot springs.

Several Japanese companies ventured into production of new small binary system. For example, KOBELCO (Kobe Steel, Ltd) developed a 72kW binary system that was made available in October, 2011. This system was installed at Beppu hot spring field in Oita prefecture and at Obama field in Nagasaki prefecture, all in Kyushu Island near a volcanic area. IHI Co. Ltd. likewise developed a 20kW class binary system which was released in August, 2013 while ULVAC-RIKO. Inc. developed a 3kW binary system.

These binary systems use Hydro Fluoro Carbon (HFC) as the heating medium. Since HFC is non-toxic and has low flammability, owners of the HFC binary systems below 300kW size have no need for a special licensed engineer for boiler and turbine in Japan. Then, the personnel expense cost for the HFC binary system is a lot cheaper which greatly influenced the choice of several hot spring owners in favor of the HFC binary system. However, the HFC binary system has several issues. One is that the Global Warming Potential (GWP) of HFC is very high, about 1,000 times that of the Carbon Dioxide gas (CO_2). Second, the cost of HFC gas may become higher in future due to increase in demand.

On the other hand, the Kalina cycle system has relatively high electrical efficiency for hot spring fluid (Osato, 2005), with no impact on global warming. However, the Kalina cycle system running cost is high due to the need for a special licensed engineer, which can be reduced if the safety and stability of the Kalina cycle system can be established. In Japan, the Kalina cycle system has already been utilized at Kashima works of Nippon Steel and Sumitomo Metal Co. Ltd. (3,400kW) since 1999 and at Sodegaura works of Fuji Oil Co. Ltd. (3,300kW) since 2007. These systems have been operational for several years without any issue. Currently, the ongoing production test of a 50kW Kalina cycle system at Matsunoyama hot spring field using a small generator (Welch et al., 2011) aims to estimate safety and stability of the Kalina cycle system and the sustainability of production from the hot spring.

Then, one of the problems of these system is corrosion and scaling on plate of heat exchanger between hot spring fluid and ammonia-water fluid similar as usual geothermal system. We carried out heat exchange test at Otari hot spring well and estimated scaling at Matsaunoyama hot spring power generation test site.

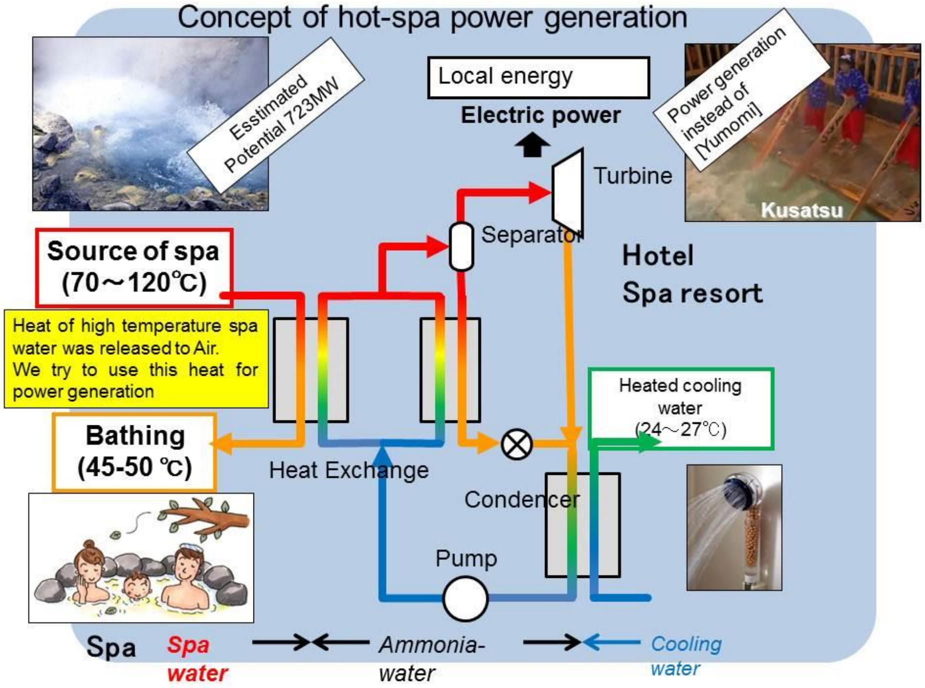

Figure 1: The concept of power generation using hot spring fluid

2. CORROSION TEST OF OTARI HOT SPRING SITE

Otari test site is north of Nagano prefecture as shown in Figure 2. In Otari, three wells were drilled and we used OT-2 well for scaling and corrosion test. The test system was connected wellhead of OT-2 and firstly hot spring fluid was supplied to corrosion test vessel. This vessel is about 50 cm long and 18 cm diameter. In vessel, five metal plates were inserted to corrosion test. The size of test plate is 3 x 5 cm and about 40 g weight and two SUS304, two copper and one iron plate were used.

