

FLUID-MINERAL EQUILIBRIA AND INJECTION IN EGS — EFFECT OF INJECTING GROUNDWATER

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ABSTRACT

Mineralization from groundwater injection augmentation in the Coso geothermal system was simulated to assess possible effects on the Coso-EGS injection well 34-9RD2. Anhydrite + dolomite or anhydrite + calcite dominate when the waters are conductively heated, while mixing produces these minerals plus a magnesium silicate. The quantities and relative proportions of the minerals are dependent on the relative rates of heating and mixing. The results of this study will be used in our ongoing petrographic and x-ray studies of injection-induced mineralization in existing wells.

INTRODUCTION

The Coso geothermal field is the site of a U.S. Dept. of Energy engineered geothermal system project (EGS; Rose et al., 2002). The goal of this project is to improve the connection between an injection and a production well on the eastern periphery of the field (Figure 1). An examination of any potential changes in permeability due to fluid-mineral interactions from the injection waters used at Coso has been undertaken in support of this program. Fluid-mineral reactions are an inevitable consequence of injecting cool water into a hot geothermal reservoir. The character of the interaction depends on the water that is injected and the difference in temperature between the injectate and the reservoir. Two compositionally distinct fluids have traditionally been used for injection, flashed reservoir fluid and condensate, although in EGS systems, low temperature groundwaters may represent an alternative source of fluid. Because the flashed reservoir fluid may contain high concentrations of silica, permeability degradation in the near well bore environment is possible. Two different approaches are commonly used to mitigate this effect. The fluid can be injected at temperatures above 150°C to avoid precipitation of amorphous silica in and around the wellbore. Alternatively the flashed fluid can be acidified with sulfuric acid to inhibit precipitation of silica. This

treatment is based on research originally performed at the Salton Sea geothermal field (Grens and Owen, 1977). Both methods are utilized at Coso. Although deposition of silica may still occur, it is more likely to be dispersed over a relatively large volume of the reservoir surrounding the well bore. Condensate, in contrast, has a very low salinity and therefore can be expected to dissolve minerals within the reservoir rock. It requires no treatment to be used as an injectate.

Outside sources of water have recently come into use as injectate. At The Geysers, CA, the injection of treated effluent from nearby population centers has been extremely successful (Goyal, 1999). Injection of groundwater from a low-temperature aquifer overlying the Dixie Valley geothermal system in Nevada has met with similar success (Benoit et al., 2000).

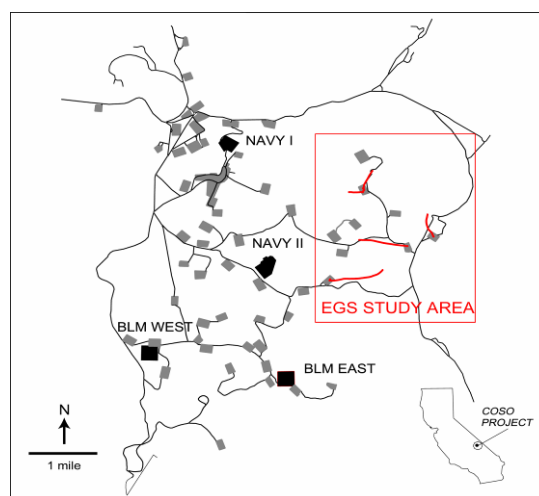


Figure 1. Location map of the Coso EGS study area.

Direct observations on the chemical reactions related to injection have been limited because reservoir rocks affected by injection are seldom sampled. Some research has been conducted on the treatment and behavior of injection waters from the Salton Sea, USA (e.g., Harrar et al., 1979), Cerro Prieto, Mexico

(Iglesias and Weres, 1981), Otake, Japan (Itoi et al., 1989) and high-temperature Icelandic geothermal systems (Gunnarsson and Arnorsson, 2003). Research specifically targeted at the injection of groundwater and low-temperature geothermal waters have been carried out by Bruton et al. (1997) and Kristmannsdottir et al. (1989).

