Production of sulfuric acid from geothermal power station exhausted gas for use in scale prevention

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Abstract

Among a number of serious problems experienced in geothermal power stations, silica scale deposition at various places has great importance in maintaining rated capacities for power generation.

It has already been known that silica deposition is prevented by keeping the pH of the solution acidic Therefore, it was considered that the pH of the brine can be controlled by sulfuric acid manufactured from hydrogen sulfide in the exhausted gases. In an experimental apparatus, the sulfuric acid for the acidification of the brine was confirmed to be manufactured from hydrogen sulfide by three different methods : ① hydrogen sulfide burning method ② thermophilic biological oxidation method. ③ biochemical reactor method.

These methods generally provide economical acidification processes to prevent silica scale deposition and would also contribute to the reduction of hydrogen sulfide emission at geothermal power stations.

Introduction

In the geothermal power stations utilizing brine dominated geothermal systems, silica scale deposition problems and air pollution by hydrogen sulfide emission from geothermal fluids are a matter of great concern.

The silica scaling 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, it is necessary to remove scale deposits from various parts of surface facilities for maintenance and / or to drill additional reinjection wells for recovering reinjection capacity. It is assumed that such maintenance costs are enormous.

On the other hand, from the environmental point of view , the amount of hydrogen sulfide extracted from the condensers in power stations should be reduced in more economical ways.

Therefore, if a newly developed scale prevention method is more effective, economical and environmentally-friendly, it will greatly contribute to the reduction of electricity generation costs in geothermal power stations. Furthermore, it may extend the effective use of geothermal brine.

Preventive effect of silica scale deposition by pH adjustment

1. Factors affecting silica scale deposition

As siliceous scale is fundamentally formed by reciprocal reaction of silanol radicals $[Si(OH)_3O^-]$, the scale deposition rate of the brine containing supersaturated silica is dependent on ①silicic acid concentration, ② temperature, ③ pH, and ④ salts concentrations. It has been shown that scaling rate can be controlled by adjusting the pH of brine while other conditions (the silicic acid concentration, temperature, and so on) can be kept constant (O. Weres et al., 1980 and others).

2. Confirmation of scale preventive effect by pH adjustment

(1) Effects on the transportation lines at surface facilities

In the Hatchobaru, Japan Power Station, brine is discharged approximately at a rate of $1000 m^3/h$ with mostly neutral pH and average silicic acid concentration of $850 g/m^3$ (as SiO_2). The scale deposition rate of raw brine is $20\text{-}80 mg/dm^2\cdot d$. On the other hand, that of the brine whose pH was adjusted to 5-5.5 by adding HCl to prevent polymerization of silicic acid is as low as $0.85 mg/dm^2\cdot d$. In fact, the scale deposition rate of individual brine discharged from Hatchobaru production wells, for example H-17 and HT-7, in which the brine pH is in acidic range of 3-5 was found to be less in comparison with those of wells H-7 and H-10, in which silicic acid concentrations were at the same level.

(2) Simulated reinjection test result

The pH of brines with different silicic acid concentration were adjusted to the range of 5-8.5. Then, the brines were transmitted into the permeable layer in a reinjection simulation test apparatus (Hirowatari, K., 1987). According to the test results, the transmission time increased with a decrease in pH for every brine. Moreover, no clogging in the permeable layer was recognized in the pH range of 5-5.5.

(3)Corrosion rate in pH adjustment

Using a test coupon, the corrosion rate of a steel material exposed in the acidified brine was measured. It was in the range of 0.017-0.023mm/yr. This corrosion rate was less than the common corrosion rate of 0.05mm/yr for steel . Therefore, it was expected that pH adjustment would not cause any corrosion problems in the actual plants.

pH adjustment using exhausted gases

The pH of main cooling waters in the Otake and Hatchobaru power stations have been controlled to neutral range by NaOH injection. The main reason for the pH decrease in the main cooling water system was presumed to be dissolution of non-condensable gas into the liquid phase. This presumption caused us to plan the fundamental studies on pH adjustment using acidic exhausted gases (CO_2, H_2S) to prevent silica scale deposition from brine. As a results of a direct contact gas absorption test, we found several problems on the application of scale prevention technology using exhausted gases from geothermal power stations, which included sulfide slime formation in the liquid phase (Hirowatari, K., 1990). Then, alternative methods described below were proposed, and the neccessary tests were carried out to investigate their feasibility.

