

## Prediction of Calcite Scaling at the Oguni Geothermal Field, Japan: Chemical Modeling Approach

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### ABSTRACT

Both calcite-scaled wells and non-scaled wells exist at the Oguni geothermal field and its vicinity. The chemical compositions among all pre-flashed waters exhibit no significant difference. The most important factor on calcite saturation at the Oguni field seems to be the degree of steam loss in addition to the reservoir temperature. The calcite saturation index ( $\log Q/K$ ) of pre-flashed water increases with steam loss in the reservoir. The anhydrite saturation index, however, is little affected by steam loss. The change in the anhydrite saturation index during production may be empirically used as an indicator of calcite scaling. The anhydrite saturation index equal to  $-0.3$  seems to correspond to the threshold for calcite scaling at the Oguni field. Calcite scaling may be decreasing in Oguni wells because the anhydrite saturation indices change to this criterion during production.

### 1. INTRODUCTION

The Oguni geothermal field is located near the border between Kumamoto and Oita Prefectures, central Kyushu. Electric Power Development CO., Ltd. (EPDC) initiated a geothermal exploration program at the Oguni geothermal field in 1983 (Abe *et al.*, 1995). Up to now, 49 wells (>500 m) including other project wells were drilled at the Oguni geothermal field and its vicinity (Figure 1). Discharge tests of some wells were carried out for more than one month. During these production tests, EPDC found calcite scaling in some GH wells, as well as DY-1 and BS wells. DY-1 kept on stable production for 9 months and stopped shortly after the total flow rate and the wellhead pressure rapidly decreased due to calcite scaling inside the well. In contrast, TY-1 and K-6 in the same area have been producing fluids for more than 15 years without any

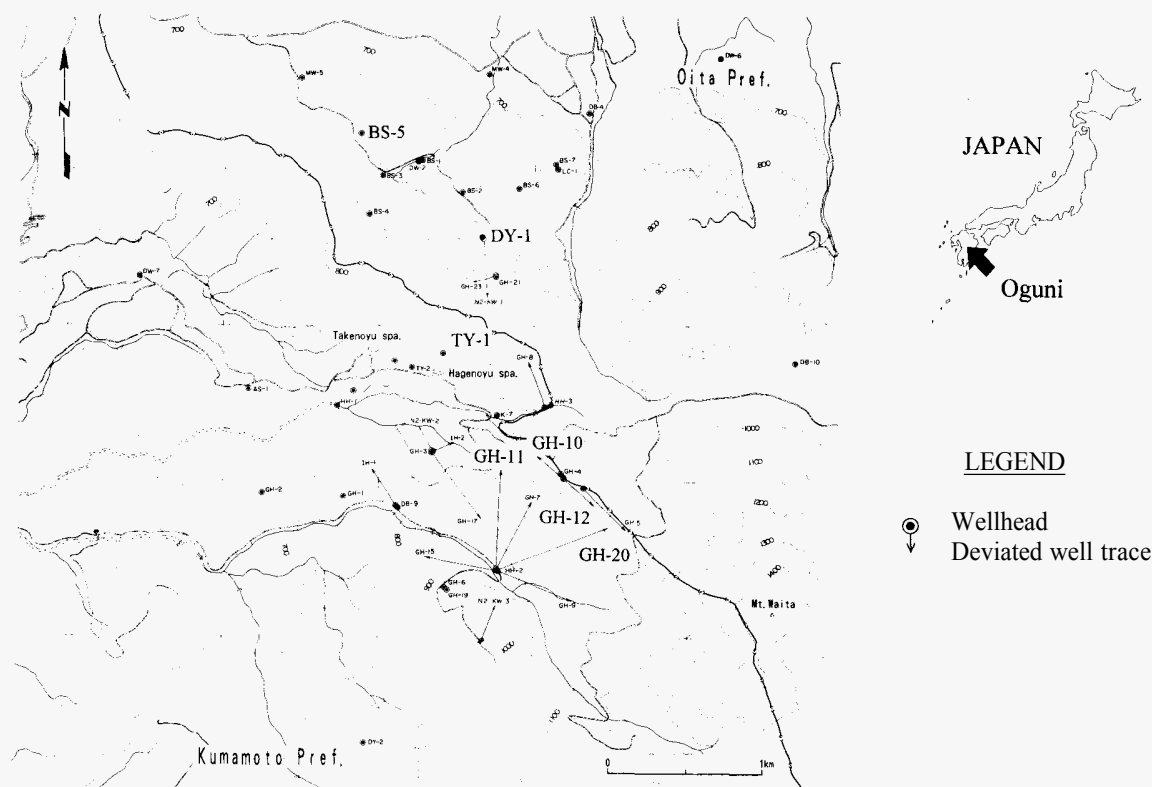


Figure 1 Location of wells at the Oguni geothermal field and its vicinity.

problems. The present study employs a chemical modeling approach to predict calcite depositions in the production wells.