At the Energy and Geoscience Institute, we have begun a three-pronged approach to the problem of investigating fluid-mineral interactions along the injection-production flow path. Moore and Norman are studying cuttings from a series of redrilled injection wells whose permeabilities had decreased after several years of use (unpublished proposal to DOE, 2004). Two sets of wells are from the Coso geothermal field. They expect to find and examine any evidence of mineralization or dissolution related to injection in these cuttings. Another study currently under way will examine the production fluids at Coso for evidence of changes in their chemical composition related to injection practices or treatment. The third approach uses batch reaction modeling to characterize the potential interactions of groundwater injected into the Coso geothermal reservoir. The effects of these interactions are discussed in this paper.

MODEL PARAMETERS

The initial-state composition of fluid from well 38B-9 was used as the reservoir fluid in the simulations. Water from this well was chosen because it is located on the East Flank, adjacent to the well that will be stimulated under the EGS project. The composition of the groundwater was taken from analyses of the water most likely to be used for augmentation. The compositions of these waters are listed in Table 1.

Data on aluminum concentrations in these waters were not available because specialized extraction and analysis techniques are required to measure monomeric aluminum concentrations in natural waters (Barnes, 1975). Aluminum was estimated for the simulations in this study by assuming equilibrium with reservoir minerals, in order to include aluminosilicate minerals which dominate the reservoir mineralogy. Magnesium was estimated for the reservoir water because it was below detection.

In this paper only the effects of injecting groundwater into the reservoir are considered. The effects of mixing injection fluids of different chemistries and dissolution of reservoir minerals will be considered in a future study.

The modeling program REACT, a code written by Bethke (1994) based on the speciation chemical model (Bethke, 1996) to examine the effects of injection. The default chemical database "Thermo.dat" was used, although the thermodynamic

data for quartz were modified to conform to those of Fournier and Potter (1982).

Table 1. Compositions of waters selected to simulate injection. Concentrations are in mg/kg of solution. NA=not analyzed. Nominal values of 0.1 mg/kg were used in the simulation for all species not analyzed but required for the mixing model. Concentrations are in mg/kg of solution. Compositions are given as the basis species input for the model, i.e., they are components, not actual chemical species. GROUNDWATER: the aluminum concentration was calculated assuming equilibrium with kaolinite. GEOTHERMAL WATER: the temperature was calculated from the NaKCa geothermometer of Fournier and Truesdell (1973). The aluminum and magnesium concentrations were calculated assuming equilibrium with albite, microcline, clinocllore, and muscovite. The measured calcium concentration was adjusted upward slightly by assuming equilibrium with calcite at the reservoir temperature to compensate for calcite deposition.

	Groundwater	38B-9
Temp. (°C)	20	274
pH	7.43	5.6
Al ⁺⁺⁺	0.003	0.0763
B(OH) ₃	NA	420
Ca ⁺⁺	97.5	30.3
Cl ⁻	67	2990
F ⁻	0.15	2.03
HCO ₃ ⁻	343	5400
HS ⁻	NA	42
K ⁺	8.66	333
Li ⁺	NA	11.3
Mg ⁺⁺	37.6	0.138
Na ⁺	136	1700
SO ₄ ⁻⁻	336	15
SiO ₂	5	612
CH ₄	NA	0.039

The composition of the water chosen to represent the reservoir fluid prior to injection was based on analyses of steam and liquid samples collected within minutes of each other shortly after initial well testing. Comparison of the total enthalpy of the well discharge with the adiabatic quartz geothermometer (Fournier and Potter, 1982) indicate that the well discharge contained no excess steam at the time of

sampling. Recombination of the steam and liquid into a reservoir fluid was accomplished by numerically reacting the gas sample with the liquid at their respective fractions, and then increasing the temperature to that of the NaKCa geothermometer (Fournier and Truesdell, 1973). As a quality check, the ion ratios of the restored reservoir fluid were examined on activity diagrams using the REACT thermodynamic database (Fig. 2). This comparison showed that the fluid plotted near the invariant point of albite, microcline, and muscovite; minerals that are present in the reservoir rocks. Another simulation was run in which the fluid was saturated with calcite, which moved the activity ratios nearly coincident with the invariant point (Fig. 2). At this point magnesium and aluminum concentrations were calculated on the assumption of equilibrium with the reservoir assemblage albite, microcline, muscovite, clinocllore (14A), calcite, and quartz. A similar procedure was followed for the groundwater sample. In all cases, the aluminum concentrations were close to those measured in Dixie Valley waters by Bruton et al. (1997) using the extraction technique of Trujillo et al. (1987).

