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SCALE PREVENTION METHOD BY PH MODIFICATION USING ADVANCED BIOREACTOR

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ABSTRACT

Silica scale deposition is one of the most serious problems in geothermal power stations using hot water-dominated geothermal systems. The scale causes plugging troubles in surface facilities and reduces the capacity of reinjection wells. A new process was proposed for scale prevention. This process is based on pH modification methods. H_2S in geothermal gas is oxidized to H_2SO_4 using sulfur-oxidizing bacteria in the bioreactor. H_2SO_4 is used for pH modification of geothermal brine. We have already reported on the field experiment carried out at Otake geothermal power station using a bubbling tower type of bioreactor. The results showed that the system could be operated stably for over 2,700 hours and was applicable to geothermal power stations, but mass transfer of H_2S at gas-liquid interface limited H_2SO_4 production rate. In this study, we replaced the bubbling tower with a packing tower to make the sulfur oxidizing reaction efficient. The packing tower type of bioreactor is filled with Raschig rings made of ceramic. The solution containing the sulfur oxidizing bacteria and nutrients is injected into bioreactor from the top and the geothermal gas is injected from the bottom. H_2S is oxidized in the zone where the gas contacts the solution. The geothermal gases are mixed with air and the H_2S concentration in mixed gas is 0.2~0.3 %. The advanced system was operated for over 3,000 hours on site. H_2SO_4 production rate was 0.07 kg-S m^{-3} h^{-1} at high H_2S removal operations (H_2S removal efficiency 95%) and 0.12 kg-S m^{-3} h^{-1} at high H_2SO_4 production rate operations (70%). This rate was 3~6 times larger than the bubbling tower type. From the estimation using the results of this study, the bioreactor volume of 12 m^3 was need for controlling the pH of the waste brine from the Otake geothermal power station.

1. INTRODUCTION

In geothermal power stations using hot water dominated geothermal systems, silica scale deposition is one of the most serious problems. Silica deposition causes plugging troubles in surface facilities such as the hot water transportation lines and a reduction of reinjection capacity. In the cases of Otake and Hatchobaru field in Japan, the average reinjection capacity has been decreasing at a rate of around 30% a year. To maintain the total injection capacity, two or three additional wells have to be drilled annually. In other geothermal stations, the brine from geothermal power station is reinjected at high temperature to avoid the scaling trouble. Direct reinjection system cannot use geothermal energy efficiently. In order to solve the silica scale problems, a number of scale prevention methods such as a centrifugation, a flotation, an ultrafiltration and a retaining tank system have been developed to date, but such operation costs are expected to be expensive. It is well known that silica deposition is prevented by keeping pH of the geothermal hot water acidic. pH modification is one of the most promising methods from the point of view that it is characterized as high effectiveness and easy installation. But pH modification of the geothermal hot water by mineral acid injection has not been commercially applied so far to geothermal power stations in Japan. On the other hand, direct emission of H_2S from geothermal power stations is also a matter of great concern from the environmental point of view. Several countries have already made environmental regulations for mitigating the H_2S emission. Geothermal power stations are under obligation to use H_2S abatement systems, which cause an increase in the costs. The new process, which uses H_2SO_4 produced from exhaust gas, was started to solve these two problems (Hirowatari et. al., 1990, 1995 and 1996). In the new process, the exhaust gas from the power station is supplied to a bioreactor in which microorganisms are cultured. The microorganisms oxidize H_2S in the exhaust gas to H_2SO_4. The produced H_2SO_4 is used for controlling the pH of the geothermal brine. This system can prevent scale deposition and H_2S dispersion simultaneously (Fujioka et.al, 1995). We have already reported on the field experiment carried out on site using a bubbling tower type of bioreactor (Hirowatari et. al., 1997, 1998). The results showed that the system could be operated stably for over 2,700 hours and was applicable to geothermal power plants, but mass transfer of H_2S at the gas-liquid interface limited H_2SO_4 production ratse. In this study, a field experiment using a packing tower was conducted to make the sulfur oxidizing reaction efficient.