1. Separated H_2S burning method

(1)Summary of the process

The hydrogen sulfide (H_2S) in the non-condensable gas extracted from the condenser is separated and concentrated in the PSA (Pressure Swing Adsorption) apparatus, and is used for the production of sulfuric acid (H_2SO_4) in the combustor followed by a SO_2/SO_3 converter and a scrubber. The recovered H_2SO_4 is concentrated in a storage tank before being used for prevention of scale deposition by pH adjustment of the brine.

The appearence of the apparatus (PSA) is shown in Photo-1 and its schematic diagram in Figure-I, respectively.

(2)Separation and concentration of H_2S

The feed gas for this experiment is the extracted gas from the condenser of the Otake power station. It contains 0.7-1.3vol% H_2S , 30-50vol% CO_2 and the other gases such as N_2, O_2 etc. The PSA system for the dry separation and concentratinn of H_2S is adopted.

In this process, a specific gas (H_2S) is adsorbed selectively from a mixed gas by an inorganic porous material like zeolite or alumina, etc., and then the adsorbed gas is desorbed (reactivated) at a depression condition for recovery. Although PSA itself became a common technology long time ago ,there has been no report where it is adopted for H_2S separation purposes (Izumi, J. et al, 1992). The PSA apparatus consists of two adsorption towers for cyclic adsorption and desorption. In this experiment, a two stage PSA system to get higher H_2S concentration is utilized.

To achieve an adequate gas separation with the PSA, we must determine an optimum condition for adsorption pressure, desorption pressure, cycle time (time span between adsorption and desorption steps),purge ratio (or counter purge flow ratio), etc.

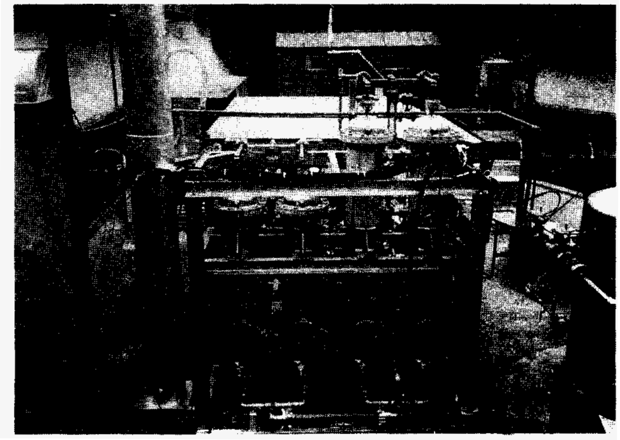

Photo-1 Appearence of the PSA apparatus

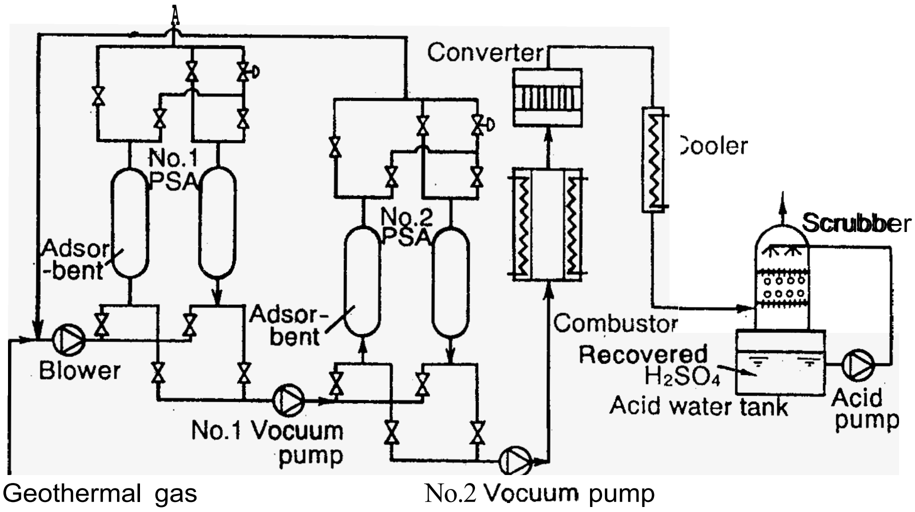

Figure-1 Schematic diagram of the H_2S·Separation Hydrogen sulfide burning method

As a result of our basic study, it was confirmed that an alumina adsorbent shows excellent performance at a low adsorption pressure and a low temperature. The increase of the purge ratio was not always effective for performance improvement. It was also confirmed that the performance is very much dependent on the cycle time. Since a relatively shorter cycle time seemed more advantageous from the view point of the adsorption tower design, we set the cycle time at about 100 seconds.

