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CHEMICAL EQUILIBRIUM MODELS FOR THE FLUIDS IN THE FUSHIME GEOTHERMAL SYSTEM: ISOENTHALPIC AND ISOTHERMAL BOILING

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ABSTRACT

Numerical modeling for fluid-mineral reactions during production-induced boiling in geothermal reservoir was carried out. The isoenthalpic and isothermal boiling processes for the geothermal waters derived from seawater were tested. The temperature decrease in the isoenthalpic boiling process causes precipitation of sphalerite and galena. In contrast, the isothermal boiling process results in dissolution of sphalerite and galena from wall rocks driven by the H_2S escape from liquid to gas phase at a constant temperature. The degassing in the isothermal process also causes continuous dissolution of pyrite from wall rocks, precipitation of magnetite and the incerases in H_2S and H_2 concentrations. As a result of these reactions, the decrease in pH with increasing enthalpy is computed. The isothermal boiling process would play an important part for the changes of fluid compositions in the high temperature reservoirs under production.

INTRODUCTION

The Fushime geothermal field is located close to the southeastern coast of the Satsuma Peninsula in Kyushu. 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 (e.g., Okada et al., 2000).

The primary geothermal water in the Fushime system is believed to be of seawater origin. Various combinations of boiling and dilution process are considered to occur in the geothermal system. The chemical composition of the waters is characterized by depletion in Mg^{2+} and SO_4^{2-}, whereas enrichment in K^+, Ca^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, SiO_2, etc. over those of seawater. The higher temperature reservoirs (over 300˚C) produce acid waters (pH = 3 - 5) containing remarkable Fe^{2+}, Mn^{2+}, Zn^{2+} and Pb^{2+}. Local near-well boiling caused by production-induced pressure decrease is common. The boiling in the reservoir sometimes involves isothermal process due to heat transfer from wall rocks to the fluid (Akaku et al., 1991). In response to the changes of physical conditions by boiling, the reactions of fluid with minerals in wall rocks may proceed. Fluid compositions should be changed. In order to know these effects, numerical modeling for fluid - mineral reactions during the isoenthalpic and isothermal boiling processes was conducted.

CALCULATION PROCEDURES

Numerical modeling was performed by using CHILLER (Reed, 1982; Spycher and Reed, 1992), a multi-component chemical equilibrium calculation program. The thermodynamic data in SOLTHERM 1992 version were basically used. However, some revisions for the equilibrium constants for sphalerite, zinc chloride complexes, H_2S (aq.) and quartz were made, based on Bourcier and Barnes (1987) and Fournier and Potter (1982). The calculation procedures were similar to those in Akaku et al. (2000).

Isoenthalpic boiling calculation was conducted from 350˚C through 250˚C. Chloride concentration of a starting solution (single-phase liquid) was set to 19,000 ppm, being equal to that in seawater. The CO_2 concentration was set to 1,230 ppm, based on the measured total discharge concentrations for the Fushime well SKG-16 (Akaku et al., 1991). Isothermal reservoir boiling calculation with a stepwise increment of enthalpy at 305˚C was initiated from a slightly dilute solution (Cl = 15,220 ppm, CO_2 = 982 ppm).

The compositions of starting solutions were computed to be exactly saturated with the observed principal alteration and scale minerals, quartz, albite, K-feldspar, muscovite, clinochlore (Mg end-member of chlorite), anhydrite, clinozoisite (Ca end-member of epidote), pyrite, magnetite, sphalerite and galena. However, when once boiling was started, precipitation and dissolution of albite, K-feldspar and clinozoisite were suppressed, assuming reactions of fluids with these minerals are too slow to attain equilibrium during local near-well boiling in the real geothermal reservoir. Therefore, the reactions of fluids with quartz, muscovite, clinochlore, anhydrite, pyrite, magnetite, sphalerite and galena were only allowed. In addition, the redox reaction for H_2 was allowed in the calculations.