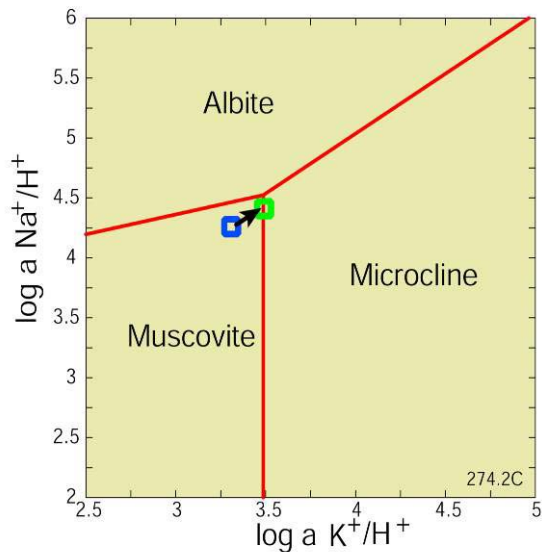


Figure 2. Activity diagram showing the reservoir composition of water from the East Flank of the Coso geothermal system. The square shows the position of recombined steam and liquid from well 34B-9 at a temperature of 274°C; the arrow and circle show the effect of saturating the fluid with calcite.

Precipitation can be handled in three different ways by the software. The first is to suppress all precipitation. This approach defines the saturation state of all of the minerals, irrespective of whether they are stable or metastable. Precipitation can be allowed with no back-reaction, which will calculate

the mineral assemblage without modifying the input fluid composition. This is a fictitious state since precipitation along the flow path would always modify the fluid composition, but it is a useful view because it compensates for the effect of delayed precipitation. For example, failure of quartz to precipitate early in the mixing process can allow magnesium silicates to form as mixing proceeds. This could occur due to kinetic inhibition or lack of nucleation.

Allowing back-reaction provides a more realistic but restricted view, in which the initial precipitation can determine the final assemblage by removing components from the fluid. Both views are shown in the following discussion to provide a wider view of possible mineral assemblages.

Temperature can be controlled in the simulations by assuming a closed system or an open system. Mixing was handled two ways in the simulations. For the case of the closed system, three kilograms of reservoir fluid were added to each kilogram of injected water. The temperature was controlled by the heat capacities of the waters. The open system only refers to conductive heat transfer, which was allowed in the open case. In this simulation one kilogram of reservoir water was added to each kilogram of injected water. The temperature and mixing fraction were a function of the final temperature, which was specified by the NaKCa geothermometer temperature of the reservoir water (274°C). The difference between the open and closed system models is illustrated in the mixing diagram in Figure 3.

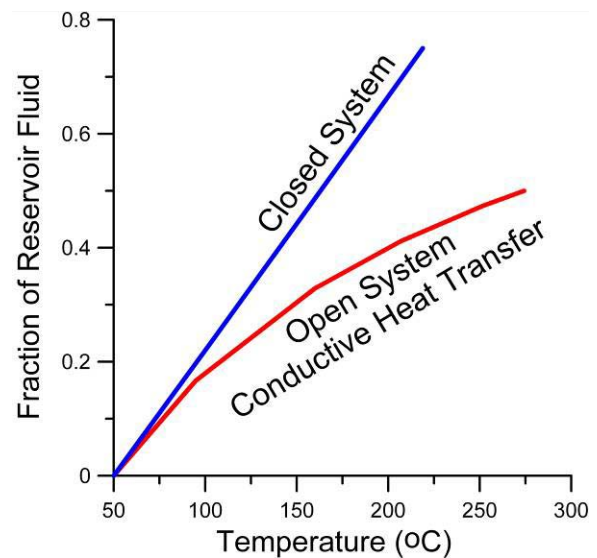


Figure 3. Temperature versus mixing fraction for the open and closed system scenarios used in the simulations. The temperatures shown apply only to a 50°C injectate temperature.

