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THE SOURCE OF ACIDITY IN WATER DISCHARGED FROM HIGH TEMPERATURE GEOTHERMAL RESERVOIRS IN JAPAN

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ABSTRACT

Acidic geothermal waters of pH 3 to 5 are discharged from the high temperature reservoirs in the Kakkonda and Fushime geothermal fields. In order to investigate the possible source of acidity in these waters, numerical modeling based on multicomponent chemical equilibrium calculations was carried out. The results of the calculation indicate that the precipitation of sphalerite from the saline Fushime water could contribute to making the acid water. In contrast, the acidity in the dilute Kakkonda water could not be caused by the precipitation of sphalerite.

However, addition of a small amount of HCI to the Kakkonda water can decrease its pH to the measured pH value. The deepest well in the Kakkonda field penetrated the Quaternary granite, a probable heat source in the geothermal system, but did not indicate the existence of HCI. The alteration mineral assemblage in the deep reservoir also argues against HCl supply from depth. If hydrolysis reactions of NaCl and $CaCl_2$ generate HCI in the Kakkonda deep reservoir during production, it could explain the low pH.

INTRODUCTION

Slightly acidic geothermal waters of pH 3 to 5 have been found in the Kakkonda geothermal field, northern Honshu (Yanagiya et al., 1996), and in the Fushime geothermal field, southern Kyushu, Japan (Akaku et al., 1991) as the geothermal energy exploitation reaches the deep and high temperature reservoirs.

The origin of the geothermal water in Kakkonda is thought to be meteoric whereas the water in the Fushime geothermal system is derived from seawater. In spite of the difference in the origin we can find some common features between the two. In both of the fields, the maximum measured temperatures in wells often exceed 350°C. The higher temperature reservoirs in these fields produce acid waters with high excess enthalpy fluids (large steam/water ratios). In contrast, the moderate temperature reservoirs in these fields discharge neutral to slightly alkaline-pH waters with little or no excess enthalpy fluids. The acid-pH waters are richer in Mg and Fe than those of the neutral to alkaline-pH waters. The occurrence of acid alteration minerals such as alunite, sulfur, kaolinite and pyrophyllite is not observed in the reservoirs which produce acid waters in Kakkonda and Fushime.

In order to consider the possible acid sources in the geothermal waters, modeling by multicomponent chemical equilibrium calculations is useful (Reed, 1991; Akaku and Reed, 1992). In this paper, we will discuss the source of acidity by integrating the geology, geochemistry and calculation results on these fields.

THE KAKKONDA GEOTHERMAL FIELD

The Kakkonda geothermal field is located inland in the

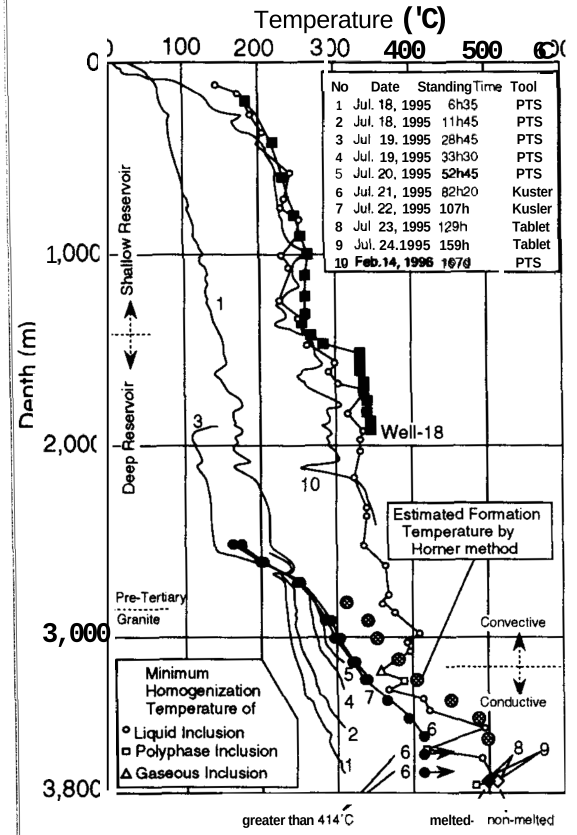

Fig. 1. Temperature profiles for NEDO WD-1 and JMC Well-18 drilled at the same site in the Kakkonda geothermal field. After Uchida et al. (1996)

rtheastern part of Japan. The first power plant, akkonda Unit 1 (50 MWe) has been operated by hoku Electric Power Company and Japan Metals and hemicals Company (JMC) since 1978. The second wer plant, Kakkonda Unit 2 (30 MWe) started eration in March 1996.

