A STUDY ON THE ABATEMENT TECHNOLOGY OF THE HARMFUL CHEMICAL COMPONENTS IN GEOTHERMAL HOT WATER

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Summary- Kyushu Electric Power Co.,Inc. and Mitsui Mining Company, Limited have jointly developed an apparatus for the abatement of arsenic(As) in geothermal hot water and conducted experiments to assess its efficiency. The concentration of arsenic in the treated water meets the environmental regulations of less than 0.01mg/L in Japan. Optimum efficiency of the apparatus could only be attained by the careful controls of the pH and of the dosed reagent. Removals on the order of 99% can be achieved.

1.0 Introduction

Most geothermal fields for development are located close to hot spring resorts in Japan. Hot water discharged from geothermal plants contains a relatively high concentration of arsenic (As). Thus, all the geothexmal hot water after a water-vapor separation is reinjected underground. If the arsenic concentration of geothexmal hot water is reduced, it could be used directly for various purposes such as hot spring water or agricultural utilization. This would be mutually beneficial to both geothermal power plants and the local community. Moreover, direct utilization of hot water can reduce the amount of water which is reinjected.

There are several methods for reducing the arsenic concentration in the water supply (Rosenblum and Clifford, 1984) and geothermal hot water (Buisson et al.,1979; Pierce and Moore, 1982). For economic and chemical reasons, dosing with an oxidizer (arsenite(III) is oxidized to arsenate(V)) and the continuous sand filter method were adopted for abatement of arsenic in geothermal hot water.

On the basis of preliminary experiments, a pilot plant with a treating capacity of 1.5 m^3/h geothexmal hot water was developed in 1990. An improved plant with a larger capacity of 15 m^3/h was constructed in 1991. This plant was designed to satisfy the environmental regulation for arsenic concentration of 0.05 mg/L. Two years later it was lowered to 0.01 mg/L. The plant was further improved to satisfy the reduced limit and has been put into practical use since 1994.

Two additional tests were carried out using the treated water: one is for scale deposition on the inner surface of the pipe when the treated water is supplied to the users and the other is for direct heat use in the green houses for flower cultivation.

2.0 Summary of the processes

The plant was installed close to the Hatchobaru geothermal power plant. It consists of transmission pipes, a reaction tank, a flocculation tank, two sets of continuous sand filters, a neutralization tank, a condensation tank, a dehydrator and four sets of reagent dosing tanks. A schematic diagram is shown in Figure 1.

2.1 The Reaction and Flocculation Tanks

Geothexmal hot water is supplied into the reaction tank with a volume of 2 m^3. Chemical reagents of polymerized ferric sulfate and sodium hypochlorite (NaClO) solutions are dosed at constant rates. The following reaction takes place in the reaction tank:

$$AsO_3^{3-} + NaClO = AsO_4^{3-} + NaCl$$

$$AsO_4^{3-} + Fe^{3+} = FeAsO_4$$

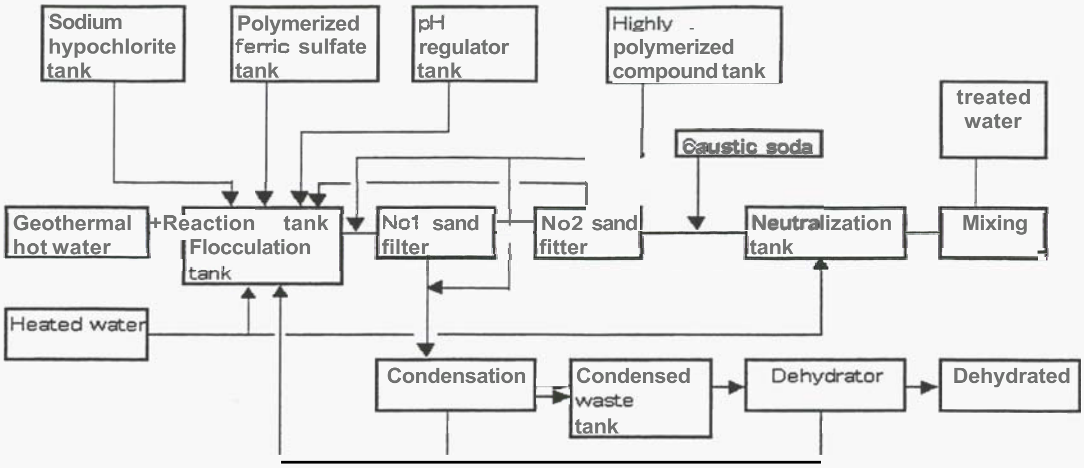

Figure **1.** Schematic diagram of the arsenic abatement plant.

The formation of $FeAsO_4$ indicates the arsenic coprecipitated with ferric hydroxide. In order to promote a growth of floc (ferric hydroxide) produced in the reaction tank, a flocculation tank was installed.

2.2 The Continuous Sand Filter

In this process, the floc coprecipitating arsenic is filtered using the upflow continuous sand filter method. This sand filter does not require backwashing in order to clean the filter beds. The **sand** bed is continuously cleaned and regenerated by internal recycling.

2.3 The Neutralization Tank

Residual flocs in the sand filter are automatically transported to a condensation tank and dehydrated by a dehydrator. The generated sludges are disposed at the controlled dumping ground.

3.0 Experimental Work

3.1 Evaluation of the Plant Performance

Geothermal water and treated water were collected at sampling points in this plant. Arsenic, total iron and other components were chemically analyzed. **A** number of experiments were undertaken at a rate of 15 m^3/h within the plant to find out following:

A. the optimum pH for coprecipitation of arsenic with ferric hydroxide by hydrolysis of polymerized ferric sulfate
B. the optimum Fe/As ratio for the arsenic concentration in treated water

C. the optimum NaClO concentration for the arsenic concentration **of** treated water

D. the physical and chemical properties of the dehydrated cake

3.2 Experiment for utilization

When using treated water, blocked pipes may occur due to scale deposition during **transmission.** This will present serious problems for the stable operation of the whole system. Therefore, experiments were carried out under practical conditions, installing four sets of test pipes at different locations as shown in Figure **5.** In these experiments, the pH effect of the treated waters on scale deposition was examined at the pH of 5.9 and **6.8** under constant flow rate and temperature.

4.0 Results and Discussion

4.1 Plant performance on arsenic abatement

Table 1 summarizes the qualities of the original geothermal water and of the treated water. Figure 2 presents the variation of the arsenic

Table 1. Characteristics of geothermal water and treated water

Item	Unit	Geothermal hot water	Treated water	Environmental regulation
Arsenic	mg/L	3—4	≦0.01	≦0.01
pH	—	6.6	6.8	0.2~1.0
BOD	mg/L	0.8	<0.2	≦1.0
SS	mg/L	0.5	0.3	≦25
Temp	℃	ca 94	ca 76	—
T-SiO2	mg/L	ca 700	ca 320	—

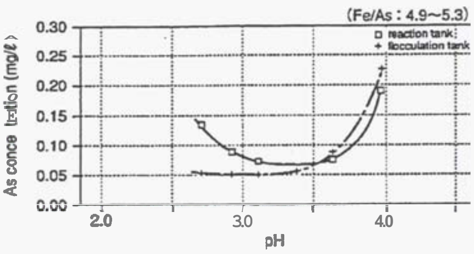

Figure 2. As concentration of treated water vs pH in reaction and flocculation tanks