RESULTS

The output of the simulations are displayed in Figures 4 through 9 as temperature versus the saturation index, $\log(Q/K)$, or the mass (in mg) of mineral precipitated. The quotient Q/K is equal to the actual concentrations divided by those expected at equilibrium. All reference to saturation in the discussion below refers to $\log(Q/K)$. The mass of mineral precipitated is normalized to one kilogram of injectate, although minerals are in fact precipitated from a mass greater than one kilogram due to mixing.

DISCUSSION

Conductive Heating.

Waters injected into geothermal systems are heated in the reservoir to some extent prior to mixing. Simulations were run in which the waters were conductively heated to 300°C to examine this effect, although it is doubtful that this temperature would be attained without mixing in the reservoir. The simulations were run with all three precipitation options. The results clearly reflect the high magnesium and calcium of groundwater. Figures 4a and 4b show the saturation states of some magnesium and calcium minerals as the water is heated. The minerals shown are either those that are present in veins within the reservoir rocks (Adams et al., 2000; Echols, 1990; Kovac et al., 2004) or have been shown to precipitate from dilute, low-temperature, conductively-heated water (Kristmannsdottir et al., 1989). These minerals are primarily carbonates and magnesium silicates. Some aluminosilicates such as saponite are also shown in figures 4a and b, although their saturation state depends on the estimated, and extremely low, concentration of aluminum. Estimation of aluminosilicate mineral saturation states also suffers from the quality of thermodynamic data for clay minerals, which is poor.

Calcite and dolomite are saturated before they are even injected, as is expected for typical groundwaters. Most of the aluminosilicates and Mg-carbonates such as huntite and magnesite reach saturation relatively quickly, at temperatures between 50° and 75°C. Sulfate minerals such as anhydrite become saturated at temperatures of 100° to 150°C.

The predicted mineral assemblage changes with the fluid composition as minerals are allowed to precipitate. Figure 5a shows the mineral precipitation sequence that develops when back-reaction with previously precipitated minerals is allowed. Dolomite dominates up to 125°C, at which point anhydrite rapidly deposits until it nearly equals dolomite at 200°C. The same simulation with suppression of dolomite, which is generally considered to be kinetically inhibited, is shown in figure 5b. In this scenario anhydrite becomes more significant as a precipitate. In addition, magnesium precipitates

primarily as silicate minerals. This precipitation is relatively minor, but would be more significant if silica concentrations were higher due to dissolution of silica. The silica could come from reservoir quartz or injection-derived amorphous silica deposited from acidified brine.

Figure 6a illustrates precipitation for the case where there is no back-reaction. The sequence and quantities are not significantly different from the previous simulations. However, where dolomite is suppressed, the early precipitation of calcite robs the anhydrite of calcium, leading to significant calcite and minor anhydrite deposition, rather than to equal amounts of both (Fig. 6b). Thus, allowing back-reactions to occur can have a considerable effect on the shape of the mineralization curves because precipitated minerals are removed from the system as the temperature is increased along the flow path.