the Kakkonda field, more than 70 wells with depths nging from 1,000 to 2,000 m were drilled and produce othermal fluid from fractures in Miocene dacitic tuffs d shales. Five deep wells drilled to depths between 463 and 3,000 m encountered productive fractures in e-Tertiary formations and a neo-granitic pluton (the akkonda granite). The Pre-Tertiary and Miocene rmations were thermally metamorphosed by the anite (Kato and Doi, 1993; Kato et al., 1993). Recently e New Energy and Industrial Technology evelopment Organization (NEDO) drilled the deepest ell (WD-1) in Kakkonda in the NEDO "Deep-seated Geothermal Resources Survey" project. WD-1 penetrated the Kakkonda granite at the depths between 2,860 and 3,729 m (Uchida et al., 1996).

The temperature profiles of the deep wells have a steep increase at around 1,500 m depth (Fig. 1) suggesting two different convection cells exist. The upper and lower convection cells are called the shallow and deep reservoir respectively. The shallow reservoir is very permeable and its temperature is from 230°to 260°C whereas the deep reservoir is less permeable and has a temperature over 300°C (probably over 350°C). Single-phase liquid feed is common in the shallow reservoir, however excess enthalpy conditions (two-phase feed) commonly develop during production in the deep reservoir (Hanano and Takanohashi, 1993).

The waters discharged from the shallow reservoir are slightly alkaline (pH = 8-9, measured at room temperature, after steam separation), but the waters from the deep reservoir are acidic (pH = 3.2-4.5). The chloride concentration in the shallow reservoir water was about 500 ppm before it was disturbed by reinjection of waste water. The deep reservoir water contains about 1,000 ppm of chloride. It is thought that the waters in both reservoirs are basically meteoric origin and that the deep reservoir water rises to the shallow reservoir with dilution by cold meteoric water (Yanagiya et al., 1995).

In the shallow reservoir, reservoir rocks are strongly altered by hydrothermal activity. Relatively recent hydrothermal vein minerals are quartz, wairakite, laumontite, K-feldspar, anhydrite, calcite, chlorite, epidote, pyrite, sphalerite and galena. In the deep reservoir, the granite, metamorphosed he-Tertiary and Tertiary formations are relatively fresh, however a little hydrothermal alteration is observed along the fractures. Anhydrite, quartz, specularite and pyrite veins are common (Kato et al., 1993; Kato and Doi, 1993). Specularite, albite, calcite, dolomite, epidote and actinolite-tremolite likely occur along the productive fractures in the deep reservoir (Kato and Sato, 1995).

At a depth of 3,700 m in WD-1, after the temperature recovery of 159 hours, temperatures over 500°C were measured using metal-base melting compounds (Fig. 1). It is believed that the boundary between the hydrothermal convection zone and the thermal conduction zone exists at about 3,100 m depth and that the Kakkonda granite is a heat source of the geothermal system (Ikeuchi et al., 1994).

Unfortunately, WD-1 did not encounter any productive fractures at the depths below 2,200 m and no discharge testing could be carried out. However, the emission of CO_2 and H_2S was observed during the drilling operation and borehole fluid samples were obtained after temperature recovery measurement in WD-1. The fluid collected near the bottom of WD-1 was hypersaline Na-Fe-K-Ca-Cl type brine to the degree that halite and other chloride salts precipitated during sampling. The brine was also rich in heavy metals such as Mn, Zn and Pb. The measured Cl concentration of the brine was 19 wt% at maximum (not including precipitated salt) and its pH was 5.2 (Kasai et al., 1996).