## 2. METHOD OF CALCULATION

The degree of calcite saturation is inferred from the calculated activity product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in the water. The methods of calculation for solution-mineral equilibria are those described by Reed (1982) and Reed and Spycher (1988). All the wells used in the present study discharge a mixture of water and steam. For calculation of a pre-flashed water composition, the steam phase including gases, is condensed back to the liquid phase in proportion to the steam fraction deduced from the total discharge enthalpy. The enthalpy of the pre-flashed water in the reservoir was estimated from dynamic temperature loggings or the silica geothermometer. All reservoir waters in the present study are presumed to flash inside the wells from the data of dynamic loggings, geochemistry and steam quality.

The aqueous speciation of the pre-flashed water in the reservoir is calculated by the SOLVEQ code using the composition of pre-flashed water and the assumed reservoir temperature. Boiling is simulated by the CHILLER code assuming a closed system and no mineral precipitation from fluid samples. The boiling process is simulated as multi-step boiling, so that aqueous speciation was calculated at each 10 °C intervals after iso-enthalpic boiling of the geothermal water. Boiling calculations were carried out from the reservoir temperature to 100 °C. The thermodynamic data base provided with SOLVEQ and CHILLER was used without modification. The fluid geochemical data of TY-1, DY-1, BS-5, and GH wells and K-6 are taken from JGEC (1979), NEDO (1983), EPDC (1988) and the unpublished data of EPDC, respectively.

## 3. RESULTS

### 3.1 Aqueous Species

Total carbonate concentrations in the geothermal waters substantially decrease during flashing due to the transfer of volatile elements including  $\text{CO}_2$  into the steam. As Arnórsson (1978) mentioned, the decrease of total carbonate concentration is always highest at the initial flashing steps (Figure 2) because of the large gas distribution coefficient. However,  $\text{CO}_2$  and the other volatile elements may not be sufficiently transferred into the steam to attain equilibrium. The ratios of sampled  $\text{CO}_2$  over calculated  $\text{CO}_2$  in steam, range from 0.74 to 0.87 at the separator in the present study. The equilibrium degassing may not further accrue at the initial flashing steps in comparison with the separator conditions (Arnórsson, 1978).

The highest pH increase of flashed water is calculated at the initial flashing steps and corresponds to the large

decrease of total  $\text{CO}_3$  concentration in the liquid phase (Figure 3). According to Arnórsson (1978), incomplete degassing may not cause a large increase of pH at the initial flashing steps. The pH of flashed water from calcite-scaled wells is lower than that from

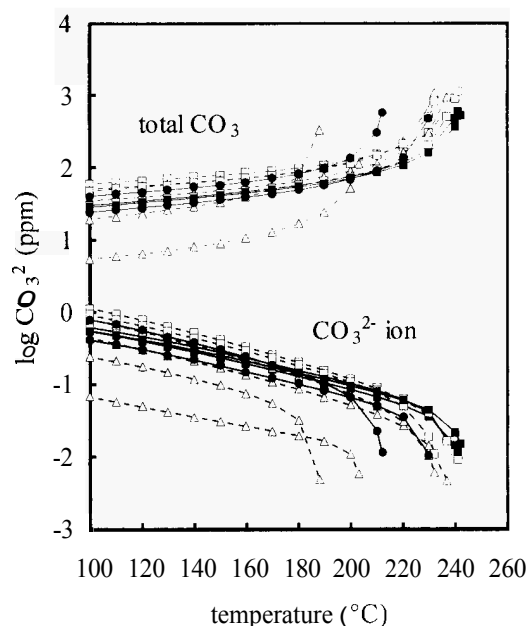


Figure 2 The variation in the concentrations of total  $\text{CO}_2$ , and aqueous  $\text{CO}_3^{2-}$  ion in geothermal waters during flashing. Closed circles indicate non-scaled wells, closed squares indicate assumed non-scaled wells, open squares indicate unconfirmed scaled wells, and open triangles indicate confirmed scaled wells.