2. EXPERIMENT

To improve the sulfur-oxidizing reaction, we designed and built the packing tower of bioreactor (advanced bioreactor) in the field. The advanced bioreactor consists of gas supply lines, circulation lines of solution, a water jacket, a concentrated nutrient solution tank, a yeast extracts solution tank and a microfiltration module and so forth. External appearance and a schematic diagram of the advanced bioreactor are shown in Figures 1 and 2. The reactor volume is about 0.35m^3. The exhaust gas from the power station contains about 0.8-1.5 vol% of H_2S, 30-50 vol% of CO_2 and the other gases such as N_2, O_2 etc. The exhaust gas mixed with air is supplied into the bioreactor from the bottom as a feed gas. The feed gas rate is 6~14 Nm^3/h and H_2S concentration in the feed gas is about 0.1~0.4 vol%. The packing tower type of bioreactor is filled with Raschig rings made of ceramic. The solution containing sulfur oxidizing bacteria and nutrients is injected into the bioreactor from the top. H_2S is oxidized in the zone where the gas contacts the solution in the bioreactor. The heater is used for fixing the temperature of the solution in the bioreactor. The microfiltration module is used for recovery of bacteria from the produced acid solution. To start up the experiment, the temperature of the solution in the bioreactor is controlled at 70-80 °C. Geothermal brine is used for keeping the temperature of the solution in the bioreactor. The solution contains 0.3 % of inorganic nutrients. The sulfur oxidizing bacteria, that are cultured in the incubator heterotrophically, are inoculated into the solution in the bioreactor. In this system, we use *Sulfolobus* sp. *Strain7* (Inatomi et.al. 1983) as the sulfur oxidizing bacteria. Under these conditions, the feed gas is supplied into the bioreactor from the bottom and oxidation reaction starts at the same time. The bacteria in the bioreactor oxidize H_2S in the feed gas into H_2SO_4 and grow using energy acquired by sulfur oxidation. The desulfurized gas is exhausted into atomosphere from the top of the bioreactor. As H_2SO_4 produced by oxidation of H_2S is accumulated in the bioreactor, pH of the solution in the bioreactor decreases. To maintain the pH, the acidic solution produced by sulfur oxidation is discharged through the microfiltration module periodically and the same volume of tap water with the concentrated nutrient solution and yeast extracts solution from each tank is supplied. The bacteria in the acidic solution are recovered at the microfiltration module and returned to the bioreactor, so concentration of bacteria in the bioreactor is kept at a certain level. The acidic solution discharge rate depends on the initial feed gas rate and H_2S concentration in the feed gas. The pH of the acidic solution also changes as the H_2S concentration in the feed gas changes. The feed gas rate and H_2S concentration in the feed gas are analyzed and used for feedback control of the acidic solution discharge rate to keep the pH in an appropriate range. During the experiment, H_2S concentration of the feed gas and discharged gas is analyzed using gas chromatography. The pH of the solution in the bioreactor is measured continuously using a glass electrode. H_2SO_4 concentrations of the solution were determined by ion chromatography, and total sulfur concentrations were also determined by ion chromatography after absolute oxidation using bromine.

3. RESULTS AND DISCCUSSION

Figure 3 shows H_2S concentration in the feed gas and exhausted gas during the experiment. The experiment was carried out for about 3000 hours. H_2S concentration in the feed gas ranged from 0.1 % to 0.4 %. In the early stages of experiment, we operated under various conditions to determine the fundamental operating parameters for packing tower types of bioreactor, so H_2S concentrations in the feed and exhausted gas were scattered. From 600 hours to 1500 hours, the bioreactor was operated under high H_2SO_4 production rate conditions. After 1700 hours, bioreactor was operated under high H_2S removal efficiency conditions and H_2S concentration in the exhaust gas was kept under 100ppmv. Figure 4 shows H_2SO_4 production rate during the experiment. H_2SO_4 production rate was calculated from the discharge rate and H_2SO_4 concentration of the solution. Maximum H_2SO_4 production rate in this experiment was 0.117 kg-S m^{-3} h^{-1}. At high H_2SO_4 production rate conditions (>0.10 kg-S m^{-3} h^{-1}), H_2S removal efficiency was relatively low (around 75%). Under the high H_2S removal efficiency conditions (H_2SO_4 production rate < 0.07 kg-S m^{-3} h^{-1}), H_2S removal efficiency was over 95%. Figure 5 shows the relationship between H_2SO_4 production rate and H_2S supply rate. The solid line shows the limiting case of H_2S completely converted to H_2SO_4. As H_2S supply rate increases, H_2SO_4 production rate also increases, but at H_2S supply rates over 0.10 kg-S m^{-3} h^{-1}, complete conversion to H_2SO_4 cannot be achieved. Figure 6 shows the relation between H_2S removal efficiency and H_2S supply rate. H_2S removal efficiency decreases under high H_2S supply rate (over 0.10 kg-S m^{-3} h^{-1}) This trend is typical for the packing tower used. In this experiment, H_2SO_4 production rate was 3~6 times larger than that of the previous experiment using a bubbling tower type. The result shows that packing tower type of bioreactor can improve sulfur oxidation reaction and be applied to H_2SO_4 production systems.