THE FUSHIME GEOTHERMAL FIELD

The Fushime geothermal field is located close to the southeastern coast of the Satsuma Peninsula on Kyushu Island. Japan Petroleum Exploration Company (JAPEX) and Japex Geothermal Kyushu Limited (JGK) have explored and developed this field. A 30 MWe geothermal power plant (Yamagawa geothermal power plant) was jointly constructed by Kyushu Electric Power Company and JGK, and went on line in March 1995.

Twenty five wells were drilled to depths between 755 and 2,600 m in the geothermal system. The temperatures measured in some wells exceed 350°C at depths below 1,500 m. The wells penetrate thick dacitic to andesitic tuffs and lavas. The most productive reservoir is situated around the intrusive dacite found at depths below 1,600 m. The principal alteration minerals observed in the production zone (commonly above 250°C) are quartz, albite, K-feldspar, sericite, chlorite, epidote and anhydrite. An abundance of K-feldspar is the most distinctive feature around the feed points of the wells (Yagi and Kai, 1990). There is no remarkable difference in alteration mineral assemblage between the high temperature (over 300°C) and the low temperature production zones

The chloride concentration and δD in the high temperature reservoir water are close to those of seawater and it is likely that the geothermal fluid originates from seawater-rock interaction at high temperature. The chemical composition of the waters is characterized by depletion in Mg and SO_4 and enrichment in K, Ca, Fe, Mn, Zn, Pb, SiO_2, etc. over those of seawater (Akaku et al., 1991).

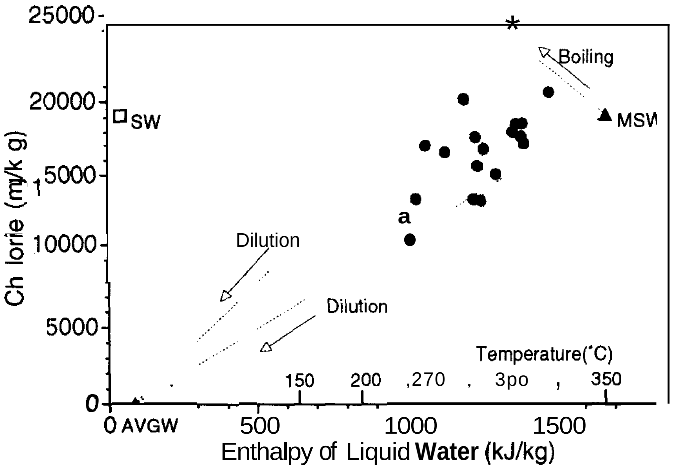

Fig. 2. Enthalpy of liquid water at quartz geothermometer temperature *vs.* chloride for the Fushime reservoir waters (solid circles). After Akaku and Reed (1995). Dotted lines represent changes of the Cl concentrations by dilution of the modified seawater (seawater reacted with rocks at 350°C) by groundwater, boiling of the modified seawater to 300°C and dilution of the boiled water by groundwater (dilution/boiling triangle). Abbreviations: SW, seawater; AVGW, average groundwater at Fushime; MSW, modified seawater.

Fig. 2 shows the relationship between the liquid water enthalpies at quartz geothermometer temperatures and the Cl concentrations in the reservoir waters corrected for steam loss and excess enthalpy. Most data points lie within the triangular boiling-dilution area connecting the points from 350°C-19,000 mg/kg, 300°C-25,000 mg/kg and 21°C-42 mg/kg (average groundwater at Fushime). The simplest explanation of these variation is that various combinations of boiling of the modified seawater and dilution by groundwater occur in the geothermal system.

During production, two-phase feed is common in the reservoir (*i.e.* excess enthalpy condition). The measured pH of the waters discharged from wells ranges from 3.8 to 8.0 at room temperature, after steam separation. The acid-pH ($pH < 5$) waters are discharged from higher temperature wells above 300°C, with higher enthalpy fluids. In contrast, the lower temperature wells (less than 300°C) produce neutral-pH waters with low excess enthalpy fluids.