RESULTS

The calculation results for isoenthalpic reservoir boiling are shown in Fig. 1. At the beginning of boiling, CO_2, H_2S and H_2 strongly partition into gas phase (Fig. 1a). The H_2S degassing drives dissolution of pyrite from wall rock and precipitation of magnetite (Fig. 1b: reaction 1). At 320˚C, pyrite turns to precipitate, whereas magnetite dissolves. The H_2S concentration in gas phase increases with decreasing temperature until 310˚C, and decreases at the later stage. Precipitation of sphalerite (reaction 2) and galena is driven by temperature decrease. The H_2 concentration in gas phase increases with decreasing temperature until 310˚C through reaction 3, and decreases later.

The water equilibrated with the principal alteration and scale minerals has a pH of 5.6 at 350˚C. A decrease in pH occurs at the early stage of boiling (5.1 at 300˚C), and slightly increases later (5.3 at 250˚C: Fig. 1c). The pH decrease results from the excess supply of H^+ from the reactions 1, 2 and 3 over the H^+ consumption by CO_2 degassing (reaction 4). For comparison, the separate calculation in which no reaction with minerals was allowed shows the pH increase with decreasing temperature (Fig. 1c). The reaction of sphalerite precipitation is the most effective supplier of H^+ in the isoenthalpic boiling process (Akaku et al., 2000).

$$\underset{\text{(pyrite)}}{3FeS_2} + \underset{\text{(aq)}}{6H_2O} \quad \underset{\text{(magnetite)}}{Fe_3O_4} + \underset{\text{(aq)}}{0.5SO_4^{2-}} + \underset{\text{(aq)}}{5.5H_2S} + \underset{\text{(aq)}}{H^+} \qquad (1).$$

$$\underset{\text{(aq)}}{ZnCl_2} + \underset{\text{(aq)}}{H_2S} \quad \underset{\text{(sphalerite)}}{ZnS} + \underset{\text{(aq)}}{2H^+} + \underset{\text{(aq)}}{2Cl^-} \qquad (2).$$

$$\underset{\text{(aq)}}{H_2O} + \underset{\text{(aq)}}{0.25H_2S} \quad \underset{\text{(gas)}}{H_2} + \underset{\text{(aq)}}{0.25SO_4^{2-}} + \underset{\text{(aq)}}{0.5H^+} \qquad (3).$$

$$\underset{\text{(aq)}}{HCO_3^-} + \underset{\text{(aq)}}{H^+} \quad \underset{\text{(gas)}}{CO_2} + \underset{\text{(aq)}}{H_2O} \qquad (4).$$

The calculation result for isothermal reservoir boiling is shown in Fig. 2. The dissolution of sphalerite and galena occurs from enthalpy of 1,338 kJ/kg (the enthalpy of the liquid water at 305˚C) through 2,092 kJ/kg. The progress of these reactions is a marked difference from that in the isoenthalpic model. The degassing of H_2S from liquid phase to gas phase at a constant temperature drives the dissolution reactions such as following:

$$\underset{\text{(sphalerite)}}{ZnS} + \underset{\text{(aq)}}{2H^+} + \underset{\text{(aq)}}{3Cl^-} \quad \underset{\text{(aq)}}{ZnCl_3^-} + \underset{\text{(aq)}}{H_2S} \qquad (5).$$

The degassing of H_2S caused by isothermal boiling also drives continuous dissolution of pyrite and precipitation of magnetite (reaction 1). This reaction results in the increase of H_2S concentration in gas phase. The H_2 concentration in gas phase increases with increasing enthalpy through reaction 3. The pH decrease is due to the combined effect of the H^+ supply from reactions with these iron-bearing minerals and the H_2 redox reaction.