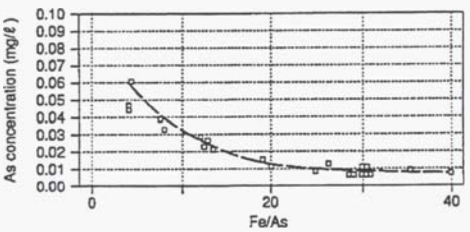

Figure 3. Concentration of As vs Fe/As ratio in the neutralization tank

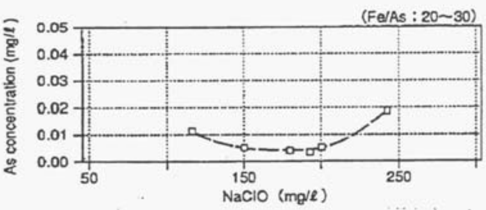

Figure 4. Concentration of As vs NaClO concentration m treated water

concentration of the treated water with pH in the reaction and flocculation tanks. The concentration of arsenic after abatement was decreased to less than 0.05 mg/L during the stable operation of this plant. The most effective aggregation of ferric hydroxide copreciptating arsenic was attained for pH values in the range of 3.0 - 3.4 as shown in Figure 2. Figure 3 shows the effect of Fe/As on the arsenic concentration in the reaction tank. From these results, for effective abatement we recommend maintaining the Fe/As ratio above 29. Figure 4 shows the effect of the concentration of NaClO on arsenic in the treated water. This indicates that the optimum concentration of NaClO is 150-200 mg/L. The production rate of the dehydrated cake was 151 - 166 kg/day, and the weight percentage in the wet base was 50%. The main components of the dried cake are Fe_2O_3(71-76%), SiO_2(9-13%) and As(1.4-1.9%).

From this evaluation, we conclude that arsenic in geothermal water is effectively abated under the given operational conditions for the flocculation reaction, although these conditions depend on the chemical characteristics of geothermal hot water. In this study, geothermal water from the Unit 1 was used, with a silica concentration of 650 mg/L, mainly in monomeric form. The concentration of silica in the geothermal water fiom the Hatchobaru Unit 2 was 800 mg/L. The induction period for silica polymerization in geothermal water fiom Unit 2 is shorter than that of Unit 1. This resulted in formation of polymerized silica within a short period in water from Unit 2. Polymerized silica is easily coprecipitated with ferric hydroxide under acidic conditions and the coprecipitation reaction prevents the abatement of arsenic. Therefore, a larger amount of polymerized ferric sulfate should be used to maintain the same extraction efficiencies of arsenic as in Unit . In this case, it is necessary to raise the Fe/As ratio for the stable operation of the arsenic abatement plant as suggested fiom the preliminary results.

4.2 Utilization of the Treated Water

The treated water was passed through the pipes in the water supply system (Fig, 5) to the greenhouse used for flower cultivation. After the treated water flowed for 3-6 months, the scale which deposited in the test pipes was collected for chemical analysis. Table 2 summarizes the chemical composition of the scales at four different points along the flow path. Figure 6 shows the amount of Si and Fe deposited on the test pipes at each sampling point in 6 months. At sampling point 1, the scale deposition rate at pH 6.8 is four times larger *than* that at pH 5.9. At other points, the scaling rate at pH 6.8 is considerably faster than that of pH 5.9.

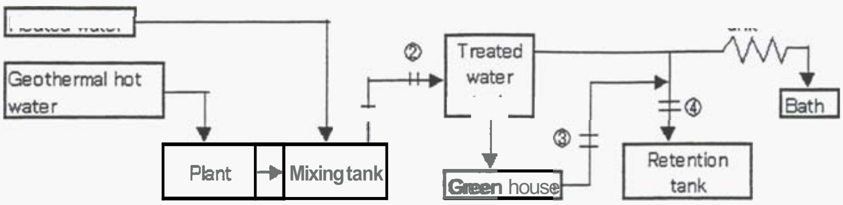

Figure 5. A schematic diagram for utilization of treated water

Table 2. The rate of deposition and the chemical composition of scale.