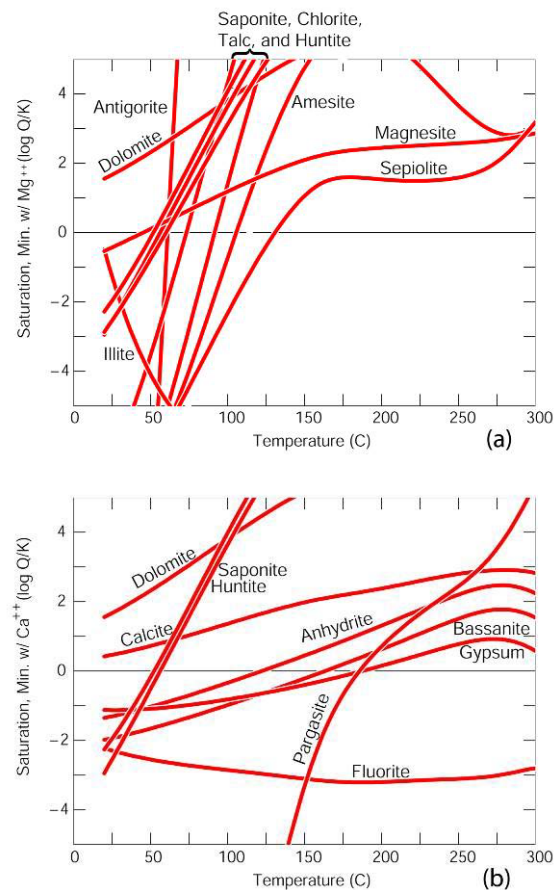


Figure 4. Coso groundwater conductively heating with precipitation suppressed to show possible (a) magnesium and (b) calcium phases.

Mixing

Mixing was simulated by incrementally combining reservoir water from 38B-9 with groundwater. A precipitation lag time, i.e., time for nucleation or conductive heating in the wellbore, was provided by

heating the injection waters to 20°, 50°, or 100°C prior to mixing. No precipitation was allowed to occur during this initial heating period. The simulations were run with all possible combinations in which back-reaction was allowed or disallowed, the system was open or closed to heat transfer, and initial heating varied from 20 to 100°C. Only a small number of the most relevant simulations are shown here due to space limitations.

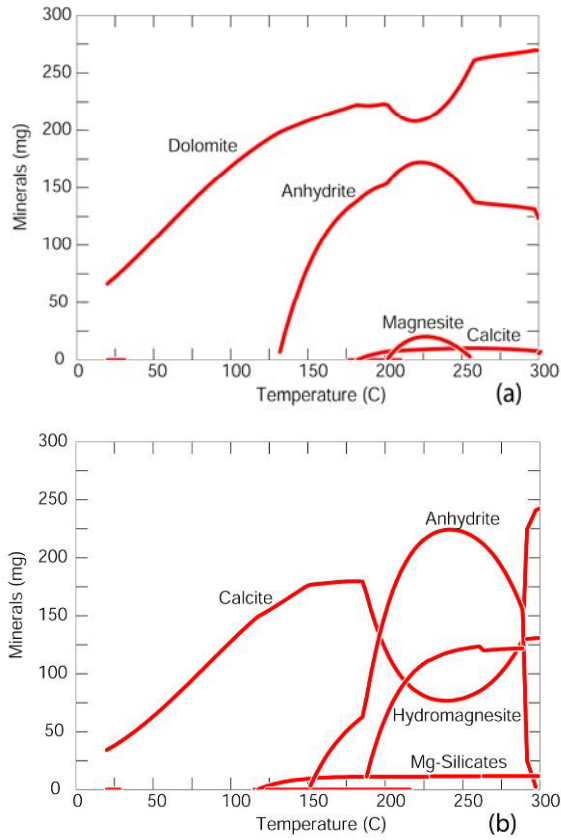


Figure 5. (a) Conductive heating of groundwater in which back-reaction with previously precipitated minerals is allowed and (b) an identical simulation in which precipitation of dolomite is suppressed.

The simulations demonstrate that the combined effects of temperature and mixing fraction are the dominant controls on the sequence of mineral precipitation. For example, consider the effect of changing the temperature of the groundwater. Although the minerals precipitated remain the same, their relative masses change considerably when the injection temperature is varied from 20° to 100°C (Fig. 7a-c). The minerals that precipitate upon mixing are mainly anhydrite, calcite, and/or dolomite. Silica as quartz is a major precipitate in the simulations. This occurs despite the fact that quartz is not oversaturated in either of the end-member waters.

However, because quartz oversaturation never exceeds 0.2, quartz may never actually precipitate.

The greatest quantity of precipitate is predicted under low permeability conditions (ignoring quartz). This condition was simulated by allowing conductive heat transfer and limiting the mixing to equal masses of injectate and reservoir water. Figure 8a shows the sequence of minerals precipitated under these conditions. The groundwater was first conductively heated to 100°C, at which point precipitation was allowed and dolomite precipitated.