COMPARISON OF CHEMISTRY BETWEEN ACID WATER AND NEUTRAL-ALKALINE WATER

In Kakkonda, acid water discharged from the deep reservoir has larger Mg/Cl and Fe/Cl ratios than in the neutral-pH water from the shallow reservoir (Fig. 3). Yamagiya et al. (1996) reported that the shallow reservoir waters are in "full equilibrium" with the wall rock but the deep reservoir waters are in "partial equilibrium" on the Na-K-Mg ternary diagram of Giggenbach (1988). It is thought that the deep reservoir water have not fully attained to the equilibrium with the wall rock and its pH is lower than that buffered by mineral reactions .

Compared with seawater, the Fushime geothermal water is depleted in Mg and *SO,* and enriched in **K,** Ca, Fe, Mn ,Zn, Pb, SiO_2, B, etc. This characteristic is common in both acid and neutral-pH waters (Fig. 4). However, the acid water has much larger Fe/Cl ratio and obviously larger Mg/Cl ratio than found in the neutral water (Fig. 4), being similar to those in the Kakkonda water. The Zn, Pb and Mn concentrations are also noticeably higher in the acid water than in the neutral water. The K/Cl and B/Cl are higher in the acid water but lower in Ca/Cl than in the neutral-pH water, though the differences in those ratios are almost invisible in the log-scale figure (Fig. 4). Akaku and Reed (1995) showed that the difference in K and Ca concentrations is clearly explained by the precipitation of K-feldspar and the dissolution of clinozoisite (Ca-epidote) followed by the temperature decrease due to the boiling and dilution processes occurring in the geothermal system. However, Mg concentrations in all of the Fushime waters depart from equilibrium with clinochlore (Mg-chlorite). Furthermore, it **is** probably difficult to explain the difference in Fe based on dilution and boiling processes alone. There is no significant difference in SO_4/Cl ratios between the acid and neutral-pH waters in both Kakkonda and Fushime. It is considered to be due to equilibrium with anhydrite (Yanagiya et al., 1995, Akaku et al., 1991).

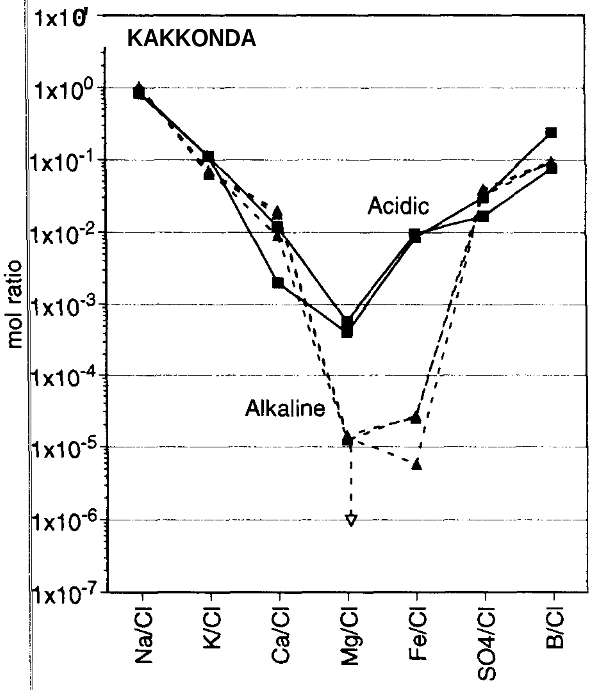

Fig. 3. Comparison of chemical composition between deep reservoir water (acidic-pH; solid squares) and shallow reservoir water (alkaline-pH; solid triangles) in the Kakkonda geothermal system.

