Characterization of acid water in the Otake-Hatchobaru geothermal field

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Abstract

Various kinds of acid waters have been recognized by well drilling in the Otake-Hatchobaru geothermal field and their formation mechanism has been studied. Shallow acid water that contains sulfate ion higher than chloride ion in content is formed by dissolved- air oxidation of hydrogen sulfide gas. Contrarily, deep acid water which has enthalpy higher than approximately 1,000 j/g contains chloride ion of high content. Zones of the latter acid water are located in and around neutral water reservoir tapped by production wells. Clarification of formation mechanism and extent of the latter acid water is indispensable for stable operation of the power plant and future development. Using recent isotopic study techniques, the deep acid water was revealed to have formed by contact of high-temperature Cl type water with sulfur-containing rocks, hydrolysis of sulfur to hydrogen sulfide and sulfuric acid. Furthermore, combining the chemical and isotopic data with geological and geophysical data, the deep acid waters are judged to be stored in restricted reservoir at relatively deep level.

1.0 INTRODUCTION

The Otake-Hatchobaru geothermal field is situated in the Kujyu volcanic area of central Kyushu, Japan. Although the chemical characteristics of the main reservoir water are neutral Cl **type,** several wells discharge acid waters. Since strong acid waters corrode hot water pipelines and surface facilities, reservoirs stored the acid water have to been kept away from drilling targets of production wells. Contrariwise, the acid water reservoirs are preferable as reinjection zone, because of depression effect of silica scaling in acid water. Therefore. clarifying the formation mechanisms and the distributions of acid waters is important to determine the future drilling targets.

Chemical data of the acid waters in the field were reported and showed various characteristics (Shimada et al.,1985). The variation of chemical and isotopic characteristics of the acid waters in the field indicates diversity of the formation mechanisms of the acid waters in this field. Formation mechanisms of the acid waters in this geothermal field were studied, considering the following mechanism generally reported.

1) Dissolution of volcanic gases and redox reaction of sulfurous acid gases (SO_2, HCI)

Due to dissolution and redox reaction of the high temperature volcanic gases containing SO_2 and HCl in water, sulfuric acid and hydrochloric acid are formed by reactions as follows.

$$SO_2(g) + H_2O = H_2SO_3$$
$$3H_2SO_3 = 2H_2SO_4 + S + H_2O$$
$$HCl\ (g) = HCl(l)$$

2) Oxidation of H_2S

Due to oxidation of H_2S gas in geothermal steam derived from geothermal reservoir, sulfuric acid is formed in water at shallow depth. Most of all acid sulfate type waters occurred at the surface are formed by this mechanism.

$$H_2S + 2O_2 = H_2SO_4$$

3) Hydrolysis of sulfur

It is reported the hydrolysis of sulfur is relevant to the formation of acid high-temperature waters within active volcanic regions (Ellis and Giggenbach, 1971). Some CI-rich acid waters at depth have been explained by this mechanism (Ellis and Mahon, 1977 and NEDO, 1993). The Cl-rich acid water is believed to form when high-temperature Cl-type water comes into contact at depth with sulfur-containing rocks, the hydrolysis of sulfur to hydrogen sulfide and sulfuric acid.

$$4S + 4H_2O = 3H_2S + H_2SO_4$$

Besides the above mechanisms, acid geothermal water was reported to be formed by reaction of chemical components contained in water at high temperature (NEDO, 1993). The acid water is characterized by low sulfate content ion and extremely high chloride ion content.

Regarding the Hatchobaru geothermal field, formation mechanisms of the deep acid waters were explained by oxidation of H_2S and hydrolysis of sulfur, using mainly chemical data. Waters acidified by oxidation of H_2S gas with contaminated air in reinjection water were found in the field (Shimada et al., 1985). In this report, chemical and isotopic characteristics and the formation mechanisms of the acid water discharged from geothermal wells, including recently drilled wells, are summarized and, based on the information of geological and geophysical data, distributions of the deep acid waters are inferred.

2.0 FORMATION MECHANISM

2.1 Characteristics of acid water

The geothermal waters in the Hatchobaru field are known to be mainly **neutral** and to have contained chloride ion of about **1,600 mg/l,** before starting waste water reinjection. The temperatures of main' production reservoir, measured and estimated fiom silica temperatures, have been around **275-280℃.** The hydrogen and oxygen isotope **data** of water indicate that the geothermal fluids originate fiom meteoric water. After starting reinjection **of** waste water, the chloride ion concentration of the reservoir water increased and the silica temperature decreased immediately, because of intlow of reinjected waste water into the main production reservoir.