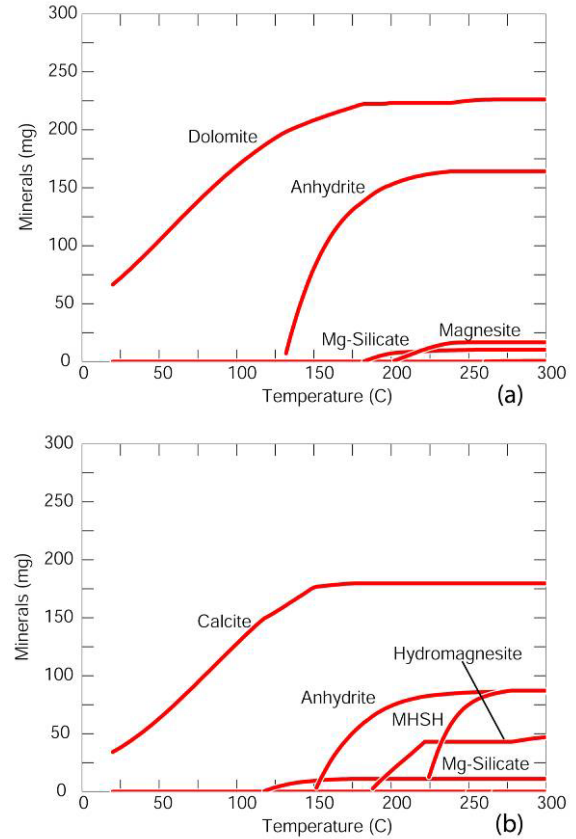


Figure 6. (a) Conductive heating of groundwater in which back-reaction with previously precipitated minerals is not allowed and (b) an identical simulation in which precipitation of dolomite is suppressed. Note that dissolution of a silica phase would prevent the formation of MSH, which is not known to form in geothermal systems.

As temperature rises and reservoir water mixes with groundwater, quartz becomes briefly saturated from 120° to 160°C. At 160°C a Mg-silicate (modeled thermodynamically as talc) replaces quartz as the stable silicate. Anhydrite also reaches saturation around 160°C and becomes the dominant precipitate by 230°C. At this temperature calcite becomes saturated and the quantity of calcite precipitated

progressively increases until it is equal to anhydrite at the reservoir temperature of 274°C. A similar sequence in which back-reaction was not allowed is shown in figure 8b. Because the dolomite and quartz that were initially precipitated do not redissolve, the amounts of anhydrite, calcite, and talc that are subsequently deposited are lower.

Simulating a high permeability environment yields the least precipitate, again assuming that silica precipitation as quartz is inhibited. This situation was simulated using a system that is closed to heat transfer and a 3:1 ratio of injectate to reservoir fluid, i.e., a higher water/rock ratio. Under these conditions, the simulations predict that dolomite will be the first mineral to precipitate, replaced by anhydrite and Mg-silicate (talc) from 160°C to 230°C (Fig. 9a). The final temperature is dictated by the temperatures of the mixing end-members. The simulation predicts that the amount of quartz deposited will be as much as three times the mass of other minerals, but as Log (Q/K) only reaches 0.2 it is problematic if quartz will actually precipitate. Altering the simulation so that back-reaction is not allowed yields similar results, except that the masses of quartz and dolomite increase and anhydrite and talc decrease (Fig. 9b).

SUMMARY AND CONCLUSIONS

The simulations in this study bring up issues that can be addressed by other techniques. For example, a petrographic and X-ray diffraction study of cuttings from a redrill of an injection well that was used for groundwater injection could reveal whether carbonates or silicates are dominant as magnesium precipitates. The identity of the magnesium minerals could also be ascertained as well. This would be of great value in showing whether dolomite, calcite, or some other carbonate dominates. Dolomite is known to be kinetically inhibited by the presence of sulfate ions at low temperatures. Since both magnesium and sulfate are present in low-temperature waters, high-magnesium calcite may form instead of dolomite.