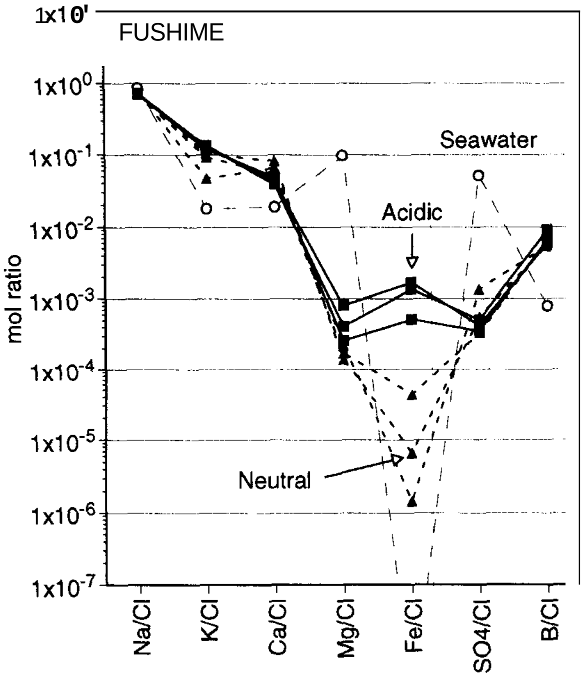

Fig.4. Comparison of chemical composition between high temperature reservoir water (acidic-pH; solid squares) and low temperature water (neutral-pH; solid triangles) in the Fushime geothermal system. The composition of seawater (open circles) is also shown.

POSSIBLE SOURCE OF ACIDITY

It is noteworthy that any acid alteration minerals such as alunite, sulfur, kaolinite and pyrophyllite are not observed in either of reservoirs in Fushime and Kakkonda which discharge acid waters. This suggests that the acidity of the waters could not derive from the reaction with these acid minerals in the geothermal system.

Akaku et al. (1991) noted that the precipitation of sphalerite and galena, which are abundant scale minerals in the high temperature surface equipment and wells in Fushime, contribute acidity. In order to test the possibility Akaku and Reed (1992) carried out numerical modeling using CHILLER (Reed, 1982; Spycher and Reed, 1992), which computes aqueous - mineral - gas equilibria. The procedure used for the model calculation is as follows:

(1) The composition of the numerical reservoir water at high temperature is calculated by the forced equilibration of seawater with quartz, albite, K-feldspar, muscovite, clinochlore, clinozoisite, anhydrite, sphalerite and galena. H_2S and CO, concentrations are set to the measured values in the Fushime field.

(2) The reservoir water boils to 100°C numerically. The boiling is iso-enthalpic with the total enthalpy of the boiling fluid set to equal the liquid phase enthalpy at the temperature of the forced equilibrium calculation.

(3) For simplicity, the precipitation of sphalerite, galena and amorphous silica are allowed in the boiling calculation. The precipitation of other minerals is suppressed.

The calculation results are shown in Fig. 5. The reservoir water equilibrated with these minerals at 350°C has a pH of 5.6. The pH of the water decreases (to 4.1 at 100°C) during boiling with the precipitation of scale

