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REACTION OF PH-ADJUSTED REINJECTION BRINE WITH GEOTHERMAL RESERVOIR: SIMULATION BY CHEMICAL EQUILIBRIUM APPROACH

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ABSTRACT

The geochemical effects caused by reinjection of a separated water mixed with sulfuric acid (pH-adjusted brine) was studied in the water-rock interactions of a reservoir. In Japan's Oguni geothermal field, the pH increase of the pH-adjusted brine (pH=5) is initially large, then approaches steady state due to the reaction of one kilogram of brine with several grams of rock. The pH is buffered by the mineral assemblage of albite, K-feldspar, K-mica and quartz. A small amount of wall rock is sufficient to neutralize the pH-adjusted brine due to the large buffering capacity of the wall rock. The chemical changes in aqueous species and alteration in mineral assemblage produced by the pH-adjusted brine are similar to those produced by the brine without added acid, independent of rock-types (andesite, dacite and tuff) and alteration degree (fresh and partially altered). Anhydrite would not precipitate from the pH-adjusted brine in the Oguni field, even when sulfuric acid was added to the system. The pH-adjusted brine would prevent the precipitation of calcite as well as amorphous silica in fractures around the reinjection well. These results suggest that the geochemical environment in the reservoir is little affected by reinjection of a small amount of brine with added sulfuric acid solution.

1. INTRODUCTION

Silica scale deposition often causes reinjection problems at geothermal power stations. In order to solve the problem, a number of scale prevention methods have been proposed, and experimental studies of silica scale prevention have been carried out at geothermal power stations. In some of Japan's geothermal power stations, the neutral brine is currently reinjected directly from the separator under high-temperature conditions to keep the amorphous silica in an undersaturated state. In geothermal power stations where brine can not be reinjected at high temperatures, a pH adjustment technique using a sulfuric acid solution can be useful for prevention of silica scaling. Gallup (1996) revealed that the silica scaling of acidified brine (pH = 5) was reduced by retarding the kinetics of silica polymerization, compared to scaling of neutral brine. In Japanese geothermal power stations, however, the pH adjustment technique using a sulfuric acid solution has not been carried out yet. It is important to assess the geochemical effect of acidified brine reinjection in the reservoir environment. A chemical modeling study was carried out to assess the effect at the Onikobe geothermal power station, Japan (Todaka and Mezaki, 1999). In this paper, the water-rock interaction calculations were carried out to study the geochemical effects caused by reinjection of the pH-adjusted brine in the Oguni geothermal reservoir, Japan.

2. METHOD

2.1 Chemical Modeling Calculation

Calculations were made using the chemical modeling code CHILLER (Spycher and Reed, 1992), which can perform rock titration calculations. Local equilibria as well as the chemical evolution of brine and wall rock were studied numerically by stepwise titration of wall rock into brine, *i.e.,* a small amount of rock (0.1 g) was successively titrated into one kilogram of brine at some constant temperature. In each titration step, the aqueous speciation was calculated. Minerals precipitated out of the supersaturated solution at each step until no mineral was supersaturated. In each titration step, the precipitated minerals were removed automatically by calculation under the chemical equilibrium condition and only the evolved solution was passed to the next step.

2.2 Starting Materials and Database

The separated brine (pH: 8.8 at 25°C, Cl: 1620 mg/l) from production well GH-20 was selected as a representative of reinjected brine in the Oguni geothermal field and used in this study. The chemical composition of the fluid (Table 1) was taken from Yamada *et al.* (in press). The separated brine was mixed with sulfuric acid by fluid-fluid mixing calculation and its pH was adjusted to 5 at 100°C. The pH-adjusted brine was mixed with the reservoir water (calculated pre-flashed water) to increase water temperature. The fluid-fluid mixing was calculated on the assumption of no mineral precipitation. Water-rock interaction calculation by rock titration was carried out at the temperatures of 100°, 120° and 150 °C at their saturation pressures. The effects of rock-type and alteration were also calculated.