The feed gas containing 0.94vol% H_2S was supplied to the PSA apparatus at a rate of $12.25Nm^3/h$ and was treated under the optimum conditions. Hydrogen sulfide was concentrated to 6.0vol% at the first stage of the PSA system and 16.8vol% at the second stage with its gas volume of $0.6Nm^3/h$. On the other hand, the H_2S concentration of the vent gas was less than $500ml/m^3$.

(3) H_2S combustion and sulfuric acid production

This apparatus consists of a H_2S combustor, a SO_2/SO_3 converter loaded with a catalyst, a H_2SO_4 scrubber, a product H_2SO_4 tank and a discharge pump, etc.

The concentrated H_2S burns in the combustor and is oxidized to SO_2. Then, the SO_2 is converted to SO_3 in the SO_2/SO_3 converter with a vanadium catalyst. When the SO_3 is absorbed by the water in the scrubber, H_2SO_4 is finally produced.

The H_2SO_4 production is influenced by the feed gas H_2S concentration, the operating temperatures of the combustor and the converter and the excess air ratio in the combustor etc. As the converted SO_3 is almost perfectly absorbed into the circulated water in the scrubber, H_2SO_4 with any specified concentration can be easily manufactured .

From the result of the fundamental experiments, it was expected that the oxidation efficiency of H_2S to SO_2 would reach nearly 100% when the temperature of H_2S combustor was kept above 550°C. However, both the SO_2/SO_3 conversion efficiency and the SO_3 absorption efficiency have not exceeded the level of 90% as yet in our present experimental apparatus.

(4) Experimental results

The flow rate of the supply (recovery) gas from the PSA system to the H_2S combustor was about $0.6Nm^3/h$ and its average H_2S concentration was about 15vol%.

This gas was combusted continuously at 550 ℃. Figure-2 shows that the H_2SO_4 concentration at the product H_2SO_4 tank which contains water in the amount of $0.29m^3$, reached 15.6wt% after a 165 hours of operation. This is equivalent to a H_2SO_4 production rate of around 280-320g/h.

The commercial plant for the Otakc power station requires a scale up of eight times from the present experimental apparatus to produce enough of H_2SO_4 to keep the pH value of the geothermal hot water with the flow rate of $350m^3/h$ at 5.5. In this plant, about one third of the total extracted gas from the condensers of this power station will be effectively used for this purpose.

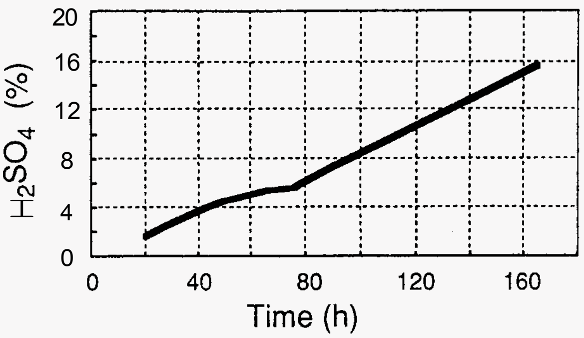

Figure-2 Production rate of H_2SO_4 by method ①

2.Thermophilic biological oxidation method

(1) Summary of the process

The gas exhausted from the Otake geothermal power station is supplied to a specific hot solution in which a thermophilic sulfur oxidizing bacterium is cultured. In this solution, the bacterium converts the H_2S in the gases into H_2SO_4. The recovered H_2SO_4 is used for controlling the pH of the geothermal brine in order to prevent the scale deposition. The appearance and the schematic diagram of the apparatus are shown in Photo-2 and Figure-3, respectively.

(2) Testing setup and experiment

The test apparatus consists of a gas supply pipe, a bacteria growth tank, a desulfurization reactor, and an acid water tank. The thermophilic sulfur oxidizing bacteria (sulfolobus) are added to the solution in the desulfurization reactor.

The temperature of the solution is controlled at about 70 ℃ . These bacteria are cultured in the bacteria growth tank. The feed gas from the geothermal power station is supplied into the desulfurization reactor at the bottom. The H_2S concentration in the feed gas is 1.2-1.3vol%. Air is also supplied into the desulfurization reactor at the bottom. Both the feed gas and the air are supplied normally at the same rate of $0.1m^3/h$, which is equivalent to $20h^{-1}$ of SV (Space Velocity) in the desulfurization reactor. Under these conditions, the bacteria oxidize the H_2S into H_2SO_4. The desulfurized gas is discharged into air from the top of the reactor.