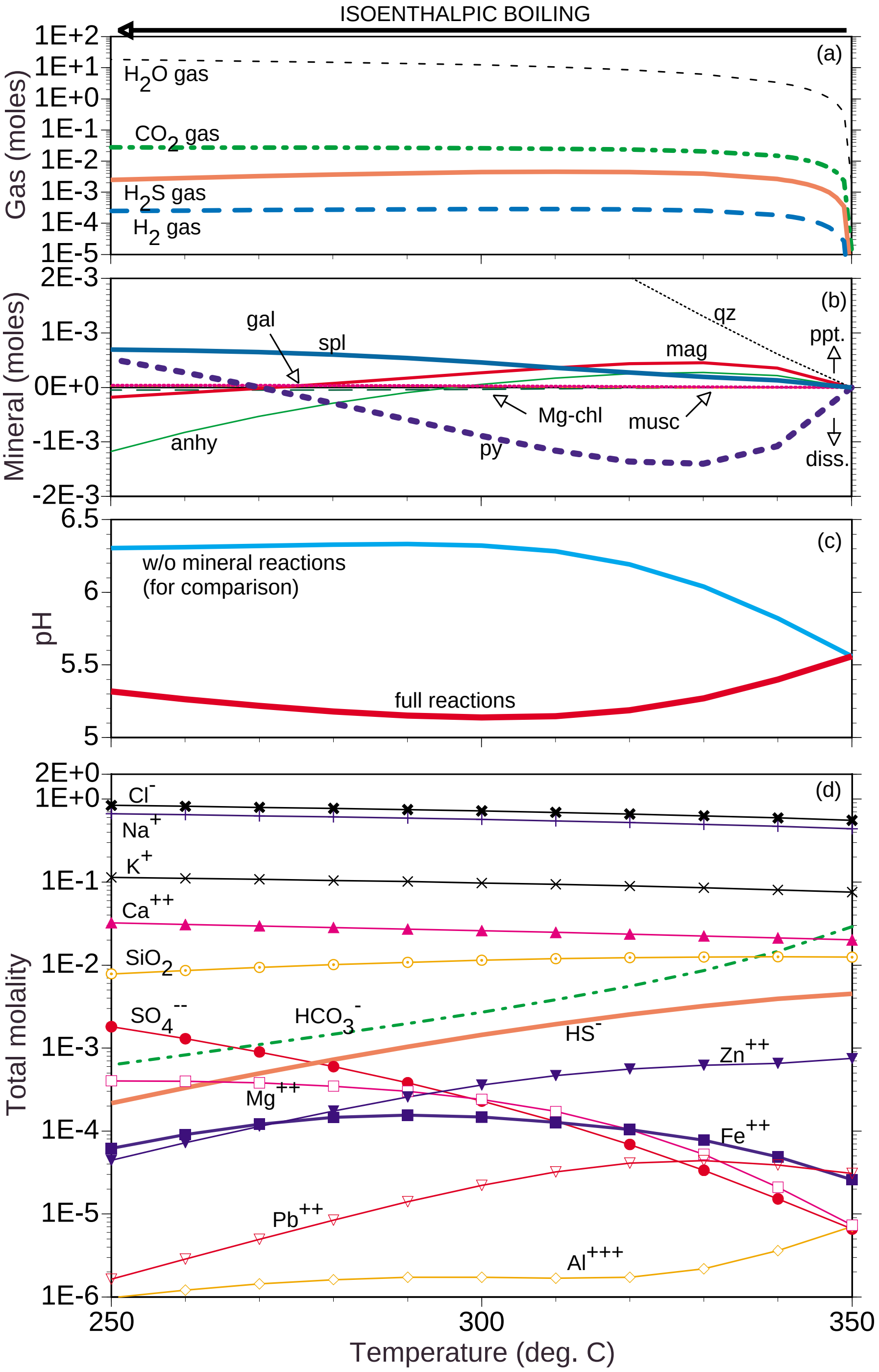

Figure. 1. Calculation results for isoenthalpic boiling process in reservoir (reproduced from Akaku et al., 2000). Boiling proceeds from the right to the left side of the graphs. The starting solution (1kg) is fully equilibrated with the alteration and scale minerals (quartz, albite, K-feldspar, muscovite, clinochlore, anhydrite, clinozoisite, pyrite, magnetite, sphalerite and galena) at 350˚C. During boiling reactions of fluid with albite, K-feldspar and clinozoisite is disallowed for kinetic reasons. (a) Gas phase composition. (b) Amounts of minerals in saturated assemblage. (c) pH. (d) Total aqueous molality of component species. Mineral abbreviations: qz, quartz; musc, muscovite; py, pyrite; Mg-chl, clinochlore (Mg end member of chlorite); anhy, anhydrite; spl, sphalerite; gal, galena; mag, magnetite.