The reinjected brine would flow through the fractures from the reinjection well and would be gradually heated from the reinjected temperature (100°C) to the reservoir temperature (242°C). The batch reaction model mentioned above is not enough to simulate this process. A model introducing pseudo flow-reaction coupling is also examined; the temperature of the system was increased after every 0.1 g or 1.0 g of rock titration at 10°C interval from 100° to 200°C at its saturation pressure. The reinjected brine evolved by rock titration was mixed with the reservoir water to make the next reaction temperature, then the next titration was carried out.

The wall rock surrounding the reinjection zone in the Oguni geothermal field consists of mainly andesite and dacite lavas of Pleistocene age, and tuffs of Pliocene age. These three rock types were selected as wall rock starting materials. The chemical compositions of the wall rocks (Table 2) were taken from GSJ (1989).

The thermodynamic data were taken from SOLTHERM (Reed and Spycher, 1992), the original database of CHILLER. In order to make the calculation fit the Oguni geothermal field, and to avoid a convergence problem, it is important to select the appropriate mineral assemblage that may appear in the calculation. The mineral assemblage at each calculation temperature (summarized in Table 3) is based on well data such as microscopic observation and XRD data of the cores and the cuttings. The secondary minerals observed at a well temperature of 100°C consist of montmorillonite, mixed-layer minerals, chlorite, kaolinite, quartz, calcite, anhydrite and pyrite. The secondary minerals at 150°C consist of laumontite, sericite, and prehnite in addition to those found at 100°C. Therefore, albite, anhydrite, calcite, clinochlore (magnesium end-member of chlorite), daphnite (iron end-member of chlorite), kaolinite, K-feldspar, muscovite (sericite), laumontite, prehnite, pyrite and quartz were selected as reaction minerals in this study. Montmorillonite and mixed layer minerals are not used because these minerals were not available in SOLTHERM and good quality thermodynamic data cannot be found in the other databases.

3. RESULTS

3.1 Reaction at Constant Temperature

pH-adjusted brine

Rock (tuff) titration calculations at 100°, 120° and 150°C were carried out. The pH of the acidified reinjection brine increased by rock titration at each temperature (Figure 1). The pH changed from 5.0 to 7.9 at 100°C and became constant after addition of 4 g of tuff into one kilogram of brine. The initial pH values at 120°C and 150°C were slightly higher than that at 100°C, because the acidified brine was mixed with the reservoir water of pH 6.9 at the reservoir temperature, 242°C. However, the similar changes in pH were calculated at 120°C and 150°C. The water-rock interaction increased the final pH of the brine to 7.7 at 120°C and 7.4 at 150°C.

The changes in aqueous chemistry and calculated mineral assemblage were almost the same at all calculation temperatures. For example, the results calculated for the reaction of the pH-adjusted brine with tuff at 150°C is shown in Figure 2. As similar to this example, chemical compositions of aqueous species became steady state after titration of several grams of rock into one kilogram of brine except Fe^{2+} and SO_4^{2-} ions. Temperature dependence of water chemistry was small except for dissolved silica concentration.

In the first titration step, quartz, muscovite, clinochlore and pyrite precipitated. Calcite and daphnite also precipitated after a small amount of rock titration. Further titration of tuff made calcite undersaturated and finally produced a propylitic mineral assemblage: calcite, K-feldspar, albite and prehnite. No anhydrite (sulfate mineral) precipitated although sulfuric acid is added into the system. Pyrite stopped precipitating after the HS^- ion was consumed in the first few titration steps.