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

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

And the fluid chemistry of hot spring fluid from OT-2 is shown in Table 1. We analyzed pH and EC at on site using pH and EC meter of Horiba D-53. We sampled hot spring fluid at inlet and outlet of heat exchanger at end of the test. HCO_3 concentration was measured using the titration with H_2SO_4. SiO_2 was analyzed by ICP method. And Na, K, Mg, Ca, Cl, F and SO_4 concentration were analyzed by ion chromatography. In Table 2, the unit of chemical composition from Na to SiO_2 is mg/l.

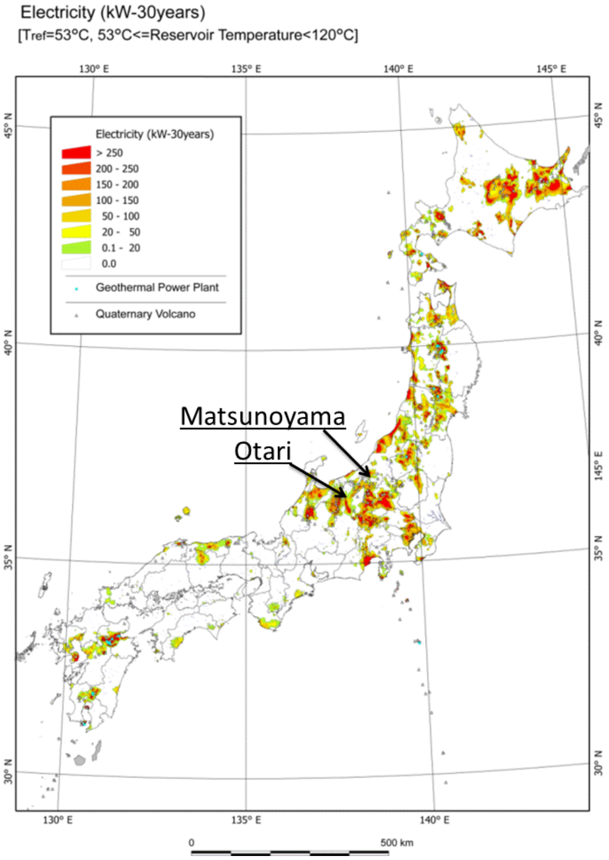

Figure 2: Potential map of hot spring power generation and test site.

Table 1: Geochemistry (mg/l) of inlet and outlet of heat exchanger of OT-2 hot spring fluid at end of 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

After 20 days test, we measured weight change of test plate and identify corrosion material by X-ray powder diffraction. The weight change of SUS304 is about 0.02g due to slightly iron oxide precipitation on SUS304. The weight change of copper depends on site in corrosion test vessel.

Figure 3 shows the photo of test plates after corrosion test. Copper plate is covered black colored sulfide minerals. And the surface of iron changed to black and red colored carrion materials. From X-ray powder diffraction, $FeCO_3$ is mainly covered on iron plate.

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

And the stainless plate, SUS304 did not suffer by fluid. Then, stainless plate is suitable for Hot Spring power generation system.

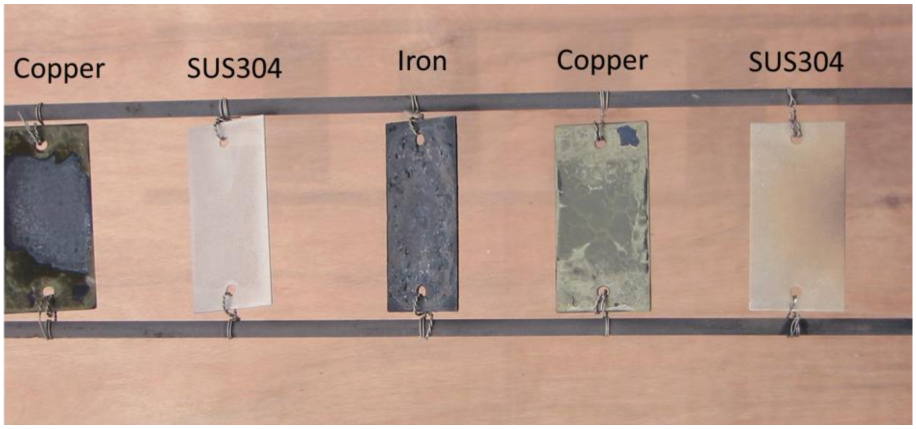

Figure 3: Test plates after corrosion test. Copper plate is covered by sulfide minerals and Iron plate is covered by carbonate.