As shown by comparing (a) and (b) in figures 5 and 6, the inhibition of dolomite will increase the amount of magnesium available for silicate deposition. Although not commonly thought of as a geothermal mineral, dolomite has been found in geothermal reservoirs in The Philippines at temperatures of up to 175°C. Ferroan dolomite has been found within shallow veins encountered in core hole TCH 74-18 (Echols, 1990). The high magnesium contents of the vein minerals and the presence of smectite in the wall rocks indicates that these veins were precipitated by low-temperature waters as they were heated. These petrologic studies of injection wells are currently underway at the Energy and Geoscience Institute by Moore and Norman.

Precipitation of silica is another issue brought up by the simulations. As we have noted, log (K/Q) never

exceeds 0.2. for the mixture of groundwater and reservoir water used in the simulations. If silica does not precipitate as a pure phase, more is available for the deposition of magnesium silicates. If silica does deposit as a pure phase, identification of the polymorph or polymorphs would help refine the simulations.

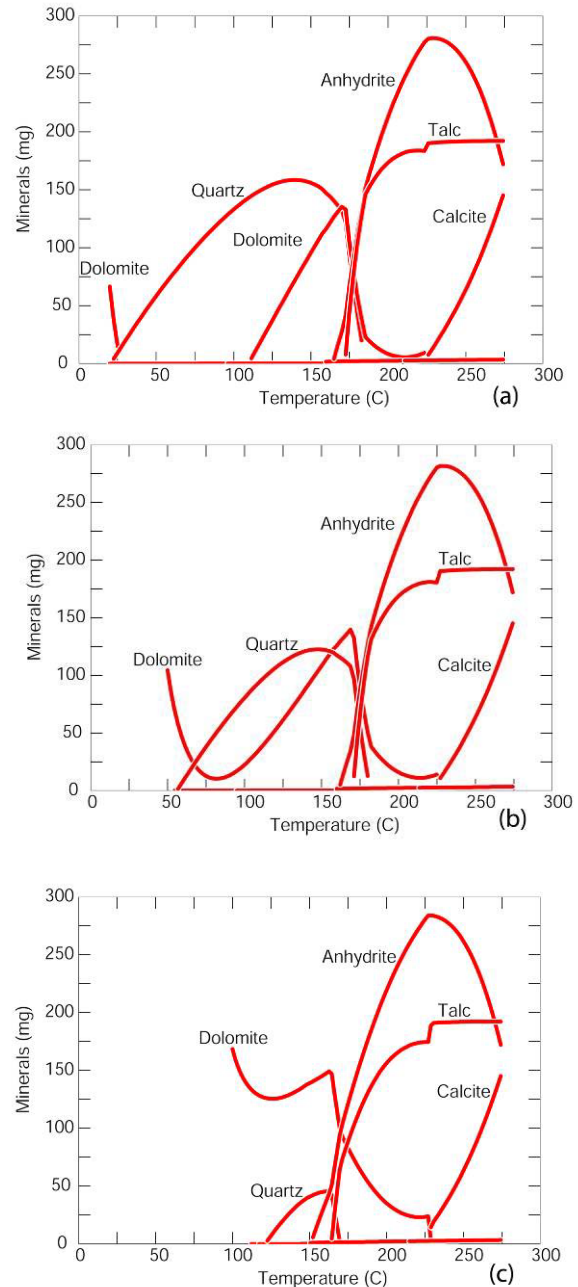


Figure 7. Variation in the temperature at which mixing starts after conductive heating (with no precipitation). (a) 20°C, (b) 50°C, and (c) 100°C.