Non-pH-adjusted brine

The pH of non-pH-adjusted brine by the reaction with tuff gradually decreased during the first few titration steps at 100°C (Figure 1). After that, it decreased from 8.4 to 7.9 between 1.0 g and 4.0 g step. The pH became constant after titration of 4.0 g of tuff. On the other hand, the pHs of non-pH-adjusted brine at 120°C and 150°C increased before it became steady state, similar to those of the pH-adjusted brine. The reaction of non-pH-adjusted brine with tuff at 150°C is shown in Figure 3. There are small differences in aqueous species concentration and mineral assemblage between the pH-adjusted and non-pH-adjusted brines at the same temperature. Water/rock ratios at which the alteration mineral formed or disappeared were slightly different between two cases (*e.g.*, calcite precipitation at 150°C: 0.2 - 6.0 g per one kilogram of non-pH-adjusted brine, but 0.8 - 6.0 g per one kilogram of pH-adjusted brine).

3.2 Effect of Rock-type

The changes in aqueous chemistry and mineral assemblage were almost the same for three rock-types: andesite, dacite and tuff. The pH changes calculated during rock titration are shown in Figure 4. The pH-adjusted brine reached pH steady state after addition of several grams of rock per one kilogram of brine in all rock-types. After reaching pH steady state, the chemical compositions of brines did not change except for Fe^{2+} and SO_4^{2-}. Tuff and dacite required slightly larger amount of titration than andesite to reach pH steady state. Only a small amount of rock was needed to reach pH steady state for both pH-adjusted and non-pH-adjusted brines. Rock type does not significantly affect the chemical evolution of brine and the alteration mineral assemblage.

3.3 Effect of Alteration Degree

The effect of wall rock alteration on the chemical evolution of brine was examined using fresh and partially altered andesites. As a result, chemical evolution of the brine by reaction with fresh and partial andesite rocks indicate similar trends; the alteration mineral assemblage was also similar in all temperature calculations. The pH-adjusted and non-pH-adjusted brines reached pH steady state by reaction with a small amount of rock. In the calculation using the pH-adjusted brine, the altered andesite required a slightly larger amount of rock titration than the fresh andesite to reach pH steady state. The reinjected brine would be neutralized if the wall rock is not so strongly altered.

3.4 Reaction around the Reinjection Well

The model introducing pseudo flow-reaction coupling is applied for geochemical evolution of the reservoir caused by brine flow around the reinjection well. Water-rock interaction was calculated in every 0.1 g or 1 g rock titration per one kilogram of brine and at the same time the temperature was increased by 10°C at each step from 100°C to 200°C. The former case (0.1 g per 10°C) corresponds to the chemically slow reacting reservoir (fast fluid flow) and the latter (1 g per 10°C) corresponds to the fast reacting reservoir (slow fluid flow). The calculated results (pH changes with flow) are shown in Figure 5. The pH changed steeply at the first step (in other words, just around the reinjection point). Then pH changed gradually corresponding to the temperature increase. In the case of 1 g per 10°C titration (fast reacting reservoir), the calculated pH for both the pH-adjusted and non-pH-adjusted brines became identical at 160°C. However, in the case of 0.1 g per 10°C, the two pHs did not agree up to above 200°C and were lower than those at 1 g per 10°C. These results indicate that, in a fast reacting reservoir, pH adjustment does not affect the reservoir condition significantly, but the pH adjustment might affect the chemical condition of the reservoir in the slow reacting reservoir. However, the maximum calculated difference is one pH unit at low temperature and becomes smaller with increasing temperature.

In the pseudo flow-reaction calculation, the HS^- ion was consumed by pyrite precipitation at the first titration step in both cases of 0.1 g per 10°C of titration (Figures 6 and 7), similar to the batch-type calculation. Anhydrite and laumontite were not formed at 100°C to 200°C, independent of pH adjustment. Calcite precipitated from pH-adjusted brine at 170°C or higher (Figure 6), and from the non-pH-adjusted brine at 150°C or higher (Figure 7). The lower pH of pH-adjusted brine than non-pH-adjusted brine probably inhibits calcite precipitation.