In the Otake geothermal field, weakly alkaline Cl type waters have been discharging from production wells and their chemical characteristics have been intluenced by the reinjection. **Though** their chemical characteristics have been similar to those of the Hatchobaru geothermal water, the chloride ion concentration and silica temperature before starting reinjection were relatively low **(1,300 mg/l** and **240°C).**

The chemical and isotopic composition of acid waters **in** the Otake-Hatchobaru geothermal field are shown **in** Table **1. These** waters are classified into Cl **type** and **Cl-SO_4** type, which contain sulfate ion of relatively **high** content, compared **with** those of the neutral waters in this field. Chloride ion content and Cl/B ratios of the acid waters varies fiom **1,300** to **3,600 mg/l** and **from 10** to **30,** respectively.

fable 1 Chemical characteristics of geothermal rater in Hatchobaru geothermal field.

WELL NAME	SAMPRING DATE	pH	Na	K	Ca	Mg	CI	SO4	HBO2	δ D	δ 18O	δ 34S	Tritium
			mg/l							per mil			T.U.
H-2	1970.8	3.4	806	166	18.7	2.0	1363	170	68				
H-3	1973.4	4.9	740	127	17.7	1.4	1274	48	82				
H-3	1978.2	4.1	1914	286	137	9.1	3623	209	250				
H-4	1977.3	5.3	1578	235	1.3	0.0	2336	38	126				
H-6	1977.12	3.5	1939	311	81.5	7.3	3607	180	214				
H-7	1977.3	4.1	1385	249	4.2	0.0	2380	43	124				
H-17	1991.10	3.5	817	143	6.5	0.5	1230	329	69	-55	-6.3	22.3	
H-28	1995.10	3.4	841	169	10.5	9.8	1190	486	63	-53	-5.8	23.2	1.3
HR-18	1981.1	3.7	792	147	26.8	2.0	1788	86	84	-57	-6.4	21.7	<0.15
HR-21	1983.12	4.6	1803	261	34.4	0.7	2904	29	153	-51	-4.9	18.9	
HT-3	1980.8	3.3	951	148	4.7	4.0	1559	244	82	-57	-5.2		3.9
HT-7	1983.10	4.4	1039	156	13.1	2.1	1647	336	78				
HT-8	1982.9	5.0	992	160	30.3	0.7	1616	229	99			21.7	15.1
ET-2	1976.5	4.0	187	43	11.6	2.5	279	141	12	-54	-7.8	16.2	
SPA1	1976.5	3.0	292	64	12.6	2.0	416	243	23	-49	-6.9	17.4	
O-20	1984.10	3.9	656	92	16.3	0.8	1110	84	51	-57	-7.3	21.6	
H-4	1973.9	7.7	863	200	0.7	0.01	1674	50	96				
O-9	1983.12	8.3	792	96	27.8	0.01	1303	84	63	-57	-6.0	18.5	

2.2 Formation mechanisms of acid water in the Otake-Hatchobaru geothermal field

The acid waters summarized in Table 1 were arranged in following groups for discussing formation mechanism, based on locations of the wells and characteristics of the acid waters.

1) H-17, H-28, HT-3, 2H-7, H-2, H-3 and HR-18

Although nearly neutral water had been discharged occasionally, acid waters have been discharged mainly fiom the H-17 well for 14 years. Geothermal waters in the reservoirs directly connected with main production zone have been influenced by reinjection water in the field. Since there is no obvious evidence that indicates inflowing of reinjection water into the H-17 reservoir, the acid water reservoir is believed to be isolated from the main production reservoir. The similarity of chemical and isotopic characteristics ofthe acid waters from the H-17, H-28, HT-3 and 2H-7 wells, these waters may be derived from the common acid water reservoir. These acid waters in reservoirs contained chloride ion of 1,200-1,800 mg/l. **As** shown in Table 1, $\delta^{34}S$ (SO_4) values in the acid waters are remarkably large for geothermal waters in the central Kyushu, and are larger than those in neutral waters in this field. These mean that formation mechanism of the acid water does not relate to oxidation of H_2S. Observation of native sulfur in drilling core of well nearby these wells suggests the geothermal waters obtained by these wells are possibly acidified by hydrolysis of sulfur in rocks.