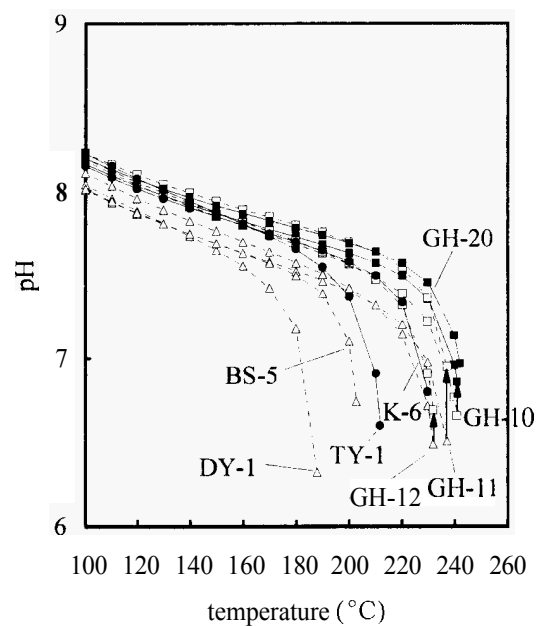


Figure 3 The variation in pH of the geothermal waters during flashing. Symbols are as in Figure 2 and arrows indicate changes during production.

non-scaled wells, independent of the initial pH of pre-flashed waters. Furthermore, the pH of pre-flashed waters increases with production time elapsed as shown by the arrows in Figure 3.

The concentration of  $\text{CO}_3^{2-}$  ion changes symmetrically to the total  $\text{CO}_3$  concentration (Figure 2). The concentrations of  $\text{CO}_3^{2-}$  ion in the waters increase radically during flashing and the increase is largest at the initial flashing steps. Incomplete degassing, however, may not cause a large increase of  $\text{CO}_3^{2-}$  ion at the initial flashing steps (Arnórsson, 1978). As the fluid cools though progressive flashing, the modeling calculation indicates that the concentrations of  $\text{H}_2\text{CO}_3^0$  and  $\text{HCO}_3^-$  continuously decrease, whereas pH and  $\text{CO}_3^{2-}$  concentrations increase.

The concentrations of total Ca and  $\text{Ca}^{2+}$  ion increase linearly during flashing (Figure 4). The increase rate of  $\text{Ca}^{2+}$  ion during flashing is larger than that of total Ca concentration. This is due to the dissociation of the complex species, in addition to the steam loss. The largest decreases in concentration during flashing are calculated for  $\text{CaHCO}_3^+$  and  $\text{CaCl}^+$  at the Oguni geothermal field. The  $\text{Ca}^{2+}$  ion concentrations in flashed waters are two or three times larger than those of pre-flashed waters. The initial decrease of  $\text{Ca}^{2+}$  ion in waters as calculated by Arnórsson (1978) is not

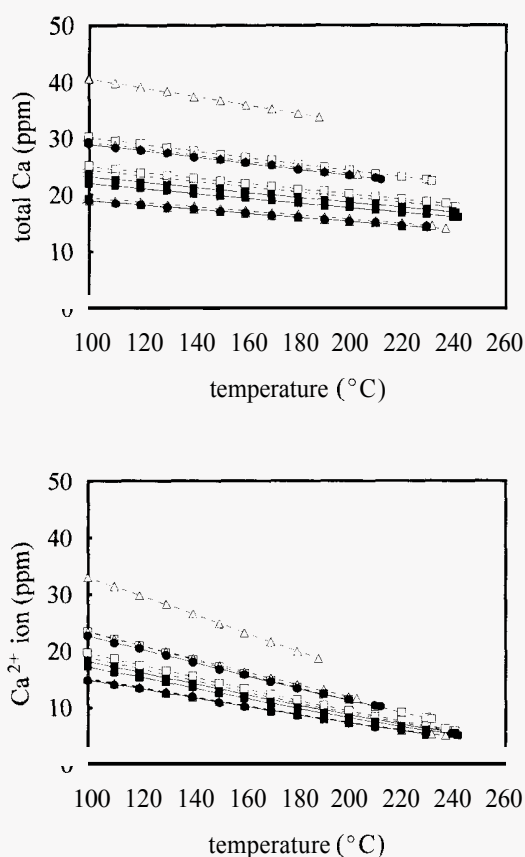


Figure 4 The variation in the concentration of aqueous  $\text{Ca}^{2+}$  ion in the geothermal waters during flashing. Symbols are as in Figure 2.

found because of the low sulfate ion concentration (<70 ppm) at the Oguni geothermal field.