4. DISCUSSION

Addition of sulfuric acid to the reinjected brine was suspected to cause precipitation of anhydrite in the reservoir. However, the present calculations indicate that anhydrite precipitation will not occur even if pH is adjusted to 5 by addition of sulfuric acid. Another possibility for absence of anhydrite in alteration minerals is lack of appropriate mineral assemblages in the thermodynamic database used in the calculation. In order to test this situation, some trial calculations were carried out including or excluding epidote, clinozoisite and prehnite in the database. Anhydrite was not precipitated in all these trial calculations. Also, laumontite, which is another Ca-bearing mineral in the database, does not appear as a precipitating mineral in all the calculation. Thus, the absence of anhydrite from the precipitating alteration minerals is not an artifact caused by the thermodynamic database used in the calculation.

Pyrite precipitated in the initial titration step at 120° and 150°C. The quantity, however, is limited to a small amount because the reinjected brine contains a very small amount of HS^- ion. The calculated small amount of pyrite precipitation may correspond to a pyritic alteration halo along veins. Pyrite precipitation would not be a significant problem for fracture sealing.

Compared to the Onikobe geothermal fluid, which is acidic and far from equilibrium with surrounding rock (Todaka *et al.*, 1999), a smaller amount of rock is needed until the brine reaches a steady-state pH in the Oguni geothermal field. This is because the fluid in the Oguni field is originally close to equilibrium with alteration minerals found in the cores. Figure 8 shows the reaction path of the brine at 150°C. The precipitation of albite establishes a feldspar-mica-quartz pH buffer that holds pH constant at each calculated temperature. The pH of this system is buffered by the following reaction:

$$\underset{\text{(K-feldspar)}}{KAlSi_3O_8} + 2\ \underset{\text{(albite)}}{NaAlSi_3O_8} + 2\ H^+ = \underset{\text{(K-mica)}}{KAl_3Si_3O_{10}(OH)_2} + 6\ \underset{\text{(quartz)}}{SiO_2} + 2\ Na^+$$

The pH buffer is particularly stable and capacious because it relies on concentrated Na^+ ions and because its constituent minerals are abundant. As shown in Figure 1, the buffered pH shifts slightly according to the temperature. After adequate reaction with wall rock, it is expected that the above reaction limits pH to 7.9 at 100°C and 7.4 at 150°C in the Oguni geothermal field. Therefore, pH adjustment would not have an impact on the reservoir environment.

5. CONCLUSIONS

The pH-adjusted brine was found to reach neutral to alkaline pH steady state after the reaction of a small amount of wall rock. The effect of rock-type, *i.e.*, andesite, dacite and tuff, on water chemistry was found to be small at the calculated temperatures. Anhydrite would not precipitate from the pH-adjusted brine by reaction with any type of volcanic rock or partially altered rock. The pH adjustment would also prevent the precipitation of calcite as well as amorphous silica in fractures around reinjection wells. The pH-adjusted brine would be neutralized by the reaction with a small amount of wall rock and have little geochemical effect on the reservoir environment.

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REFERENCES

Gallup, D. L. (1996). Brine pH Modification Scale Control Technology. *Geothermal Resources Council Transactions*, Vol. **20**, pp.749-755.

Geological Survey of Japan (GSJ) (1989). Well Data Compiled from Japanese Nation-Wide Geothermal Surveys, Part 1 Core Sample Data, -Physical Properties, Geology, Age, Chemical Composition-. *Rept. Geol. Surv. Japan*, Yano, Y., Suda, Y. and Tamanyu, S. ed. No.271, 832pp (in Japanese with English abstract).

Reed, M. H. and Spycher, N. (1992). SOLTHERM: Data Base of Equilibrium Constants for Aqueous-Mineral-Gas Equilibria. Dept. of Geological Sciences, Univ. of Oregon. 64pp.

Spycher, N. and Reed, M. H. (1992). Users Guide for CHILLER: A Program for Computing Water-Rock-Gas Equilibria. Dept. of Geological Sciences, Univ. of Oregon.

47pp.

