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EXPERIMENTAL STUDY ON A SCALE PREVENTION METHOD
USING EXHAUSTED GASES FROM GEOTHERMAL POWER STATIONS

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ABSTRACT

For the utilizations of geothermal energy, prevention of scale deposition is one of the most important factors. In general, scale deposition is recognized at various places inside of transportation lines in geothermal power stations.

The silica scaling from geothermal fluids is brought about by a solution that is supersaturated with silica. It is known that silica deposition is prevented by controlling the pH of the solution by maintaining it in an acidic condition (about 5.0). There are various methods to control the pH of fluids. One is the addition of mineral acid to the solution. However, this method has not been applied until the present time because of its environmental impact. An alternative pH control method using geothermal gases discharged from geothermal power stations was studied. From the environmental view point, this method is more desirable than the former because the gases are mainly composed of carbon dioxide.

In this paper, the experimental study on the prevention of silica deposition will be described.

INTRODUCTION

In geothermal power stations utilizing a brine-dominated geothermal system, scale deposition from geothermal fluids not only causes troubles in the surface facilities such as the brine transportation lines, but also causes the decrement of reinjection capacity. For this reason, a lot of maintenance is necessary to remove scale deposition in the surface facilities or to drill additional reinjection wells for recovering the decrement of reinjection capacity. Therefore, a method of reinjecting high temperature fluid (direct reinjection) has been applied in some geothermal power stations to prevent scale deposition even though the geothermal fluid is ineffectively used. Then, if a new scale prevention method which is more effective and economical compared with the conventional method is developed, it will contribute to the decrease of electric generation cost. Furthermore, this may enlarge the effective use of the geothermal fluid.

Prevention of Siliceous Scale by pH Adjustment

Siliceous scale is initially formed by the reaction between silanol radicals (Si-OH). The speed of the reaction is dependent on such factors as temperature, pH, and the concentrations of coexisting salts. This

means that the formation of siliceous scale is affected by (1) silicic-acid concentration, (2) temperature, (3) pH, and (4) salts concentrations.

Figure 1 gives the relationship among actual scale deposition rate, pH and silicic-acid concentration in Otake and Hatchobaru brines. The scale deposition rates of wells H-17 and HT-7 in which the brine pH is in the acidic range of 3-5 were found to be very slow in comparison with those of wells H-7 and H-10 in which silicic-acid concentrations were at the same level.

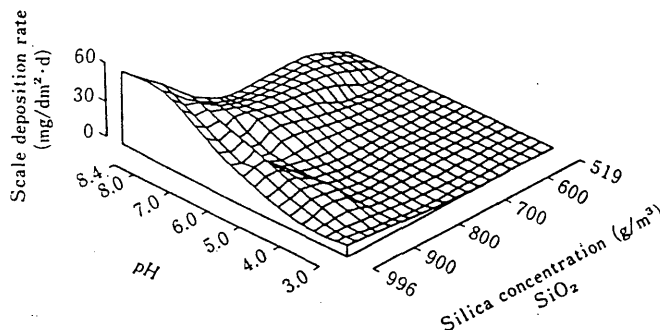


Figure 1. Relationship among scale deposition rate (measured value), silica concentration and pH for Otake & Hatchobaru brines.

In the Hatchobaru power station, brine is discharged at a volume of about 1000 m³/hr, with a pH value of about 7.5, and an average silicic-acid concentration of 850 g/m³ (as SiO₂). The scale deposition rate is measured as 20-80 mg/dm²·d. When HCl was added to the brine and pH value was adjusted to 5-5.5 to prevent polymerization of silicic-acid, scale deposition rate decreased to very small value of 0.85 mg/dm²·d. In addition, using test pieces, the corrosive rate of steel material caused by acidic brine was measured as 0.017-0.023 mm/yr, which was smaller than the common corrosive rate of steel of 0.05 mm/yr. Therefore, it is considered not to cause any problem.

The relationship between the pH of brine flowing in the heat exchanger and the scale deposition rate was studied using test pieces. When brine temperatures were set at 90 and 50°C and pH was in the range of 5-9, scale deposited faster in the case of Hatchobaru brine in which the concentration of silicic acid was higher, and the scale deposition rate was smaller in case of low supersaturation. The scale

deposition rate increased with a decrease in cooling temperature. But the preventive effects of scale deposition in each case were remarkable when the brine was adjusted to pH 5-6.5.