Regarding the H-2, **H-3** and HR-18 wells, the wells are situated near the reinjection area. The acidification does not relate to the reinjection, because pHs of waters discharged from these wells were acidic before starting reinjection. Since the $\delta^{34}S(SO_4)$ value of the water of HR-18 is similar to those of the H-17 and H-28 wells, these waters may be acidified by the same as those of these wells.

pH of the H-17 water has varied between 3.3 and 8.0. Two main feed zones of this well were detected by well log and acid and neutral waters are considered to inflow separately from these zones. Chemical and isotopic characteristics of the H-28 well hear the H-17 well are similar to those of the H-17 water. Drilling mud contamination of the H-17 discharge during the H-28 well drilling at the same depth of shallower reservoir of the H-17 well indicates that the H-28 well taps a common acid water reservoir to the H-17 well. According to the data of lost circulation zones of these wells, the acid water reservoir may be stored at -200 to -300 meters in an altitude in this area.

2) H-4, H-6, H-7 and HR-21

These wells discharged acid water occasionally, and the acidification of discharged water had observed immediately after the reinjection started at near these wells. The increase of chloride ion concentration with lowering of pH and relatively larger δD and $\delta^{18}O$ values of the waters indicate inflow of reinjected waste water to the reservoir. The simultaneous increase of N_2 gas concentration in steam suggests air contamination inro reinjected water. The relatively small $\delta^{34}S$ value is due possibly to admix of sulfate ions formed by H_2S oxidation and dissolved from reservoir rocks. There is possibility that air contaminated into reinjection water, because the reinjection was operated in open-air system. Sulfuric acid formed by air oxidation of H_2S gas would acidify reservoir water.

3) ET-2 and hot springs

The ET-2 well, hot spring well (about 7-00 m depth) and hot springs which are situated near fumaroles and surface alteration zones by acidic water, discharge SO_4 or Cl-SO_4 type acid waters containing chemical components of low content. This suggests that these hot waters were formed by steam-heated ground water and/or mixed with neutral Cl type water. The small $\delta^{34}S$ (SO_4) values of these waters indicate that sulfuric acid in these waters was formed by oxidation of H_2S.

4) *0-20*

The 0-20 well was only one production well discharging acid water in the Otake geothermal field. Chloride ion concentration of this water was relatively low, but the silica temperature and δD and $\delta^{18}O$ of water were the same as those of main reservoir water in the Otake geothermal field. These suggest that the 0-20 water is stored at relatively deeper level and is not formed by mixing of shallow ground water. The large $\delta^{34}S$ (SO_4) value of 21.6 ‰ which is larger than those in the neutral waters indicates no connection with H_2S oxidation. Since these chemical and isotopic characteristics of this water are similar to those of the H-28, H-17 wells etc.. the water is believed to be acidified by hydrolysis of sulfur in rocks.

3.0 VARIATION OF $\delta^{34}S$ (SO_4) VALUE

As mentioned in previous sections, acidification of the geothermal water in this field is caused by sulfuric acid. The sulfuric acid in the water was formed by two kinds of formation mechanism; oxidation of hydrogen sulfide by air and hydrolysis of sulfur by high temperature Cl type water. $\delta^{34}S$ (SO_4) in the acid water is of interest in connection with formation mechanism of the acid water. The characteristics of $\delta^{34}S$ (SO_4) of geothermal waters in this field are summarized as follows;.

The $\delta^{34}S$ (SO_4) values of production well waters in this field range from 16 to 20 ‰. $\delta^{34}S$ (SO_4) ofthe water discharged from the HT-5-1 exploratory well which was the deepest in the this field and tapped the reservoir in the basement rocks is the minimum value as 9 ‰. Difference of the $\delta^{34}S$ (SO_4) value between the production wells and the deepest exploratory well is considered to indicate the difference of rocks between the both reservoirs.

Large $\delta^{34}S$ (SO_4) values of acid waters (discharged from the H-28, H-17, 2H-8 and HR-18 wells) which are not considered to be formed by oxidation of H_2S gas, have a linear relationship with sulfate ion concentrations, as shown in Fig.1. $\delta^{34}S$ (SO_4) value of the water is proportional to sulfate ion concentration (Fig.1). This indicates that mixing between strong acid water of large $\delta^{34}S$ (SO_4) (larger than *23* ‰) and neutral water of relatively small $\delta^{34}S$ (SO_4)(16 - 20‰) occurs in reservoir or wells.