Todaka, N and Mezaki, Y (1999). Study on Silica Scale Prevention -pH Modification Technique and Geochemical Evolution of pH-modified Brine in Reservoir-. *Jour. Geothermal Association,* Vol. **36**, No. 3, pp.25-40 (in Japanese with English abstract).

Yamada, M., Iguchi, K., Nakanishi, S. and Todaka, N. (2000). The Reservoir Characteristics and Development Plan of the Oguni Geothermal Field, Kyushu, Japan. *Geothermics* (in press).

Table 1. Chemical composition of fluid from well GH-20 in the Oguni geothermal field.

	pH	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	Al mg/l	Li mg/l	SO_4 mg/l	Cl mg/l	T-CO_2 mg/l	SiO_2 mg/l	H_2S mg/l
liquid phase	8.8	950	134	22.0	0.01	0.01	0.77	5.22	58	1620	56.9	615	0.05

	Noncondensable gas vol%	CO_2 vol%	H_2S vol%	H_2* vol%	O_2* vol%	N_2* vol%	CH_4* vol%	Ar* vol%	Separation pressure kg/cm2, gauge
steam phase	0.054	93.0	2.5	0.07	<0.01	4.17	0.21	0.05	2.8

*: data added to Yamada *et al* . (in press)

Table 2. Chemical compositions of rocks distributed in the Oguni geothermal field.
ho: hornblende, px: pyroxene, Da: dacite, An: andesite

unit: wt%

rock name	SiO_2	TiO_2*	Al_2O_3	Fe_2O_3	FeO	MnO*	MgO	CaO	Na_2O	K_2O	P_2O_5*	H_2O^+	H_2O^-	S	total	well name (depth)
ho-Da	60.7	0.75	18.75	2.64	2.46	0.14	0.99	3.58	3.5	3.4	0.22	0.57	0.3	0.0	98.00	DW-2 (495m)
2px-An	52.88	0.43	18.33	4.92	3.14	0.21	3.29	9.06	2.86	1.4	0.21	0.85	1.65	0.0	99.23	DB-9 (498m)
px-An	60.1	0.75	18.0	2.79	1.36	0.08	0.98	4.8	4.64	3.15	0.21	1.3	0.35	0.0	98.51	DB-4 (419m)
lapilli tuff	65.2	0.49	14.84	0.72	2.52	0.08	1.39	3.55	2.87	3.56	0.11	1.89	0.65	0.0	97.87	DW-2 (1497m)

Reference: GSJ (1989)
*: not used in this calculation

Table 3. Alteration mineral assemblage in the Oguni geothermal wells as a function of temperatures. lm: laumontite, wa: wairakite, mo: montmorillonite, mlm: mixed-layer minerals, ch: chlorite, se: sericite, ka: kaolinite, ep: epidote, pr: prehnite, qz: quartz, cc: calcite, an: anhydrite, py: pyrite

temperature (°C)	lm	wa	mo	mlm	ch	se	ka	ep	pr	qz	cc	an	py
100			┃	⋮	⋮		⋮			┃	┃	⋮	⋮
120	⋮		┃	⋮	⋮		⋮			┃	┃	⋮	⋮
150	⋮		┃	⋮	⋮	⋮	⋮		⋮	┃	┃	⋮	⋮
200	⋮	⋮	⋮	┃	┃	⋮	⋮	⋮	⋮	┃	┃	⋮	⋮
230～240	⋮	⋮		⋮	┃	┃		⋮	⋮	┃	┃	⋮	⋮

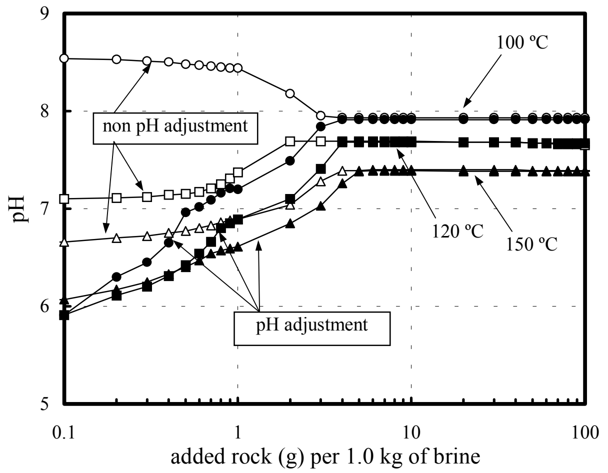

Figure 1. Calculated pH changes of pH-adjusted and non-pH-adjusted brines by the reaction with tuff. Open symbols are pHs of non-pH-adjusted brine and closed symbols are those of pH-adjusted brine.