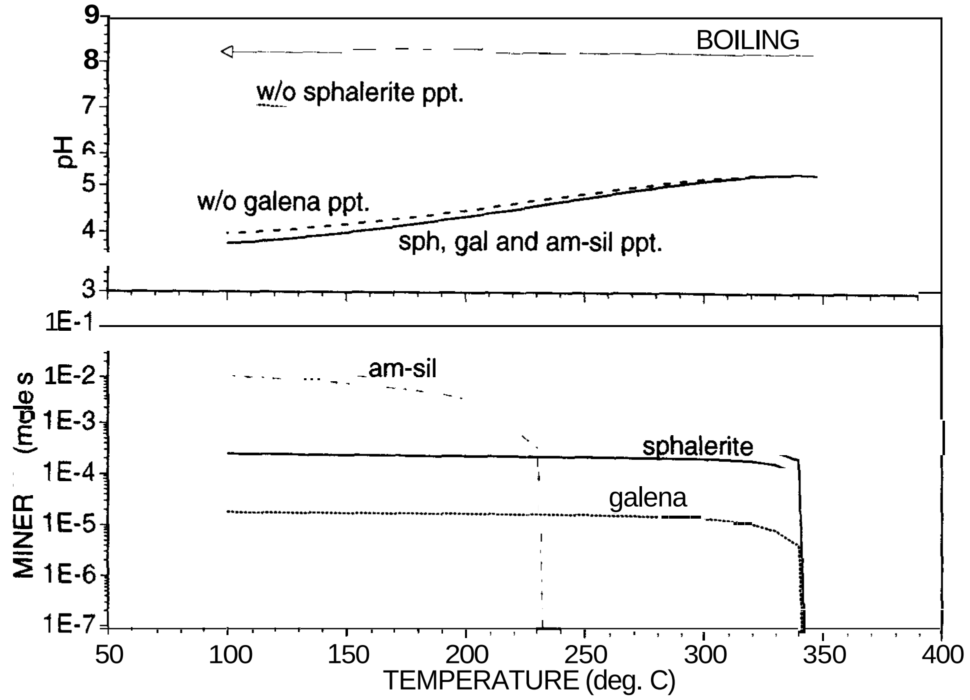

Fig. 5. Numerical boiling of the Fushime-type water, seawater equilibrated with quartz, albite, K-feldspar, muscovite, clinochlore, clinozoisite, anhydrite, sphalerite and galena at 350°C. The boiling proceeds with decrease of pressure and temperature from 350°C to 100°C. The H_2S and CO, concentrations are set to the measured values in the Fushime field. The pH of the water decreases with boiling when the precipitation of sphalerite, galena and amorphous silica is allowed. If precipitation of sphalerite is suppressed, the pH increases with boiling. The suppression of galena precipitation results in the slight positive pH shift from that of the full mineral precipitation. It is suggested that the precipitation of sphalerite is a major source of acidity, and that the precipitation of galena has minor effect.

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$$\text{HCO}_3^- + \text{H}^+ \text{--->} \underset{(aq, gas)}{\text{H}_2\text{O}} + \underset{(gas)}{\text{CO}_2} \qquad (1)$$

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The calculated pH with the precipitation of scale minerals is fairly close to the measured pH for the acid water discharged from high temperature reservoirs in Fushime. The results of the calculation indicate that the precipitation of the sphalerite could contribute to making the acid water.

In Kakkonda, it is observed that the deep reservoir water also precipitates sphalerite and galena as scale minerals (Yanagisawa et al., 1995). We performed the same type of the model calculation applied to Kakkonda as we did for the Fushime water. The Cl concentration of the numerical reservoir water is set to 1,000 ppm, based on the data in Yanagiya et al. (1996). The pH increases upon boiling, from **6.4** at 350°C to 7.2 at 100°C (Fig. **6)** because the supply of H^+ from precipitation of sphalerite and galena is too small to exceed consumption of H by CO_2 degassing. The contrast of the calculations between the Fushime and Kakkonda models is due to the difference in stability of zinc chloride complexes. For low Cl water such as the Kakkonda water it is not likely that the precipitation of these minerals is the cause of acidity.

It is possible that acid volatiles such **as** HCl contribute to the acidity of the high temperature reservoir water. At 350°C, addition of 0.1 and 0.5 millimoles of HCI to **lkg** of the Kakkonda-type equilibrated water lowers