In this experiment, when the pH of the solution in the desulfurization reactor decreases to a certain level, the solution with concentrated H_2SO_4 is discharged from the desulfurization reactor where the same amount of neutral solution is supplied. The discharged H_2SO_4 solution is stored in the acid water tank. The bacteria in the solution is supplied from the bacteria growth tank into the desulfurization

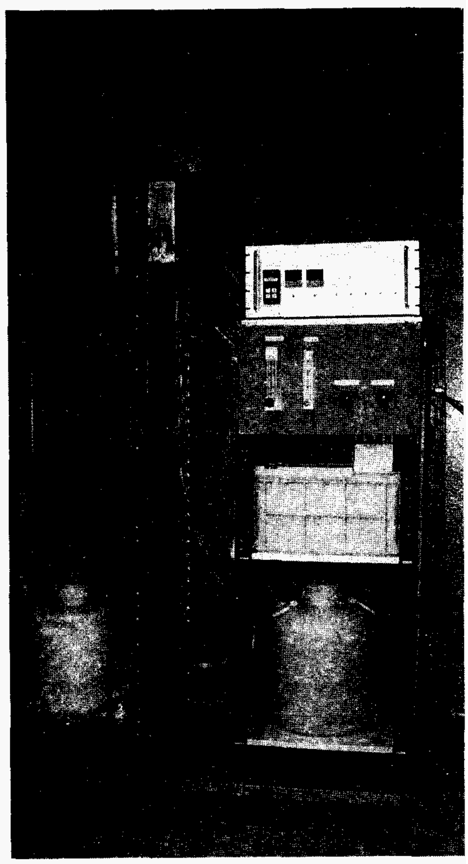

Photo-2 Testing setup of thermophilic biological oxidation reactor

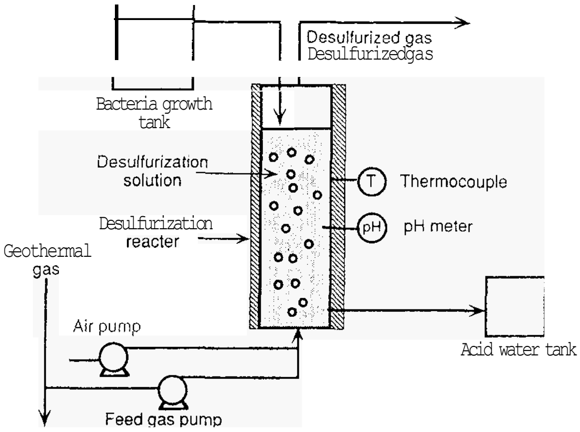

Figure-3 Schematic diagram of the thermophilic biological oxidation method

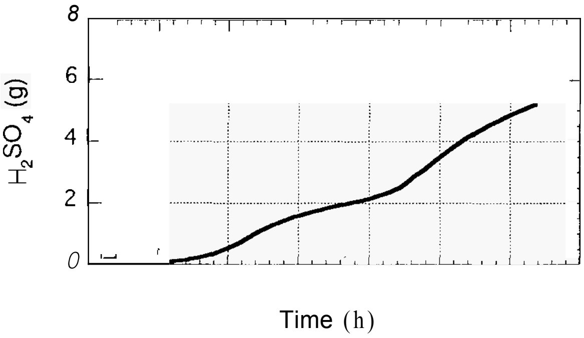

Figure-4 Production rate of H_2SO_4 by method ②

reactor to keep the number of the bacteria in an appropriate range.

(3)Experimental results

As the bacteria oxidized H_2S in the gases to H_2SO_4 in the desulfurization reactor, the pH of the solution decreased in a short time. After 40 hours of operation, the pH value reached 2.0. Then, the solution with concentrated H_2SO_4 was periodically discharged from the desulfurization reactor to the acid water tank. As a result, 5g of H_2SO_4 was manufactured in 60 hours as shown in Figure-4. The production rate of H_2SO_4 per unit volume of the solution in the desulfurization reactor was about 35g/h・m^3. The desulfurization efficiency, defined as $(H_2S_{feed}-H_2S_{discharged})/(H_2S\ feed)\times 100$ was 20-40% in this experiment. The desulfurization efficiency at the constant feed gas rate increased in proportion to the solution volume in the desulfurization reactor.