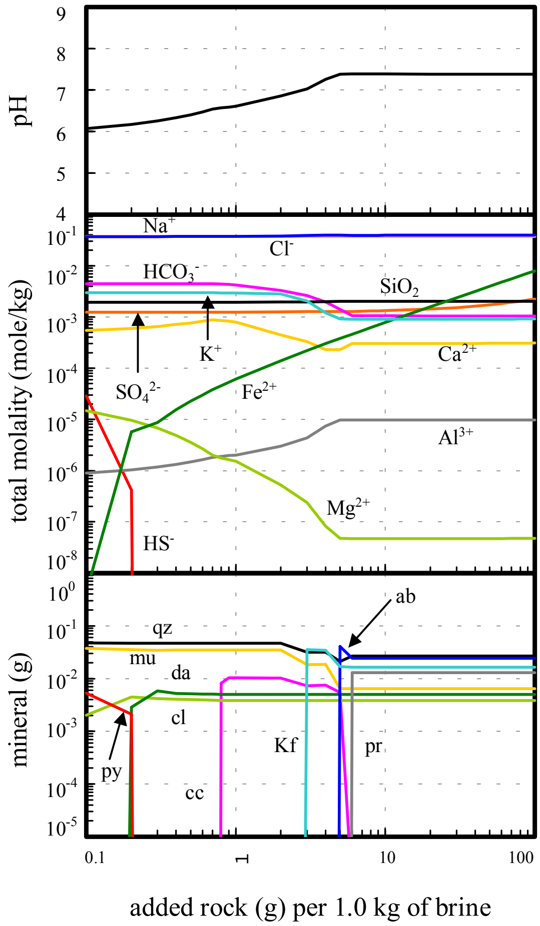

Figure 2. Reaction of pH-adjusted brine with tuff at 150°C. Kf: K-feldspar, ab: albite, cl: clinochlore, da: daphnite, mu: muscovite, pr: prehnite, qz: quartz, cc: calcite, py: pyrite

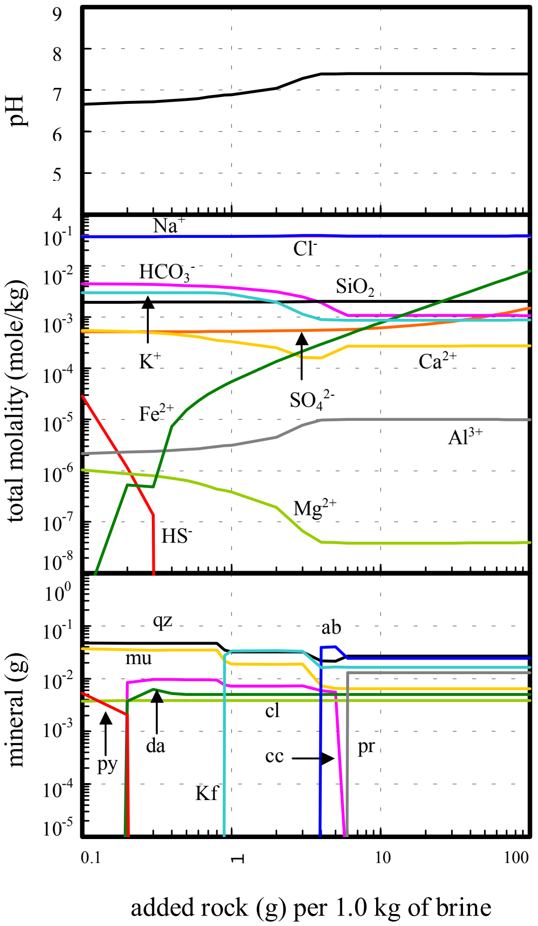

Figure 3. Reaction of non-pH-adjusted brine with tuff at 150°C. Abbreviations are as in Figure 2.