3. SCALING TEST OF OTARI HOT SPRING SITE

After 20 days test, scale precipitated on plate of heat exchanger. Figure 4 shows the photo of hot spring fluid side of heat exchanger. About 0.4g scale precipitated on one plate. Main composition is amorphous silica, calcite, aragonite and iron oxide. Figure 5 shows the photo of cooling water side of heat exchanger. Scaling depends on temperature and much precipitation of high temperature region at inlet of hot spring fluid and outlet of cooling water. And the range of scaling weight is from 1 g to 10g per plate depends on flow rate and temperature on plate. Due to scaling, the flow rate of cooling water decreased from 20 l/min to 13 l/min. And main composition of scale is calcite and aragonite. This scaling is due to lower solubility of calcium carbonate. Especially, we used high Ca and HCO_3 fluid, cooled hot spring fluid, as shown in Table 1. This is reason to amount scale precipitation. Then preventing scaling technology need for not only hot spring water path but also cooling water path.

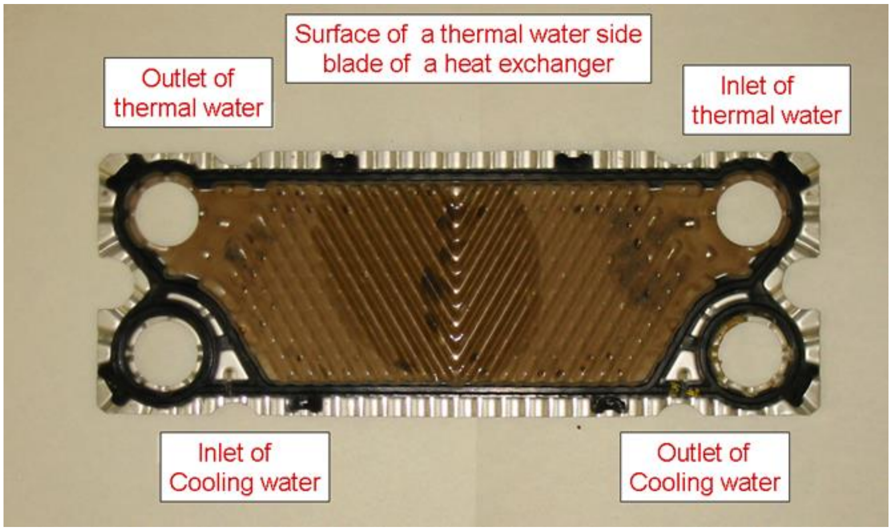

Figure 4: Scale on hot spring fluid side on heat exchanger.

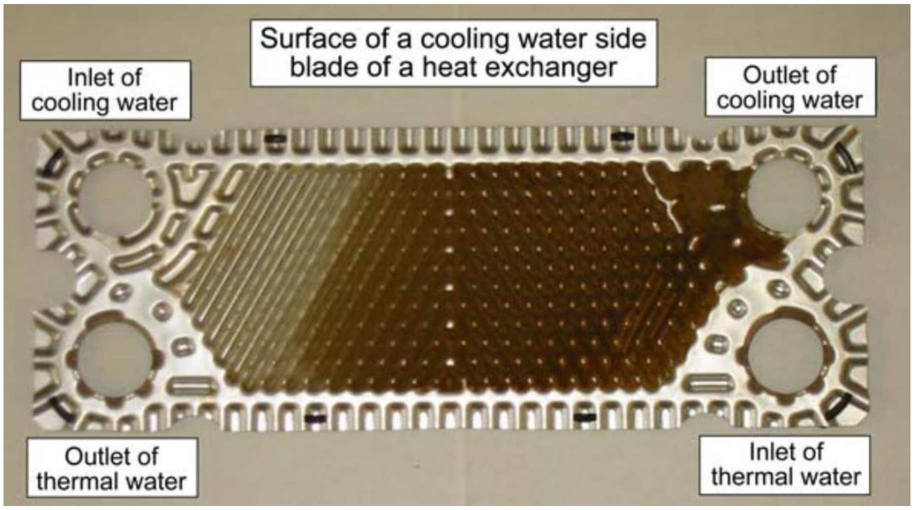

Figure 5: Scale on cooling water side on heat exchanger.