Chiba (1991) recalculated the  $(\text{Ca}^{2+})/(\text{H}^+)^2$  curve in Icelandic geothermal waters as shown in Figure 5. The result is different from Arnórsson (1983) because of the difference in thermodynamic data used. The  $(\text{Ca}^{2+})/(\text{H}^+)^2$  ratios of non-scaled wells are plotted above the curve. The points of calcite-scaled wells, except BS-5, however, are plotted below the curve. This may be due to the deficiency of  $\text{Ca}^{2+}$ . In contrast, some points above the curve may result from steam loss. The arrows in Figure 5 indicate the change in  $(\text{Ca}^{2+})/(\text{H}^+)^2$  ratios during production. It is estimated that prolonged production may cause  $(\text{Ca}^{2+})/(\text{H}^+)^2$  ratios to increase as a result of steam loss.

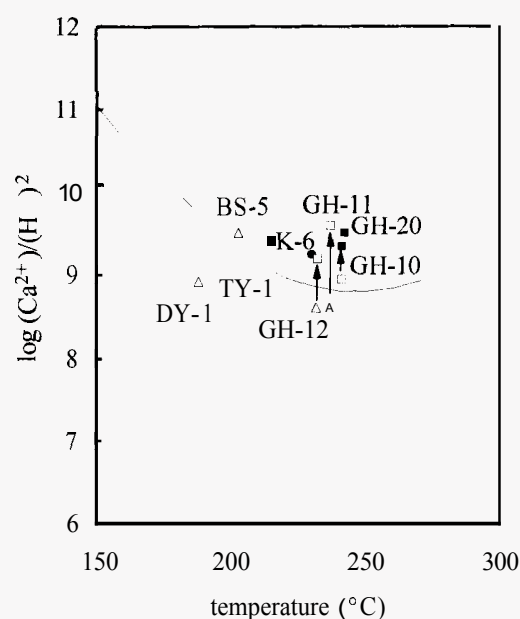


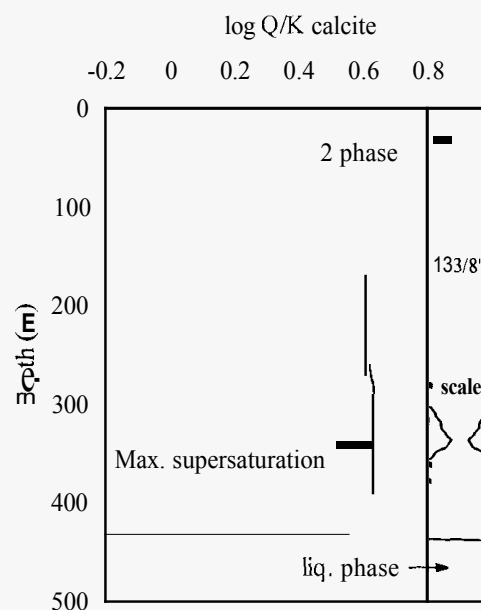
Figure 5 The temperature dependence of  $(\text{Ca}^{2+})/(\text{H}^+)^2$  ratios of the waters from the Oguni geothermal wells. Symbols and arrows are as in Figure 3.

### 3.2 Gaseous Species

Gaseous species are treated in the manner described by Giggenbach (1980). The analytical equilibrium constants ( $\log K_c$ ) of the  $\text{CO}_2\text{-H}_2\text{-CH}_4$  system from geothermal wells are plotted in Figure 6. The curve at the center corresponds to the equilibrium for all species dissolved in a single liquid phase. All fluids from the Oguni geothermal system are plotted below the equilibrium curve. The degree of steam loss is indicated by the contours of steam fraction and increases with production time elapsed as shown by the arrows in Figure 6. Similar small steam loss was calculated on the  $\text{CO}_2\text{-H}_2\text{-CH}_4$  diagram in the Nigorikawa geothermal system (Chiba, 1991) where calcite is apparently precipitated (Fujii, 1988). This means that the decrease of total  $\text{CO}_2$  concentration in water by calcite precipitation is extremely small.