pH	Location of pipe		Scale deposition rate (g/100cm2/month)	Chemic; l mmmsiti ns			
				SiO_2	Fe_2O_3	Al_2O_3	others
6.8	①	outlet of MT[*1]	0.83	42.7	32.2	6.82	18.2
	②	Inlet of GH[*2]	0.49	33.6	41.7	4.65	20.1
	③	Outlet of GH	0.09	47.4	27.8	5.82	19.C
	④	Inlet of RT[*3]	0.11	64.1	12.5	5.57	17.9
5.9	①	Outlet of MT[*1]	0.22	91.1	5.33	3.11	0.46
	②	Inlet of GH[*2]	0.02	87.2	9.09	3.36	0.35
	③	Outlet of GH	0.03	71.5	12.C	4.74	11.a
	④	Inlet of RT[*3]	0.00	46.4	32.C	4.08	11.5

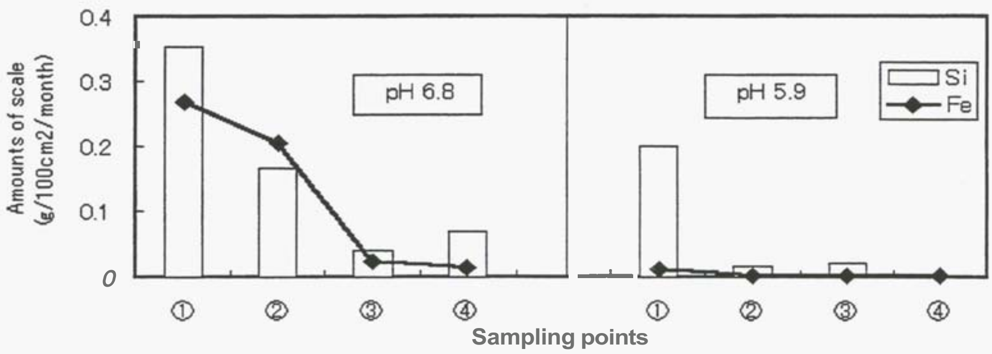

Figure 6. Amount of Si and Fe deposited in the test pipes at each sample point

Except for the case of sampling point 1 at pH 5.9, the amount of Si deposited is correlated to the concentration of Fe. It is well known that ferric hydroxide can coprecipitate a significant amount of silica. The results indicate that scale deposition, mainly consisting of Fe_2O_3 and SiO_2, depends on the deposition of ferric hydroxide. As a result, the formation mechanism of scale is reasonably understood to be a coprecipitation of silica with ferric hydroxide which is not filtered by continuous sand filter. In the Figure 6, it is remarkable that the deposition rate of Fe at pH 5.9 is slower than that of pH 6.8. The difference in the deposition rate is reflected in the color of the scale. At pH 6.8 the scale is brownish, whereas at pH 5.9 it is almost white. For utilization of treated water, the pH adjustment to below 6 is a practical and simple method to retard the scale deposition.

5.0 Countermeasures for Long-term Operation of the Plant

For practical applications, the deposition of silica scale may be a serious problem. The following are countermeasures for reducing the scale deposition rate.

(1) Maintain the pH of the treated water below *6*
(2) Dilution by adding fresh water
(3) Increasing the amount of heated water for dilution in the neutralization *tank*
(4) The pipe diameter for transmitting the treated water should be large for ease of maintenance.

6.0 Conclusions

Arsenic commonly occurs as a toxic material in natural ecosystems. The plant which we have developed is useful for abating arsenic in geothermal water. The results of this study show that arsenic was coprecipitated with polymerized ferric sulfate in the pH range of 3.0-3.4. Thus, the arsenic concentration of treated water was lowered below 0.01 mg/L. The treated water can be supplied not only to hot spring resorts, but also for agricultural use such as greenhouse cultivation. In the Hatchobaru area, treated geothermal water has been used for heating a greenhouse where moth orchids are grown as well as for bathing. **A** large capacity plant of 100 t/h has been constructed at Hatchobaru by New Energy Foundation(NEF).

7.0 References

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