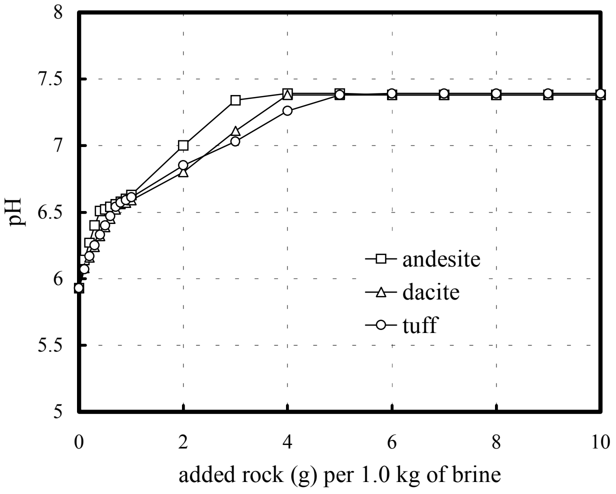

Figure 4. pH changes of pH-adjusted brine by the reaction with andesite, dacite and tuff.

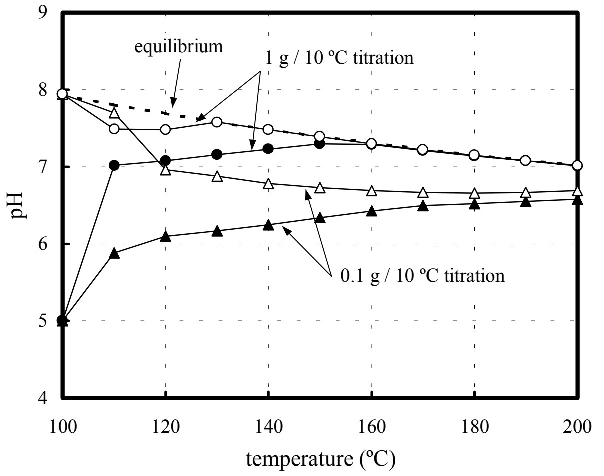

Figure 5. pH changes of pH-adjusted and non-pH-adjusted brines by the reaction with tuff. A small amount of tuff (0.1 g or 1 g) was titrated into one kilogram of water in each 10°C step calculation. Open symbols are the pHs of non-pH-adjusted brine and closed symbols are those of pH-adjusted brine.