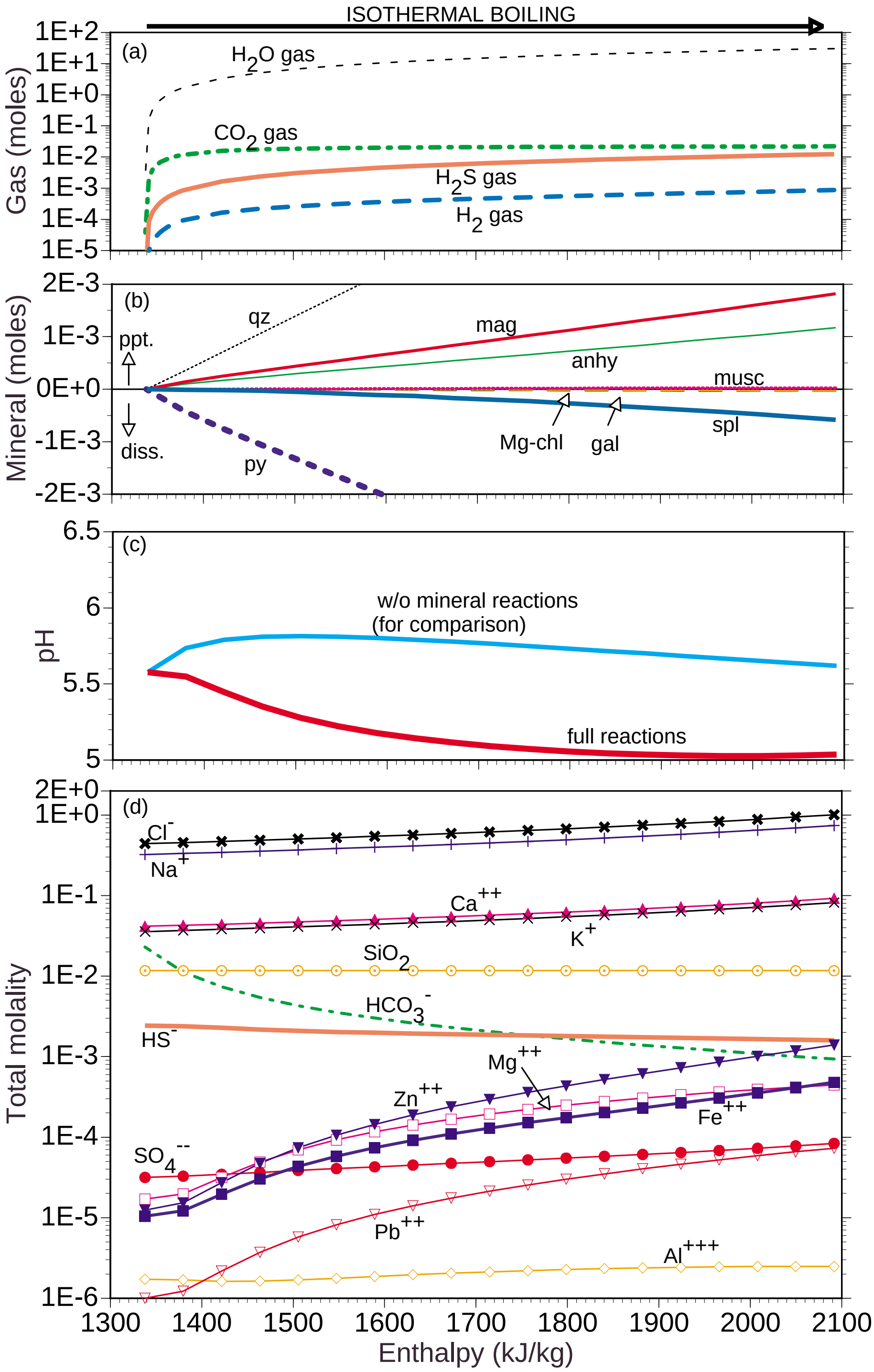

Figure. 2. Calculation results for isothermal boiling process in reservoir. Boiling proceeds from the left to the right side of the graphs. The starting solution (1kg) is fully equilibrated with the alteration and scale minerals (quartz, albite, K-feldspar, muscovite, clinochlore, anhydrite, clinozoisite, pyrite, magnetite, sphalerite and galena) at 305˚C. During boiling reactions of fluid with albite, K-feldspar and clinozoisite is disallowed for kinetic reasons. (a) Gas phase composition. (b) Amounts of minerals in saturated assemblage. (c) pH. (d) Total aqueous molality of component species. Mineral abbreviations are same as those in Fig. 1.

CONCLUSIONS

The model calculations show that the isothermal boiling process results in dissolution of sphalerite and galena from wall rocks driven by the H_2S escape from liquid to gas phase at a constant temperature. The degassing in the isothermal process also causes continuous dissolution of pyrite from wall rocks and precipitation of magnetite. In addition, the H_2S and H_2 concentrations of fluid increase with increasing enthalpy. As a result of these reactions, the decrease in pH could occur.

Local near-well boiling caused by production-induced pressure decrease is commonly observed in the high temperature reservoirs. The boiling in the reservoir sometimes involves isothermal process due to heat transfer from wall rocks to the fluid. The isothermal boiling process would play an important part for the changes of fluid compositions in the reservoir under production.