4. ESTIMATION OF THE SIZE APPLIED FOR ACTUAL PLANT

Keeping the pH of geothermal brine under 5.5 can prevent the silica scale deposition. We estimated the reactor volume for this system applied for the Otake geothermal power station using the H_2SO_4 production rates from this experiment. The Otake geothermal power station discharges 350 m^3 h^{-1} of the total waste geothermal brine and 290 N m^3 h^{-1} of the total exhaust gas. 1.2 L of 0.1 N H_2SO_4 is needed to control the pH of 1 m^3 of the Otake geothermal brine at 5.5. The result of the estimate shows that a reactor volume of 6 m^3 (in the case of H_2SO_4 production rate operation) or 12 m^3 (in the case of H_2S removal efficiency operation) and about half of the exhaust gas from the geothermal stations was needed for controlling the pH of the waste brine from the Otake geothermal power station.

5. CONCLUSIONS

To enhance the H_2S removal and H_2SO_4 production reaction, an advanced bioreactor was designed and installed in Otake geothermal field. A packing tower type of bioreactor was used as the advanced bioreactor because previous studies indicated that mass transfer limited H_2S removal and H_2SO_4 production using a bubbling tower bioreactor. The experimental results are summarized as follows.

1) A packing tower type of bioreactor could be operated over 3000 hours at site. H_2SO_4 production rate was 3~6 times larger than bubbling tower type.
2) H_2SO_4 production rate was 0.07 kg-S m^{-3} h^{-1} at high H_2S removal operation (H_2S removal efficiency 95%) and 0.12 kg-S m^{-3} h^{-1} at high H_2SO_4 production rate operation (70%).
3) From the estimation using the results of this study, the bioreactor volume of 12 m^3 was need for controlling the pH of the waste brine from the Otake geothermal power station.

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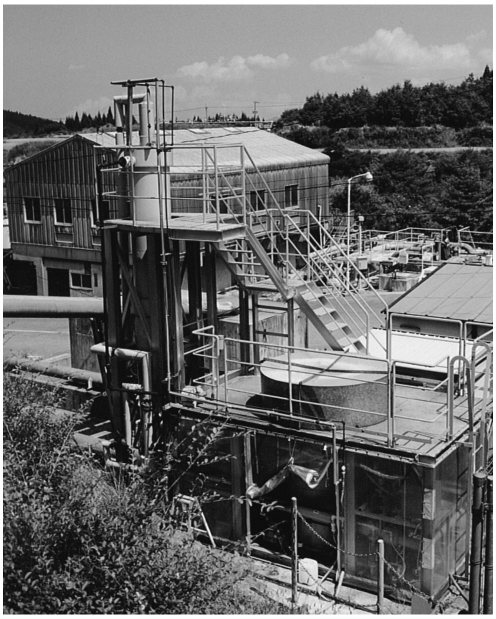

Figure 1. External appearance of the advanced bioreactor

Inatomi, K., Ohba, M. and Oshima, T. (1983) Chemical properties of proteinaceus cell wall from an acido-thermophile, *sulfolobus acidocaldarius*. *Chem Lett.* Vol. 8, 1991-1994.

