EXPERIMENTAL AND MODELLING STUDY OF CAUSTIC-DOSED BRINE/ROCK INTERACTION

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ABSTRACT

A laboratory experimental simulation and geochemical modelling study of the re-injection of caustic-dosed brine into diorite have been performed.

The experimental simulation (at 150°C) used a one-pass, continuous-flow, fluid-rock interaction apparatus. The experimental fluid was caustic-dosed re-injection brine and the rock material was crushed, sieved and cleaned diorite. At 150°C, the behaviour of SiO_2, Ca and Al were indicative of precipitation of a Ca-aluminosilicate mineral, likely a zeolite or clay. SEM-EDS examination of the run products showed dissolution of the primary minerals. Precipitated phases were a Ca-aluminosilicate, conjectured to be a zeolite but could also be a Ca-rich clay mineral, and calcite.

Eight geochemical software models were performed simulating interaction between re-injection brine and bypass fluid both with and without caustic dosing. Fluid-rock interaction with the various fluid compositions results in increases in rock mass due to precipitation of secondary phases including quartz, K-feldspar, muscovite, zeolite, clay and calcite. In three of the models, where amorphous silica was assumed to be the stable polymorph, mineral precipitation ceased at high water/rock ratio.

The experimental results provide information on fluid/rock interactions during the initial stages of re-injection while the modelling provides information on the longer term effects of these interactions. In the case of three of the geochemical models, it is possible that fracture permeability will remain open and caustic dosing may be at least partially effective.

1. INTRODUCTION

The chemical treatment of geothermal brines to prevent mineral scaling is a common industrial process utilised at modern geothermal power stations (Gallup, 2009). Anti-scalants are used to prevent calcite precipitation in production wells (Moya et al., 2005). Acid dosing is used to slow down quartz precipitation kinetics in plant and in re-injection aquifers (Gallup, 2011a, b). A further possibility is the dosing of brine with caustic soda to maintain high silica polymorph solubilities (Erstich et al., 2012), however, the effect of high pH on the saturation state of other minerals is poorly constrained. This contribution reports results from: 1) an experimental study simulating the interaction between caustic-dosed re-injection brine and a diorite aquifer and 2) geochemical modeling simulating the interaction between both untreated and treated re-injection brine and plant bypass fluid with a hypothetical diorite. The results from both approaches are interpreted in terms of their relevance to a real injection scenario both in the short and long term.

2. EXPERIMENTAL SIMULATION OF BRINE-DIORITE INTERACTION

2.1 Experimental Method

A high temperature-pressure apparatus (Figure 1) was used to simulate brine-diorite interaction with a continuously-flowing fluid. Continuous flow is achieved in the system by a computer-controlled double-piston pump with a flow rate range of 0.001 – 15 ml/min. The pump injects distilled water into a titanium separator containing a movable diaphragm. The brine is contained above the diaphragm. As the pump injects distilled water below the diaphragm, this forces the experimental fluid through the pressure vessel. This set-up allows corrosive and/or saline fluids to be used without damage to the pump. The diorite is contained in a titanium pressure vessel that is externally-heated in an insulated oven. Temperature is monitored by a thermocouple inserted in the top of the pressure vessel. The pore fluid pressure is maintained by a digitally-controlled back pressure regulator. The exit valve and effluent path were continuously heated to approximately 160°C using heating tape. All components wetted by the pore fluid are composed of titanium except for the Teflon diaphragm in the back pressure regulator. The sample was collected in a standard luer lock disposable syringe. A computer is connected to the equipment and regularly records pressure, temperature and pumped volume.

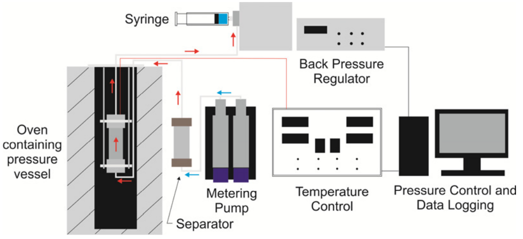

Figure 1: Schematic diagram of the one-pass, continuous-flow, fluid-rock interaction apparatus. Blue arrows show the flow path of distilled water and red arrows show the path of the experimental fluid.

The diorite is holocrystalline with crystal sizes up to several millimetres. The major mineral phases include subhedral to euhedral oligoclase (~50%), interstitial hornblende (~30%) and magnetite (~5%). Less abundant phases include titanite, apatite and quartz. The rock was coarsely-crushed and sieved to extract the 0.5 – 2 mm size fraction. This was cleaned using an ultrasonic bath and then repeatedly rinsed with distilled water. The rock particles were dried at 40°C and then packed into the pressure vessel (Figure 1). The weight of rock particles in the pressure vessel was 26.99 g.

The experimental fluid used in the simulation was separated geothermal brine from a New Zealand power station dosed using 1 molal NaOH solution.

Fluid sampling was carried out at regular intervals, typically every 24 hours for a flow rate of 1 ml/hr. At each sampling time, 10 ml of effluent was collected and acidified with two drops of concentrated ultrapure nitric acid for analysis of cations and two (2) ml of un-acidified effluent for analysis of anions. The quench pH was measured immediately upon sampling using the remaining effluent with a pH meter calibrated using standard pH buffers.