In reinjection simulation tests, the pH of the brines in different silicic-acid concentrations was adjusted to the range of 5-8.5 and brines were transmitted into the permeable layer. The transmission time turned longer with a decrease in pH in the case of every brine. Clogging in the permeable layer was not recognized in the pH range of 5-5.5. As a result if the brine pH can be controlled to 5-5.5, not only scale deposition in surface facilities of power plants, but also the decrement of reinjection capacity can be prevented.

pH Adjustment Using Exhausted Gases

In the Otake and Hatchobaru power stations, NaOH is injected to the main cooling system and the pH is adjusted to a neutral range to prevent its corrosion. According to the results of experiments on the mechanism of corrosion in the system, the cause of the decrease in the pH of the main cooling water is presumed to be the dissolving of noncondensable gases into the liquid phase. This suggested to us to make a fundamental study on pH adjustment using exhausted gases to prevent scale deposition.

Exhausted gases containing 70 percent of CO₂ and 2 percent of H₂S were introduced into the gas absorption vessel in which brine was transmitted continuously. The effect of the pH adjustment was confirmed. The pH of the brine tended to decrease with an increase in the liquid-gas ratio. However, the pH value remained constant when the ratio was above 15.

Brine pHs were adjusted to 5.8 and 5.3 by means of gas absorption. The brines were kept at 80-89°C and room temperature, respectively. The variation of monosilicic-acid concentration with time, the so called polymerization speed was measured. As a result, polymerization of supersaturated silicic acid was recognized to have been prevented for about 2 hours after the brine pH had been adjusted to 5.3. Besides, monosilicic silica decreased more slowly later in comparison with the case when the pH was adjusted to 5.8.

Exhausted gases from power stations were introduced continuously at a gas-liquid ratio of 14.5 into the Hatchobaru brine in silicic-acid concentrations of 840-850 g/m³ and at a pH of 7.0. The pH value of the brine was adjusted to 5.2 (59°C) after gas absorption. A test piece was inserted into the treated brine and the quantity of scale deposition was measured every 24, 48 and 72 hours. The scale deposition rate was 0.5 mg/dm²·d, which was approximately 1/30 that of brine without pH adjustment. Therefore, scale deposition was thought to be prevented.

In the Hatchobaru power station, exhausted gas from the condenser is expelled at a speed of 1200-1800 Nm³/hr. Supposing that the total quantity of gas is used in the pH adjustment at a gas-liquid ratio of 10, about 120 m³/hr of brine, that is only 10 percent of the discharged brine can be treated, while the actual quantity of gas consumed in pH adjustment by the gas absorption set-up decreases slightly. Therefore, multiple gas absorption set-ups shown in Figure 2 are

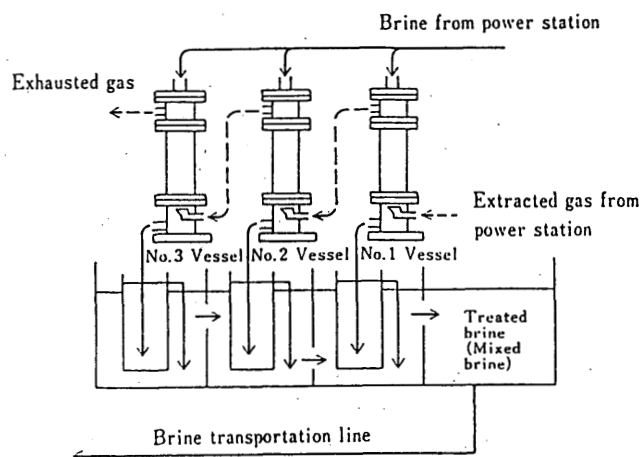


Figure 2. Gas and absorption set-up

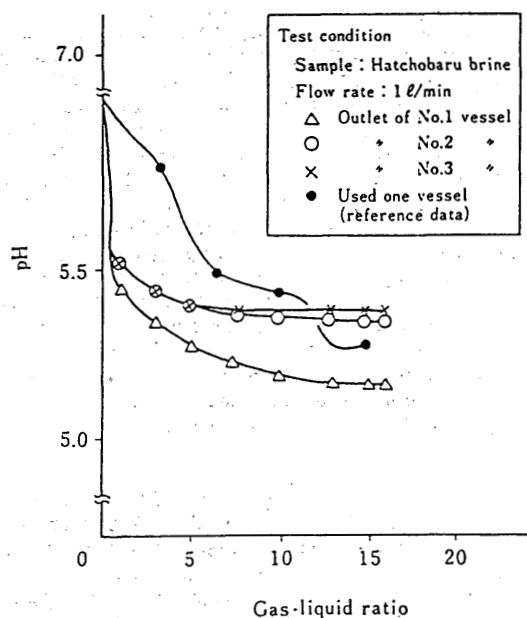


Figure 3. Relationship between pH and gas-liquid ratio for each vessel.

adopted. The method is studied by circulating and reutilizing the exhausted gas to increase the quantity of brine to be treated. In fact, the gas-liquid ratio decreased substantially. As a result of the experiment using the multiple gas absorption set-up, the pH value of brine at the outlet of each vessel can be controlled to below 5.5 under the temperature condition of 85°C (shown in Figure 3).