### 3.3 Calcite Saturation

According to Arndrsson (1978), the magnitude of calcite supersaturation is largely controlled by the reservoir temperature and the ionic strength of pre-flashed water. The measured reservoir temperatures at the Oguni field and its vicinity range from 188 to 242 °C. Calcite obviously precipitates in the low temperature wells (<210 °C). Almost all the pre-flashed waters at the Oguni geothermal field are estimated to have similar NaCl concentrations. Cl concentrations corrected to reservoir conditions range from approximately 800 to 1000 mg/l. Variations in Cl concentrations of flashed waters may result from subsurface mixing with dilute water and steam loss. Thus, the chemical compositions of all pre-flashed waters in the Oguni geothermal field are similar and



there is no a significant difference in ionic strength.

If boiling is adiabatic, the degree of calcite supersaturation attains a maximum after a temperature drop of about 10 to 30 °C (Figure 8). Temperatures at which calcite supersaturation reaches a maximum correspond to the significant decrease of total CO<sub>3</sub> concentration at the initial flashing steps. Although both activities of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> increase during

flashing, the log Q/K values continue to decrease to 100 °C after the maximum supersaturation, because the calcite solubility increases with decreasing temperature. Incomplete degassing, however, may not provide such a high degree of calcite supersaturation at the initial flashing steps.

Ion activity products,  $(\text{Ca}^{2+})(\text{SO}_4^{2-})$  and  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$ , are plotted as log Q against reservoir temperature in Figure 9. The upper line indicates the solubility product of anhydrite and the lower is calcite. At the Oguni geothermal field, the calculated  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$  values of the pre-flashed waters from the calcite scaled wells, such as DY-1 and BS-5, are apparently just saturated with respect to calcite. Also, GH-11 and GH-12 at the initial stage of production are close to the saturation of calcite. However, the others are calculated to be supersaturated. If a small amount of steam is lost by subsurface boiling, as mentioned above, much  $\text{CO}_2$  escapes from the liquid to the steam phase. The removal of  $\text{CO}_2$  from the reservoir water causes an increase in pH and  $\text{CO}_3^{2-}$  ion, which results in an increase of the calculated  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$ . The calculation indicates qualitatively that the observed supersaturations of the pre-flashed waters, except scaled wells, result from  $\text{CO}_2$  loss. The difference between the  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$  values of pre-flashed waters may also indicate the degree of steam loss in the reservoir.

On the other hand, all calculated  $(\text{Ca}^{2+})(\text{SO}_4^{2-})$  values indicate minor undersaturation with respect to anhydrite (Figure 9). According to Chiba (1991), Japanese geothermal wells are approximately saturated

with respect to anhydrite. Geothermal fluids in Broadlands, New Zealand, however, are obviously undersaturated with respect to anhydrite. Although it is not clear why the Oguni geothermal waters are undersaturated with respect to anhydrite, the  $(\text{Ca}^{2+})(\text{SO}_4^{2-})$  values in the pre-flashed waters become obviously larger with production time. The  $(\text{Ca}^{2+})(\text{SO}_4^{2-})$  values are little affected by steam loss compared to  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$ . The changes may indicate a decrease of calcite scaling.

Figure 10 shows a diagram for the saturation index (log Q/K) of calcite versus anhydrite. The calcite-scaled wells are plotted in the bottom left of the diagram. The non-scaled wells are plotted in the top right. Furthermore, the anhydrite saturation indices of non-scaled wells approach -0.3 with production time. The field observations of calcite scaling suggest that pre-flashed waters, whose anhydrite saturation indices are larger than approximately -0.3 in the top right of the diagram, may precipitate no calcite at the Oguni geothermal field. The increase of the anhydrite saturation index with production time agrees with the increase of calcite supersaturation. This means that the wells with an anhydrite saturation index close to -0.3 do not precipitate calcite effectively inside the well. The anhydrite saturation index equal to -0.3, seems to correspond to the threshold whether calcite effectively precipitates or not. The dotted line (log  $K_{\text{anhydrite}} - 0.3$ ) in Figure 9 may indicate the limit of calcite scaling. According to this criterion, calcite scaling in GH-10, -11 and -12 may become smaller during production and little calcite may ultimately precipitate in the wells.