The conversion efficiency from H_2S to H_2SO_4 (H_2SO_4 production per feed gas volume) is still too low to adjust the pH value of all geothermal hot water (flow rate of $350m^3/h$) to 5.5 in Otake geothermal power station. If the conversion efficiency is improved to 4-5 timrs the present experimental value, it can be adjusted to 5.5.

Both of the high desulfurization efficiency and the H_2SO_4 production rate are necessary to improve the conversion efficiency. Desulfurization efficiency and H_2SO_4 production rate in the preliminary study in our laboratory experiment were higher than those in this study. The temperature and the volume of the solution in the desulfurization reactor, the gas flow rate (SV), the air mixing ratio and the bacteria injection rate were the major parameters which gave significant effects on the desulfurization efficiency and H_2SO_4 production rate.

3. Biochemical reactor method

(1)Smmary of the process

Certain sulfur oxidizing bacteria , sampled from the secondary aeration tank for a biochemical sludge treatment process, are acclimatized and grown on a charcoal bed material, and are used for a biochemical reactor. The exhausted gas from power station is continuously blown into this reactor, and the produced H_2SO_4 is recovered into the water intermittently sprinkled from the top of the reactor and is discharged from the reactor.

The appearance of testing setup is shown in Photo-3, and the schematic diagram is shown in Fig-5.

(2)Testing setup and experiment

This testing setup consists of a reactor, an air blower, an acid solution transfer pump, an acid water tank and other equipment. The major pipings of the reactor include a gas feeding pipe , an air supplying

Photo-3 Appearence of the biochemical reactor

pipe , a sprinkler pipe and a H_2SO_4 discharge pipe. The reactor contains 0.77m^3 of the charcoal as the bed material for sulfur oxidizing bacteria. The mean micro-pore radius of the chacoal is 2.5 × $10^{-3}\mu m$ and the specific surface area 260m^2/g. The grain size is 5-10mm.

The sulfur oxidizing bacteria (Thiobacillus thioparus), which were grown in a separate facility, are scattered on the charcoal from the top of the reactor, while the exhausted gas from the power station is fed at the lower part of the reactor after adjusting the concentration ratio of CO_2/O_2 by diluting it with air. At this time, the H_2S concentration in the mixed gas becomes about 0.25vol%. The mixed gas flowed through the charcoal-filled layer in the reactor at a SV of about 10h^{-1}. Thus the bacteria are acclimatized. As the acclimatization advances, the H_2S in mixed gas is oxidized by the bacteria into H_2SO_4. The water is sprinkled from the top of the reactor for the purpose of adjusting the multiplying condition for sulfur oxidizing bacteria and discharging the produced H_2SO_4 from the system. Since the pH of the H_2SO_4 discharged from the reactor becomes lower than 2 in about one week after the start of gas feed, this is regarded as the acclimatizing period of the bacteria. On the other hand, the concentration of H_2S in the vent from the reactor becomes remarkably low.

The factors that control the production of H_2SO_4 and desulfurization in the reactor are the temperature in the reactor, the CO_2/O_2 ratio of mixed gas, the flow rate of gas (SV), the quantity and the intervals of water sprinkling, etc. As the sulfur oxidizing bacteria adhering to the charcoal in the reactor are basically self-sustaining, no supplement of the bacteria is required.

(3)Experimental results

The exhausted gas from the power station was diluted with air to about four times in volume, and the CO_2/O_2 ratio was adjusted to about 0.85. The diluted gas was continuously fed at 7.2m^3/h into the reactor shown in Photo-3. The H_2S concentration in the mixed or diluted gas was 0.25-0.26vol%, while the H_2S in the vent gas from the top of the reactor ranged from 200-400 ml/m^3 corresponding to a desulfurization efficiency of more than 90%. This efficiency decreased with the increased CO_2/O_2 ratios or the increased space velocity. Therefore, it was necessary to determine these optimum conditions in relation to the H_2SO_4 production rate.