In order to confirm the preventive effect of scale deposition by the pH control method, a test piece was dipped into brine at every outlet of the vessel and the scale deposition rate was measured. As shown in Figure 4, the scale deposition rate at every outlet decreased to 1/20-1/30 of that of brine without treatment. However, when the gas absorption set-up is operated continuously for a long period, red-brown

slime deposits on the surface of the packing materials filled the inside of the gas absorption set-up for better contact between phases of gas and liquid.

The deposition rate of slime in the gas absorption set-up was as high as 5-10 mg/dm²·d. If the brine was transmitted into an imitation permeable layer, the layer clogged in a short time. Slime quantity was recognized to be dependent on the gas-liquid ratio and the mixing of air. Slime is mainly composed of SiO₂ and S. The contents of the sulfides of Fe, As and Hg, which are slight components of brine, are comparatively high. From these results, the reasons for preventing slime formation is considered as firstly the formation of sulfides from H₂S in exhausted gas and metal ions in brine; secondly, the release of colloid sulfur from H₂S by a reaction similar to the Claus Reaction; and thirdly, the coagulation of SiO₂, connected with the above two phenomena.

Slime removal and preventive methods were studied by physical means such as the improvement of the gas absorption vessel, prevention of air mixing, and setting a filter in the treated-brine transportation line. But the desired effect has not been obtained. The test was then done by adjusting the brine pH using CO₂ only with the aim of investigating the affect of H₂S on the exhausted gases. As a result, the brine pH could be adjusted to 5.2-5.4 (at 87°C) and slime formation was prevented in the outlet of the gas absorption set-up and the waste-water transportation line after commingling of treated brine. This means that pH adjustment by exhausted gases after removing the H₂S is effective for slime formation and deposition.

From the results to date, it is clear that continuous removal of H₂S from the exhausted gases is desirable for decreasing scale quantity (preventing slime deposition) in the brine-transportation lines after gas absorption. A removal method using Cl₂ or O₃ was tried but proved to be ineffective. Therefore, selective separation of H₂S by the pressure swing absorption (PSA) process was adopted.

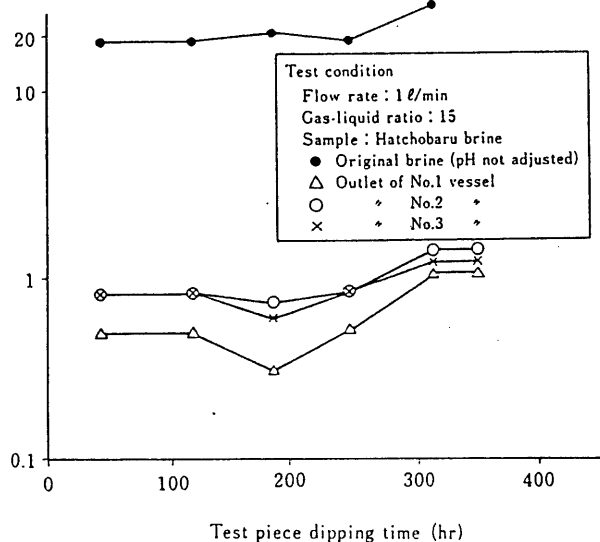


Figure 4. Change of scale deposition rate of the brine treated by gas absorption.

In the PSA process, an inorganic absorbent such as zeolite is used to separate a certain gas selectively from a mixture of gases. Scrubbing (regeneration) is done by controlling the gas pressure. Selectivity is realized by fitting the pore size of the absorbent. This is the first trial for the author to apply the PSA process to H₂S separation.