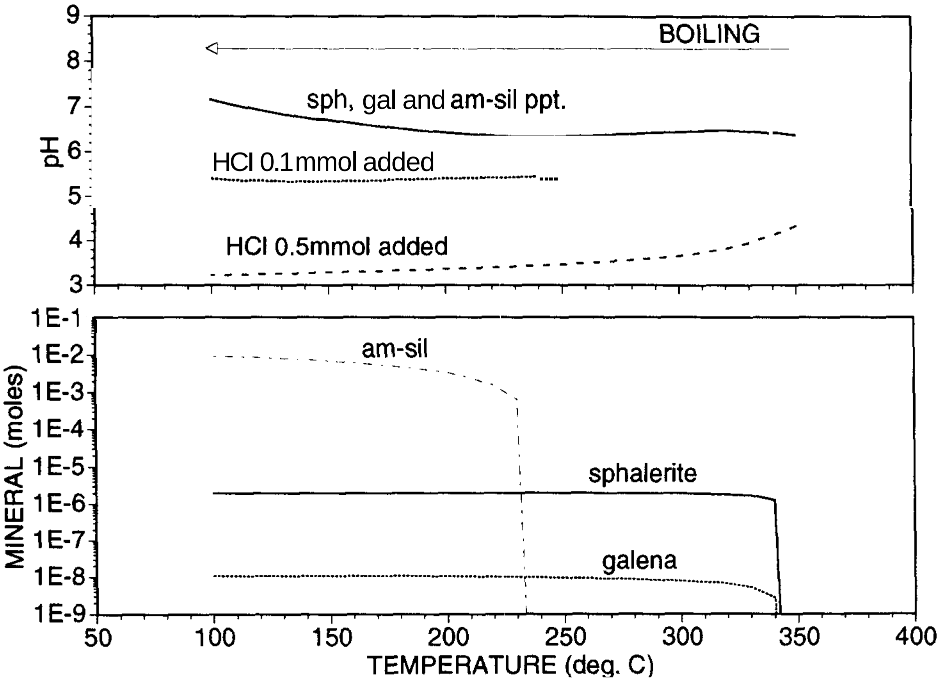

Fig. *6*. Numerical boiling of the Kakkonda-type water, the dilute water (Cl = 1,000 ppm) equilibrated with quartz, albite, K-feldspar, muscovite, clinochlore, clinozoisite, anhydrite, sphalerite and galena at 350°C. The boiling proceeds with decrease of pressure and temperature from 350°C to 100°C. The H_2S and CO_2 concentrations are set to the measured values in the Kakkonda field. The pH of the water increases with boiling in spite of the precipitation of sphalerite and galena. In contrast, addition of 0.1 and 0.5 millimoles HCI per kg of the equilibrated water lowers pH, suggesting that a small amount of HCl is a possible source of acidity.

pH to 5.4 and to 4.3 respectively (Fig. 6). Boiling calculations indicate that the pH of the water with 0.1 millimoles HCl added is almost unchanged (about 5.4), but the pH of the water with 0.5 millimoles HCl added decreases to 3.2 at 100°C. These changes result from the shifting balance of H^+ production by dissociation of HCI and consumption depending on CO, degassing (Reed, 1991). The calculated pH is consistent with the measured pH, suggesting that quite a small amount of HCI could contribute to the acidity in the deep reservoir water. It is not easy to detect such a small amount of HCI by Cl analysis in both vapor and liquid phase samples.

WHERE DOES HCl COME FROM?

The deepest well in Kakkonda, WD-1 penetrated the Quaternary granite that is a probable heat source of the geothermal system. The emission of CO, and H_2S gas was experienced during drilling. The hypersaline Na-Fe-K-Ca-Cl type brine was obtained from the bottom of the well but its pH was 5.2. Consequently we could not find any symptom of the existence of HCI in the granite. Furthermore, acidic alteration minerals are not observed in the deep part of the geothermal system, arguing against HCl as the cause of the acidity in the deep reservoir water.

The formation of HCl by the hydrolysis reaction of NaCl a high temperatures and low pressures was reported by several researchers (*e.g.* Fournier and Thompson, 1993; Shinohara and Fujimoto, 1994). Recently, B schoff et al. (1996) showed the generation of HCI in the vapor phase buffered by the liquid in $CaCl_2$-H_2O system at relatively high pressures (≤ 230 bars at 380°C, ≤ 580 bars at 500°C). If these reactions occur in the Kakkonda deep reservoir driven by the production-induced depressurization it would be a possible explanat on for a link between the acidity in the deep reservoir water and HCI.

CONCLUSIONS

The acidity in the low chloride water discharged from Kakkonda deep reservoir could not be caused by the precip tation of sphalerite and galena, in contrast with the saline Fushime water. Addition of a small amount of HCl to he deep reservoir water could contribute to the acidity of the Kakkonda water.

The deepest well in Kakkonda penetrated the Quaternary granite, a probable heat source in the geothermal system, but did not indicate the existence of HCI. The alteration mineral assemblage in the deep reservoir also argues against HCl supply from depth. If the hydrolysis reactions of NaCl and $CaCl_2$ generate HCl in the Kakkonda deep reservoir during production, it could explain the low pH.

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