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REFERENCES

Akaku, K., Reed, M. H., Yagi, M., Kai, K. and Yasuda, Y. (1991), "Chemical and Physical Processes Occurring in the Fushime Geothermal System, Kyushu, Japan," *Geochemical Journal*, **25**, 315-333.

Akaku, K., Kasai, K. and Nakatsuka, K. (2000), "Modeling of Formation of Acid Water Discharged from High Temperature Geothermal Reservoir," *Proceedings of the World Geothermal Congress 2000*, 895-900.

Bourcier, W. L. and Barnes, H. L. (1987), "Ore Solution Chemistry - VII. Stabilities of Chloride and Bisulfide Complexes of Zinc to 350˚C," *Economic Geology*, **82**, 1839-1863.

Fournier, R. O. and Potter, R. W. (1982), "A Revised and Expanded Silica (quartz) Geothermometer," *Geothermal Resources Council Bulletin*, November, 3-12.

Okada, H., Yasuda, Y., Yagi, M and Kai, K. (2000), "Geology and Fluid Chemistry of the Fushime Geothermal Field, Kyushu, Japan," *Geothermics*, **29**, .279-311.

Reed, M. H. (1982), "Calculation of Multicomponent Chemical Equilibria and Reaction Processes in Systems Involving Minerals, Gases and Aqueous Phase," *Geochimica et Cosmochimica Acta*, **46**, 513-528.

Spycher, N. F. and Reed, M. H. (1992), *"Users guide for CHILLER: A Program for Computing Water-rock Reactions, Boiling, Mixing and Other Reaction Processes in Aqueous-mineral-gas Systems,"* University of Oregon, 64pp.