4. HOT SPRING POWER GENERATION TEST AT MATSUNOYAMA

After material test at Otari site, the Ministry of the Environment (MOE) of Japan started to support hot spring power generation project from fiscal year 2010. In this project, power generation test by 50kW class Kalina cycle system using about 100 ºC hot spring water is carried out at Matsunoyama hot spring field in in Tokamachi city of middle part of Niigata prefecture about 200km NNW from Tokyo shown in figure 2 (Yanagisawa et al., 2011)..

At Matsunoyama, new hot spring well, Takanoyu#3, was drilled until about 1,200 meters depth in 2007. At the first production test, the fluid temperature is about 97 ºC and flow rate is about 630 l/min. This production rate is the largest in Matsunoyama hot spring resort. After this test, the production rate from Takanoyu#3 is about 230 l/min and about 100 l/min fluid is not used for bathing and released to river directly due to over production for hotels. Then, Takanoyu#3 is selected to the test well foe the hot spring generation project.

And the power plant system was installed at Takanayu#3 at December of 2011. The power generation system is contains about one meter length power generator, heat exchanger for hot spring fluid with ammonia/water mixture, separator ammonia gas from water, ammonia tank and pumping system. The system size is about 5 meter cubic as shown in figure 6 (Welch et al., 2011).

Figure 6: Kalina power generation system using hot spring fluid at Matsunoyama

After October 2010, we started the flow rate, temperature and geochemical monitoring of Takanoyu#3 for generation test well and Kagaminoyu, Yusaka well and Koshinnoyu as surrounding well from Takanoyu#3.

Table 2 shows the fluid composition of Matsunoyama wells with high Cl concentration about 10,000 mg/l in all wells measured at November 2010. Takanoyu#3 has about 3,700 mg/l Na, 200mg/l K, 2,100 mg/l Ca and 36 mg/l HCO_3 and did not change from production start at September 2007.

Table 2: Geochemistry of hot spring of Takanoyu#3 and surrounding wells (mg/l)

	Na	K	Cl	Ca	SO4
Takanoyu#3	3661.0	195.9	10140	2100.0	90.7
Takanoyu#2	3785.0	208.0	9495	2162.0	94.4
Yusaka	3526.0	162.2	10297	1957.0	89.1
Kagaminoyu	3720.0	129.2	9421	1981.0	84.8
Kousinnoyu	5493.0	50.1	9724	222.0	0.0
					(mg/l)
	HCO3	Mg	Si	T_{NaKCa}	Depth
Takanoyu#3	36.1	0.4	50.1	161	1260
Takanoyu#2	39.1	0.6	59.2	162	287
Yusaka	30.5	5.5	40.2	153	1100
Kagaminiyu	39.1	14.4	29.3	141	410
Kousinnoyu	344.7	44.9	9.4	106	356
			(mg/l)	(°C)	(m)

5. ESTIMATION OF SCALING POSSIBILITY

We estimated the possibility of scaling in this system at Takanoyu#3 by calculating equilibrium of silicate and carbonate minerals using Solveq-Chiller by Reed (1982). The diagram of mineral equilibrium is shown in figure 7.

During cooling process of hot spring fluid from 100 to 40 ºC, on 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 under saturation.

From figure 7 we estimated the scale problem will be not so serious because silica scaling usually as amorphous silica under saturation over 40ºC at Matsunoya#3 and the degree of super saturation of calcite is decrease with temperature deceasing. Then to prevent scaling, we have to take care to prevent vaporize fluid and pH change in heat exchanger.