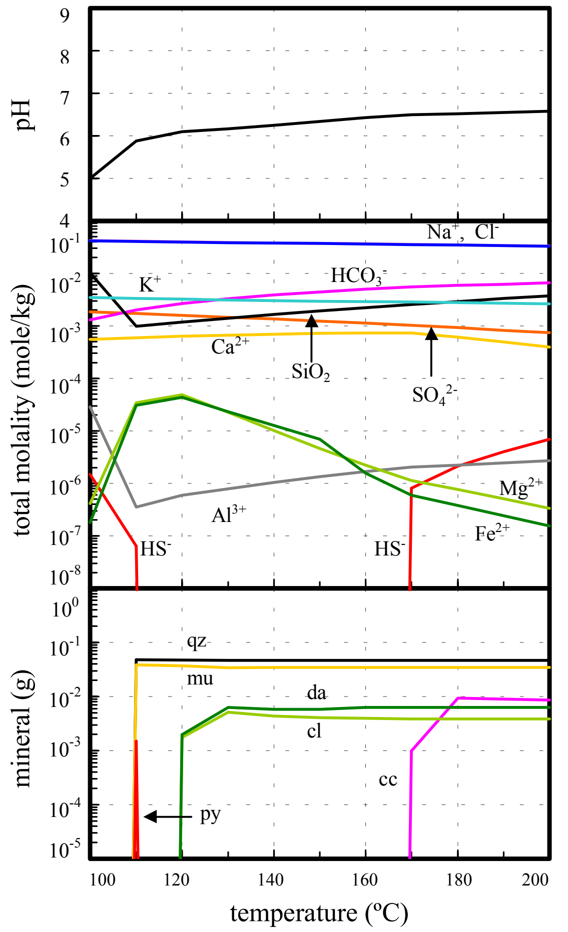

Figure 6. Pseudo flow-reaction of pH-adjusted brine with tuff. The calculation titrated 0.1 g per 10°C increase in one kilogram of brine. Abbreviations are as in Figure 2.

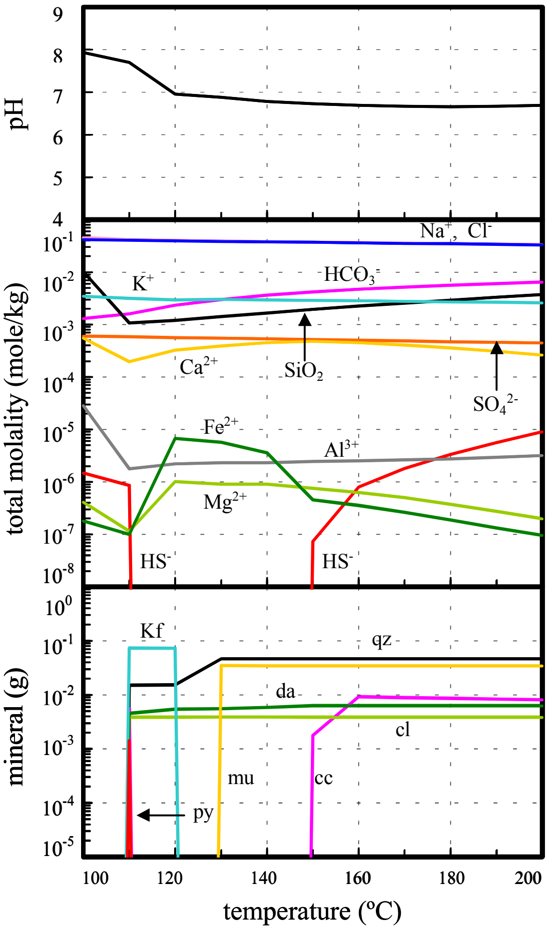

Figure 7. Pseudo flow-reaction of non-pH-adjusted brine with tuff. The calculation titrated 0.1 g per 10°C increase in one kilogram of brine. Abbreviations are as in Figure 2.

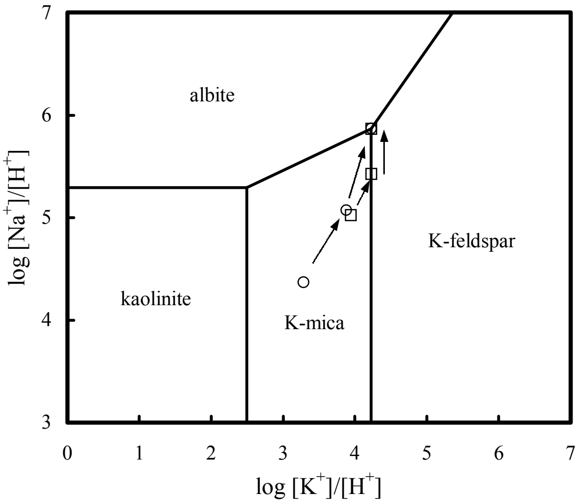

Figure 8. Calculated reaction path in Na^+-K^+-H^+ system at 150°C. Open circles and squares stand for pH-adjusted and non-pH-adjusted brines, respectively.