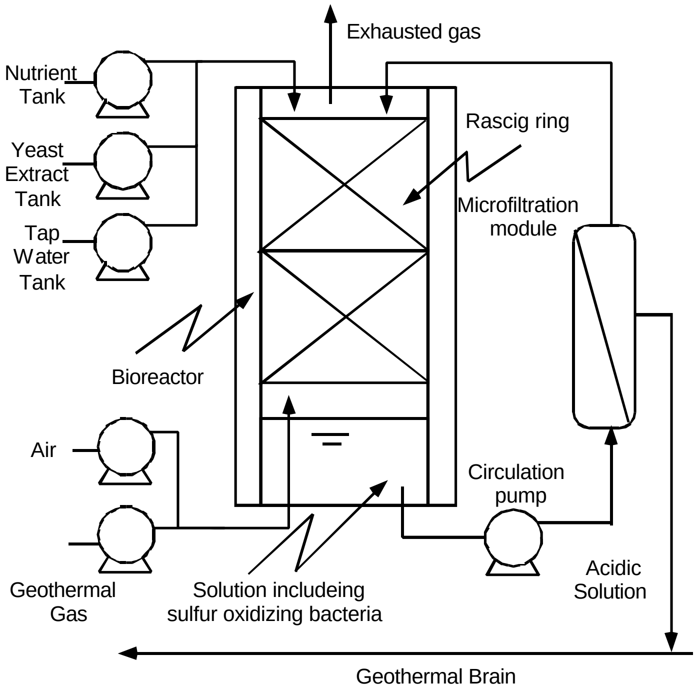

Figure 2. Schematic diagram of the advanced bioreactor

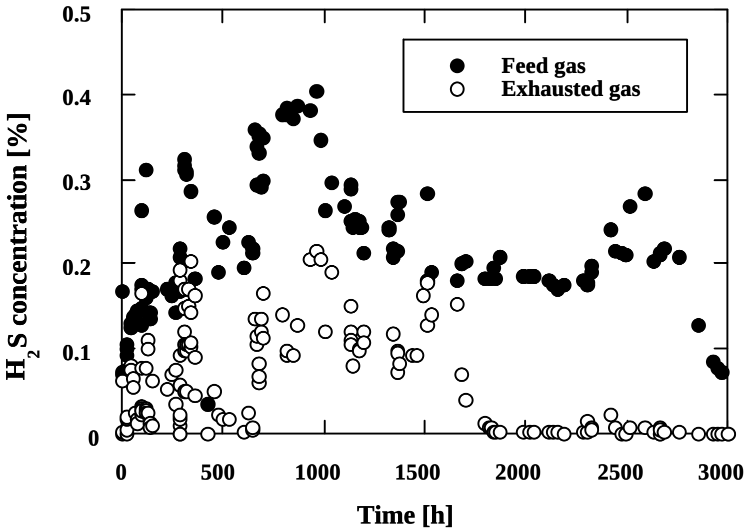

Figure 3. H_2S concentration in the feed gas and exhausted gas during the experiment.

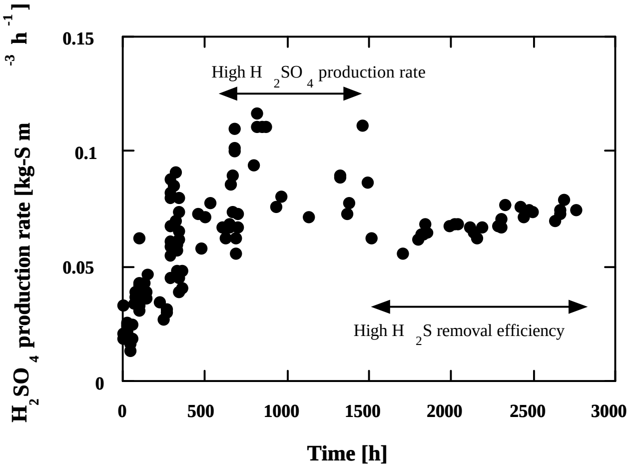

Figure 4. H_2SO_4 production rate during the experiment

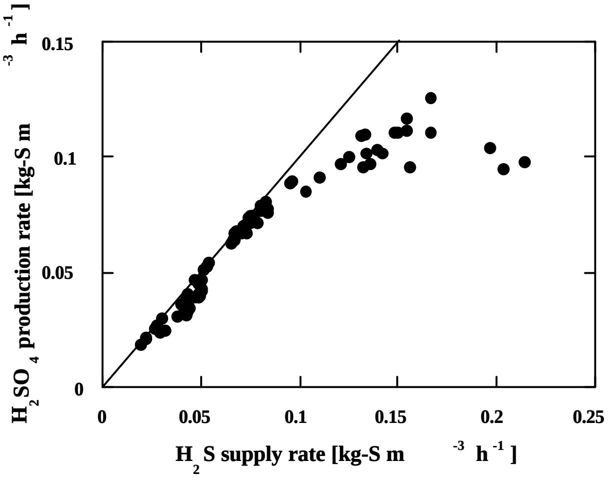

Figure 5. The relation between H_2SO_4 production rate and H_2S supply rate.

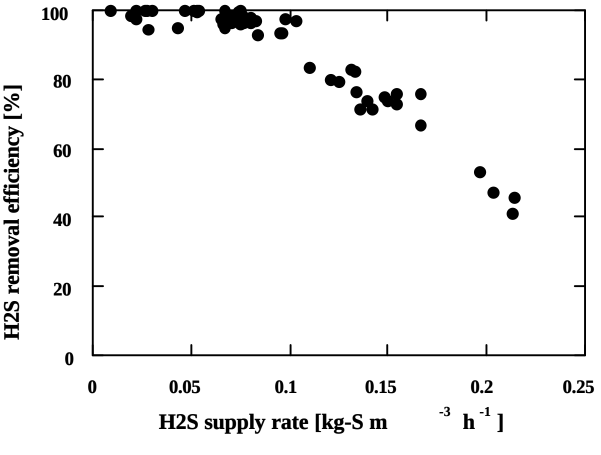

Figure 6. The relation between H_2S removal efficiency and H_2S supply rate