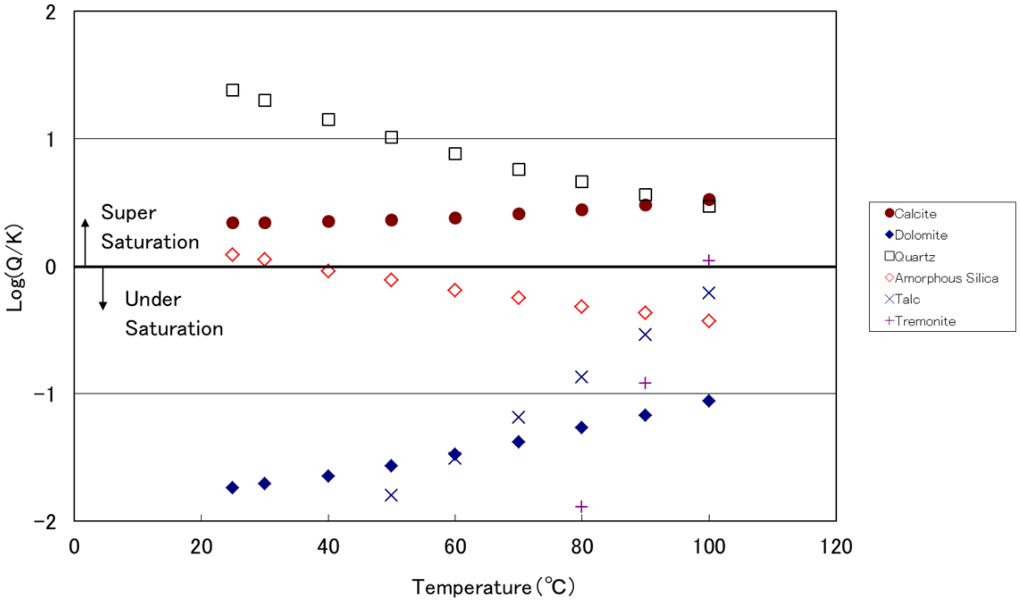

Figure 7: Estimation of equilibrium of scale minerals of Takanoyu#3

As describe above, the scaling risk is estimated low using Takanoyu#3. But at Otari, calcite and silica precipitated on plate of heat exchanger. Then, we calculate the equilibrium of minerals using Otrai composition data of Table 1. And the result is shown in Figure 8.

In Figure 8, magnesium silicates, tremolite is super-saturated above 50°C. And dolomite is super-saturated and the Log(Q/K) is more than 2 above 50°C. The Log(Q/K) of these Mg including minerals at Otari is higher than Takanoyu#3 due to high Mg concentration, 11mg/l. And the Log(Q/K) of calcite at Otari is from 1 to 1.5 between 60 and 100 °C. This Log(Q/K) is higher than that of Takanoyu#3 from 0.3 to 0.5 due to high HCO_3, 2,162mg/l. Then, the fluid of Otari has higher scaling possibility than that of Takanoyu#3.

The reason of low risk of scaling is due to low HCO_3 and Mg concentration at Takanoyu#3. Then, the scaling risk will increase in high HCO_3 and Mg region.

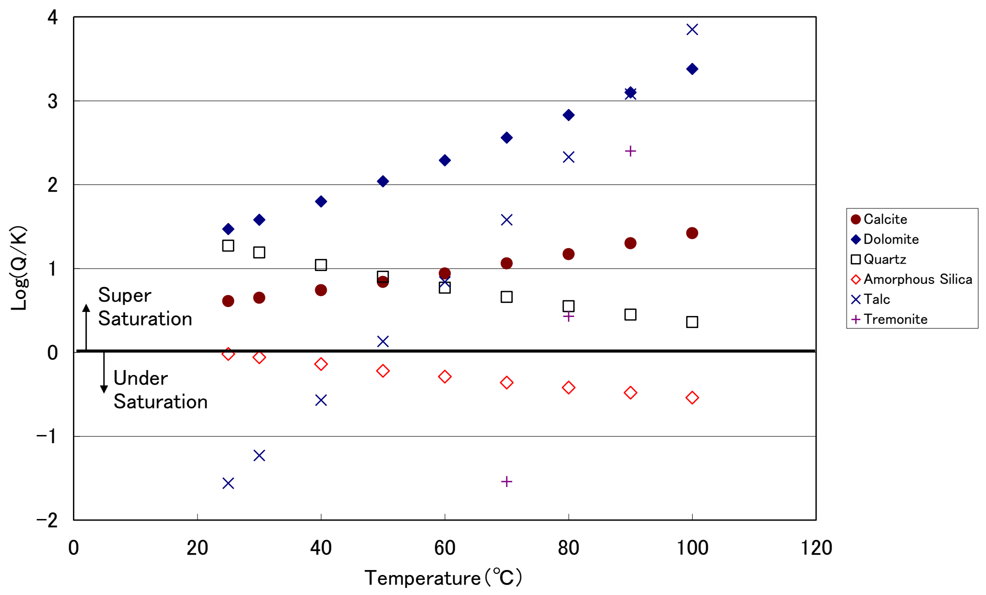

Figure 8: Estimation of equilibrium of scale minerals of Otari

6. SUMMARY

To promote power generation system using hot spring water, estimation of scale and corrosion is carried out. Main results are as follows;

1) In hot spring fluid, copper plate reacted with sulfur, iron plate reacted with CO_2 and SUS304 was stable.

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

3) The scale problem at Takanoyu#3 of Matsunoyama region will be not so serious because silica scaling usually as amorphous silica under saturation and the degree of super saturation of calcite is decrease with temperature deceasing. The reason of low risk of scaling is due to low HCO_3 and Mg concentration at Takanoyu#3.

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