$\delta^{34}S$ (SO_4) values of the waters from the H-4, H-6 and HR-21 wells tend to decrease with time. Considering the chemical characteristics of the waters, the reservoir water was considered to be mixed with reinjection water. The $\delta^{34}S$ (SO_4) value of reservoir water influenced with reinjection water was low due to the oxidation of H_2S gas dissolved in water by contaminated air.

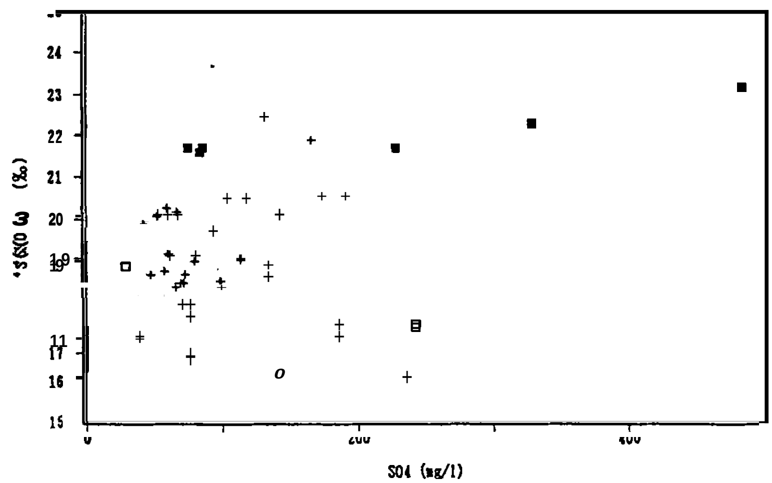

Fig. 1 Relationship between SO_4 ion concetrations and $\delta^{34}S(SO_4)$ value in water.
■:Acid water. □:Acid water formed by oxidation of H_2S. +:Neutral water.

4.0 ACID WATER FLOW

Although some of the wells in the main reservoir of the Hatchobaru geothermal field, which extends along the Komatsuike sub-fault, occasionally discharged relatively small amounts of acid waters probably formed by mixing of reinjected water, the wells in the area generally produce only alkaline to neutral water. On the contrary, the acid water reservoirs tapped by the H-28, H-17 and HT-3 wells seem to extend along the Hatchobaru fault lying west of the Komatsuike sub-fault. However, as mentioned above, the H-17 well has occasionally produced neutral water. The HT-6 and HT-5-1 wells close to the west side of the Hatchobaru fault discharged nearly neutral waters. Moreover, no alteration minerals by the acid water were found in the feed zones of the H-28 and H-17 wells. Therefore the acid water discharged from these wells is probablynot stored in large amounts in permeable zone along the Hatchobaru fault, and is thought to be drawn up to the wells from somewhere near the fault. If the acid water is formed by hydrolysis of native sulfur, it may be stored in limited area where native sulfur occurs. In any case, the acid water flows are restricted to small zones and the reservoirs are isolated from the main reservoir extending along the Komatsuike sub-fault..

5.0 CONCLUSIONS

In the Otake-Hatchobaru geothermal field, various kinds of acid waters are formed by several chemical reactions and mixing. Formation mechanisms of the acid waters were estimated using data of chemical and isotopic characteristics of the waters. In particular, isotopic study of sulfur have been used effectively for clarification of formation mechanism of the acid waters in this field. Based on the clarified formation mechanisms, the acid water which was mainly found in western part of the Hatchobaru geothermal field is considered not to be formed by inflow of shallow acid water or reinjected water, but to be formed by hydrolysis of sulfur in rocks. This water may be stored in limited zone near the Hatchobaru fault and isolated fkom the main reservoir.

Generally speaking, determination of sulfur isotope of sulfate ion in acid water is effective for revealing the formation mechanism of acid geothermal water. Analyses of sulfur isotope of hydrogen sulfide and sulfate minerals in core and cuttings must turn more precious interpretation into a possibility. Furthermore, combining the clarified mechanism with geothermal and geological structures inferred by geological and geophysical studies are indispensable for locating the acid water reservoirs.

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