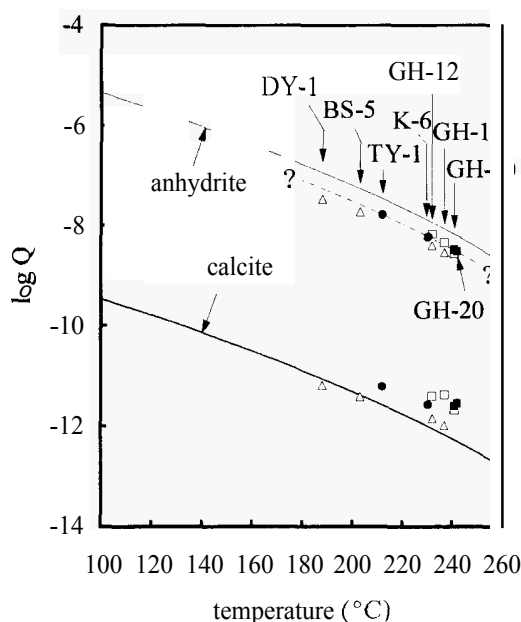


Figure 9 Relationship between activity product (log Q) versus reservoir temperature. Symbols are as in Figure 2.

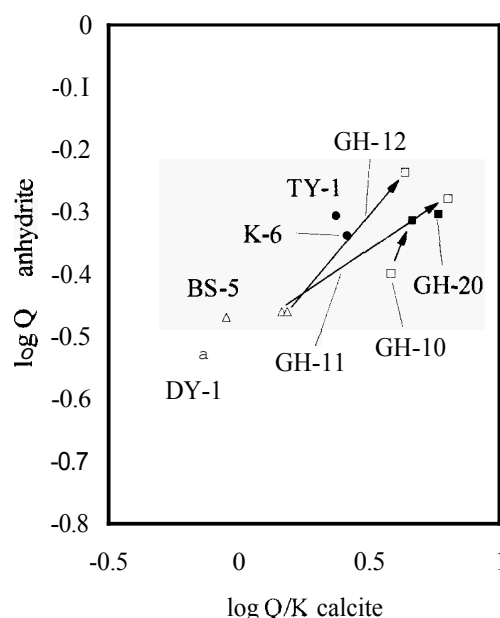


Figure 10 Relationships between activity product and solution product ratios (log Q/K) of calcite and anhydrite. Symbols and arrows are as in Figure 3.

#### 4. CONCLUSIONS

Both calcite-scaled wells and non-scaled wells exist at the Oguni geothermal field and its vicinity. The chemical compositions of all pre-flashed waters exhibit no a significant difference. The measured reservoir temperature at the Oguni field and its vicinity, ranges from 188 to 242 °C. Calcite obviously precipitates in the low temperature wells (<210 °C).

The most important factor on calcite saturation at the Oguni geothermal field seems to be the degree of steam loss in addition to the reservoir temperature. The magnitude of calcite supersaturation is strongly affected by CO<sub>2</sub> loss. The calcite saturation index of pre-flashed water increases with steam loss in the reservoir. The anhydrite saturation index, however, is little affected by steam loss. The increase of anhydrite saturation index with production time correlates with the increase of calcite supersaturation. The field observations of calcite scaling suggest that pre-flashed waters, whose anhydrite saturation indices are greater than approximately -0.3, may precipitate no calcite at the Oguni geothermal field. The anhydrite saturation index equal to -0.3, seems to correspond to the threshold for calcite scaling. The change in the anhydrite saturation index with production time may be empirically used as an indicator of calcite scaling at the Oguni geothermal field. Calcite scaling in GH-10, -11 and -12 may diminish with production time, and very little calcite may ultimately precipitate in the wells because the anhydrite saturation indices change from the initial values to -0.3 during production.

EPDC will inject polyacrylic acid into wells using a double tubing pipe system to inhibit calcite scale during initial exploitation. Fluids discharged from wells are routinely sampled and their aqueous speciations are also calculated periodically. The indicator proposed in this study may help EPDC to plan the proper inhibitor injection program to prevent calcite scaling. The future task is to make clear the reason why calcite does not precipitate from waters supersaturated with respect to calcite in non-scaled wells.

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