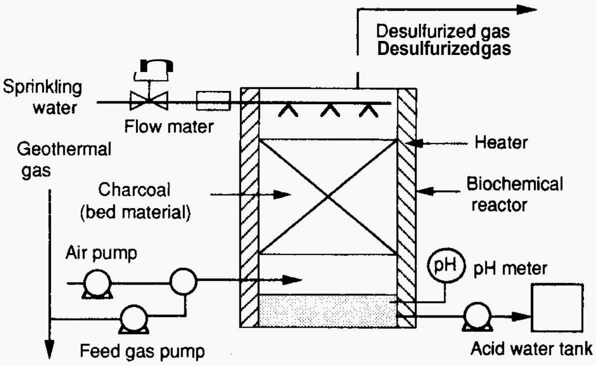

Figure-5 Schematic diagram of the biochemical reactor method

In order to investigate the relation between the concentration of the recovered H_2SO_4 (pH of the liquid) and the specific flow rate of sprinkled water, tests were conducted with the spare velocity and other conditions kept constant, where the specific flow rate of sprinkled water was changed in the range of 200-800l/m^3 as C·day. The results obtained are shown in Fig-6, which indicate that the H_2SO_4 concentration was inversely proportional to the specific flow rate of the sprinkled water, and that a H_2SO_4 concentration equivalent to 0.036 N was achieved at 800l/m^3 as C·day. The average H_2SO_4 production rate obtained was 32.3g/h.

Under these conditions, attempts to reduce the pH of Otake geothermal hot water at a flow rate of 350m^3/h to about 5.5 , requires a facility about 70 times as large as the present testing setup, having a reactor with the charcoal quantity of about 55m^3, as well as 1/2 of the total exhausted gas quantity of the power station. As the H_2SO_4 production rates 3-4 times as high as the present value were obtained temporarily in this test, efficiency improvement in the future can be expected.

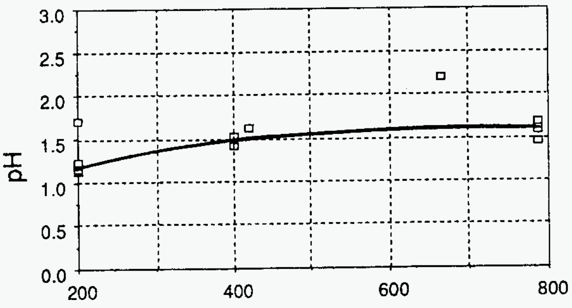

Figure-6 Production rate of H_2SO_4 by method ③

Confirmation of the effects to prevent the scale deposition and the clogging in the water permeable layer.

Using the geothermal brine with its pH adjusted by the H_2SO_4 that was produced from the H_2S in exhausted gases, a series of experiments were conducted to confirm the effects to prevent scale deposition and clogging of permeable injection layers. The scale deposition preventing effect was confirmed by comparing the growth rate of scale on test coupons. The scale deposition rate of the Hatchobaru brine with the pH of 7.0 and a Si02 concentration of 850 g/m^3 was 20-80$mg/dm^2 \cdot d$, while that of the pH-adjusted geothermal brine was as low as 0.2-0.8$mg/dm^2 \cdot d$. The effect to prevent the clogging of the permeable layer was confirmed by comparing the time for the pressure difference of the simulated permeable layer to increase by 0.5 MPa due to the clogging. The time for the raw (without pH-adjustment) geothermal brine was 180 hours, while that oi the pH-adjusted geothermal brine exceeded 1300 hours . It was confirmed that pH adjustment of geothermal brine is effective in preventing scale deposition as well as clogging in the permeable layer (Hirowatari,K., 1992).

Conclusion

Among a number of methods to prevent the silica scale deposition, the adjustment of the pH of geothermal brine by mineral acid injection seems promising. However, this method has not been applied in geothermal power stations in Japan so far, because of its potential impact to groundwater environments.

In order to avoid such potential impact, an alternative pH-control method has been proposed, where the sulfuric acid made from geothermal gas is used instead of mineral acid. After various kinds of preliminary experiments and field tests, we developed a new acidification process incorporating on oxidization reaction of hydrogen sulfide.

Outline of the experimental results are summarized below.

- Sulfuric acid was made from hydrogen sulfide in exhausted gas from a geothermal power station in three different ways.
- Hydrogen sulfide was recovered in a final form of sulfuric acid so that it may solve both the air pollution problem and silica scale problem.
- It was confirmed that the scale deposition in brine and the clogging in the permeable layer of reinjection wells can be mitigated by acidification.

These silica scale prevention methods with an acidification process using exhausted gas will be put into practical use in the near future. They will contribute to the effective use of geothermal energy for multipurposes, and will provide a solution to the utilization of power generation in double-flash cycle plants.

However, several problems still remain in the application of scale prevention technology for practical use, where less expensive and reliable systems are always required. We believe these problems will be resolved in the near future.

Acknowledgments

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