For investigating the proper conditions for selective separation of H₂S from exhausted gases whose main component is CO₂, imitation gases were transmitted into the PSA test apparatus consisting of two small vessels (shown in Figure 5). As a result, a kind of aluminum was recognized to be an effective absorbent. Suitable operation conditions such as absorption temperature, scrubbing pressure and others were obtained. The gas balance in a continuous gas-separation test under these conditions is also shown in Figure 5. Using the PSA process, a gas mixture containing 70 percent of CO₂ and 2 percent H₂S was separated into gas containing H₂S, at a ratio of 3:1, respectively. However, under the test conditions colloidal sulfur was deposited and the absorption ability decreased. This problem can generally be solved in combination with the temperature swing absorption (TSA) process. Hopefully, it can also be solved by proper selection of other adsorbents according to experiments.

SUMMARY

Outline of Experimental Results

- (1) Brine pH can be controlled to about 5.5 using exhausted gases from power stations.
- (2) H₂S in exhausted gases causes the formation of slime but it can be effectively separated by the PSA process.
- (3) The method of circulating and reutilizing gases is effective in increasing the treating capacity of brine.
- (4) The pH value of the brine after gas absorption is comparatively constant for as long as the temperature does not decrease.

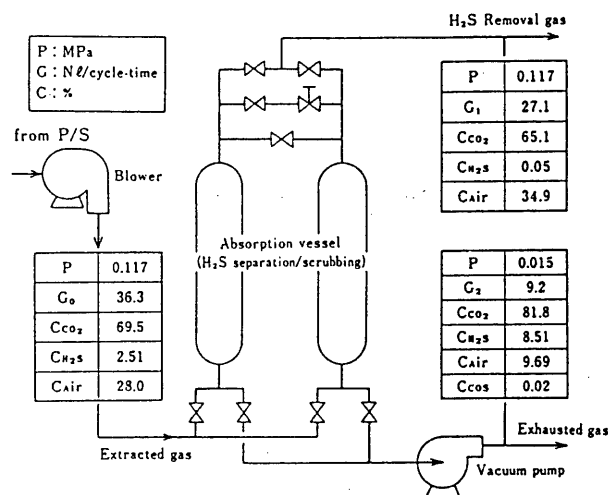


Figure 5. Schematic of PSA process and gas balance for H₂S separation from extracted gas.

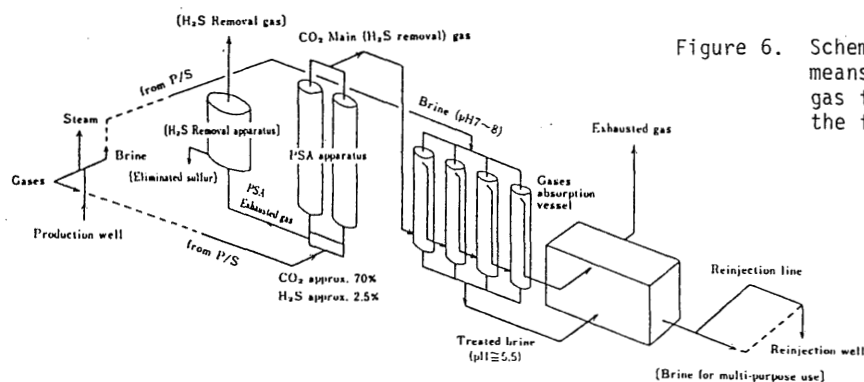


Figure 6. Schematic of scale prevention process by means of pH adjustment using extracted gas from geothermal power station (in the future).

Besides, polymerization of supersaturated silicic acid in brine can be prevented.

- (5) The scale deposition rate in brine after pH adjustment can be decreased to 1/20 of that in brine without treatment.
- (6) Prevention of scale deposition by pH control is effective in the heat exchanger and it prevents clogging in the permeable layer.

Characteristics and Prospective Effects

A schematic of the scale-prevention process by means of the pH-control method using exhausted gases is shown in Figure 6. The system has the following characteristics and effects when it is put into use.

- (1) Cost is lower than that of the other processes for scale prevention like floating separation.
- (2) Environmental problems can be avoided because no chemical reagent is used, and the CO₂ gas which had been exhausted to atmosphere up to now is only utilized in this process.
- (3) The process is not only effective for preventing scale deposition in surface facilities but also for preventing a decrease in reinjection capacity.
- (4) The multipurpose use of brine discharged from power stations is realized owing to this process.
- (5) It will contribute to the dissemination of power generation with double-flash cycle.
- (6) Based on this process, the development of H₂S removal techniques can be promoted.

APPENDIX

Several problems remain in the application of the scale-prevention technique using exhausted gases from geothermal power stations. However, these are considered to be solved in the future. If the process is put into practical use at low cost as a simple preventive method of scale deposition, it will contribute to the effective use of geothermal energy.

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