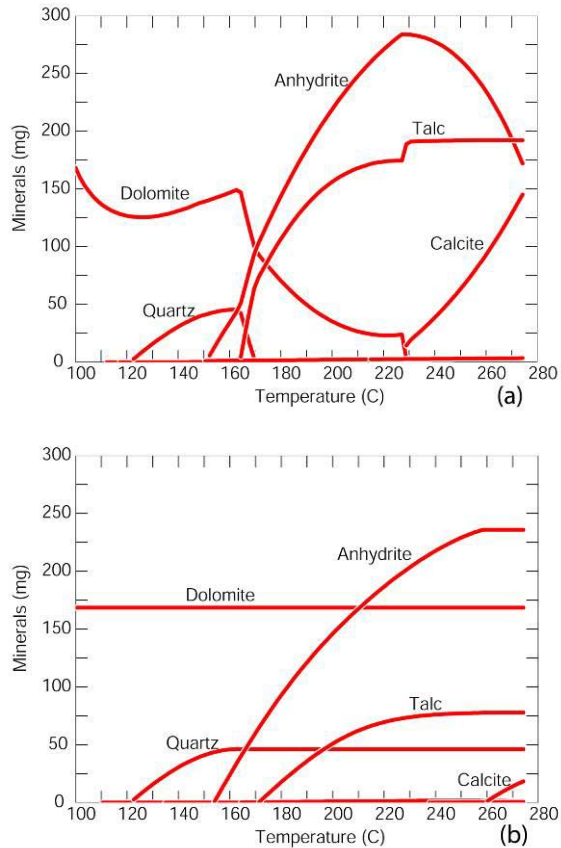


Figure 8. Simulation of injection into low permeability area. Simulation includes small amount of mixing (1:1) and conductive heat transfer (see fig. 3). (a) Back-reaction is allowed. (b) Back-reaction is disallowed.

The simulations also show the relevance of the previous history of the injection well. The length of time an injection well is in service will affect the temperature of the flow path, resulting in different amounts of heating before mixing. As previously discussed and shown in figures (6a-c), this can change the composition of the precipitated mineral assemblages and mineral ratios. The type of fluid that was previously injected can also have an effect on the behavior of injection induced mineralization. For example, if amorphous silica was deposited from injectate consisting of flashed brine, silica will be readily available for dissolution and reprecipitation as a magnesium silicate during subsequent injection and heating of silica deficient groundwater. The deposition of silica may be further confounded by acidification of the injectate. In addition to delaying the precipitation of amorphous silica by interfering with polymerization, acidification may progressively

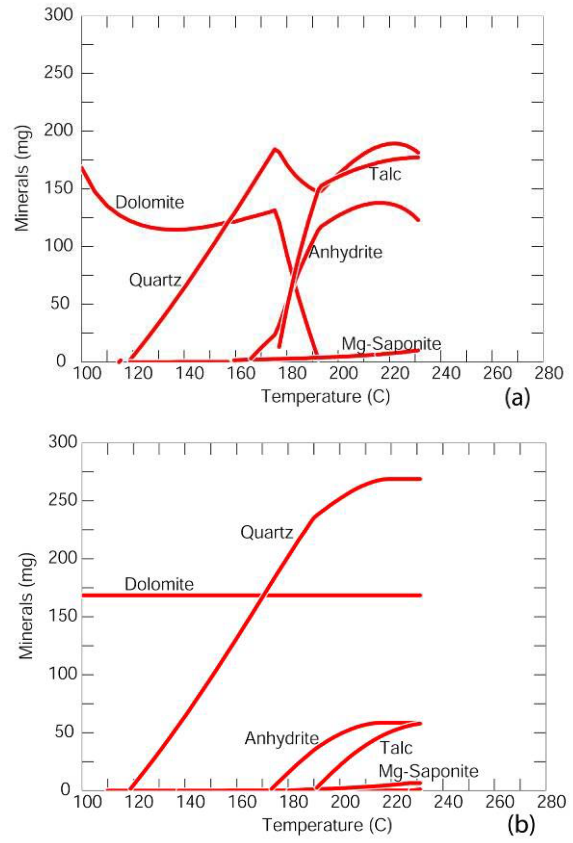


Figure 9. Simulation of injection into high permeability area. Simulation includes large amount of mixing (3:1, reservoir to injectate) and no conductive heat transfer (see fig. 3). (a) Back-reaction is allowed. (b) Back-reaction is not allowed.

lower the buffering capacity through reactions with vein carbonate minerals and the wall rocks. This may have the effect of maintaining the low pH and delaying silica precipitation, allowing the silica deposition to move further from the well bore.

Further simulations will be conducted for this study. One of the topics will be the benefits of alternating condensate, acid brine, and groundwater injection compositions in injection wells to minimize the persistence of scale.

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