During the experiment, fluid flow was initiated at room temperature (~20°C) and maintained for one week after which the temperature was increased to 150°C (Figure 2). This was done in order to observe the shift in fluid composition in response to temperature change. The flow rate during this period was 1 ml/hr. A change in flow rate, from 1 ml/hr to 0.5 ml/hr, was made at 28 days in order to observe any changes in fluid composition due to longer residence time and hence an indicator of steady state versus chemical equilibrium. If the fluid is not at equilibrium with the rock minerals, steady state concentration will change depending on the flow rate.

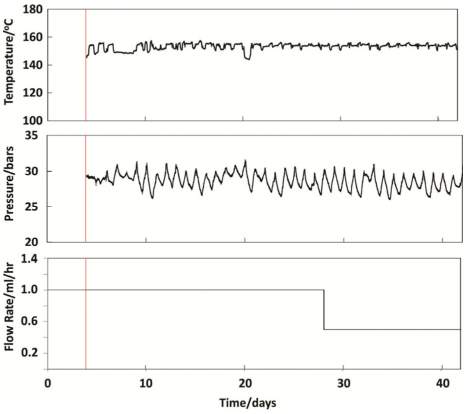

Figure 2: Temperature, pressure and flow rate of fluid-rock interaction simulation. Vertical red line represents time of temperature shift from 25°C (data logging started at this point). For the remainder of the simulation, the median temperature was 153°C and median pressure was 29 bar.

At the end of the experiment (after 42 days), the oven was turned off and flow was discontinued. Pressure was maintained by closing the exit valve of the pressure vessel. The vessel was cooled to room temperature using a stream of compressed air. This process took approximately two hours over which time the pressure was also allowed to decrease. The small volume of pore fluid in the pressure vessel during quenching is unlikely to cause precipitation of any significant amount of secondary phases when compared with the total flux over the whole experimental time. Upon opening of the pressure vessel, the rock grains were removed and placed on absorbent paper. The grains were rinsed with distilled water to remove any soluble salts that precipitated during quenching. The reacted grains were divided into five portions based on their position in the pressure vessel.

2.2 Analytical Methods

Effluents were analysed for Li, Na, K, Mg, Ca, Sr, Mn, Fe, As, Al, B and Si with inductively coupled plasma-optical emission spectroscopy (ICP-OES); F, Cl, Br and SO_4 with ion chromatography (IC). Detection limits vary between elements: Li, 0.01; Na, 0.8; K, 0.9; Mg, 0.01; Ca, 0.05; Sr, 0.003; Mn, 0.007; Fe, 0.08; As, 0.015; Al, 0.15; B, 0.3; Si, 0.6; F, 0.03; Cl, 0.04; Br, 0.1 and SO_4, 0.1 (mg/kg). Sample results are shown in Figure 3. The results are plotted at the time of sampling and thus represent the average concentration between sampling points. Scanning electron microscopy (SEM) using energy dispersive spectroscopy (EDS) was used to characterise the mineral/chemical composition of the diorite and its run products.

2.3 Results

2.3.1 Effluent Chemistry

Figure 3 shows water chemistry results for selected elements in the treated and untreated brine as well as for the output solutions collected during the experiment. The pH value of the untreated brine is 4.18 reflecting the acid dosing of this fluid at the power station. This also explains the high sulphate concentration (124 mg/kg) of the starting brine. After caustic dosing with NaOH solution in the laboratory, the brine's pH is increased to 10.15. The caustic dosing also elevates the Na concentration by 100 mg/kg to 717 mg/kg. Other solutes decrease slightly reflecting dilution by the NaOH solution. The starting brine contains no detectable H_2S.

Effluent compositions from the experiment show the response of the fluid to reaction with the diorite. For the first four days, fluid was passed through the diorite at 25°C at a rate of 1 ml/hr. During this period, the pH remained at ~10.14 indicating that there was minimal fluid-rock interaction. Elements that behave conservatively include B, Li, K, Na, and Cl. Other elements demonstrate measurable changes due to fluid-rock interaction. Sulphate concentration increased relative to the starting caustic-dosed brine composition due to anhydrite dissolution. Aluminium decreased slightly presumably due to mineral precipitation. Calcium concentration increased to a maximum of 20 mg/kg again reflecting anhydrite dissolution. SiO_2 concentration is only about 200 mg/kg during the first four days. This is low relative to the starting brine composition of 1089 mg/kg. This is explained by the filtering out of silica polymers by the back pressure regulator leaving only monomeric silica. This is not a result of fluid-rock interaction and is an experimental artefact.

After the temperature shift to ~150°C at Day 4 (vertical red line in Figure 3), the pH increased slightly and then dropped to a minimum of 9.7 after which it rose to a steady value of about 9.9. B, Li, K, Na and Cl remained conservative through the remainder of the experiment. Sulphate concentration rose sharply to 284 mg/kg and then declined to a steady value of ~115 mg/kg. The sharp increase in sulphate after the temperature increase is attributed to the dissolution of anhydrite. Without CO_2 analyses it is not possible to confirm whether calcite was in equilibrium with the fluid (calcite was not reported in the petrographic analysis of the original diorite). Mineral saturation indices for anhydrite show that this mineral remained under-saturated throughout the experiment so it could respond kinetically to a temperature increase. Calcium shows similar behaviour reaching a maximum one day after the temperature shift and then declining rapidly to near detection limit within ten days. Aluminium concentration responds similarly; however, peak Al concentration is not reached until eight days after the temperature shift. Aluminium concentration then declines to near detection limit concentrations.

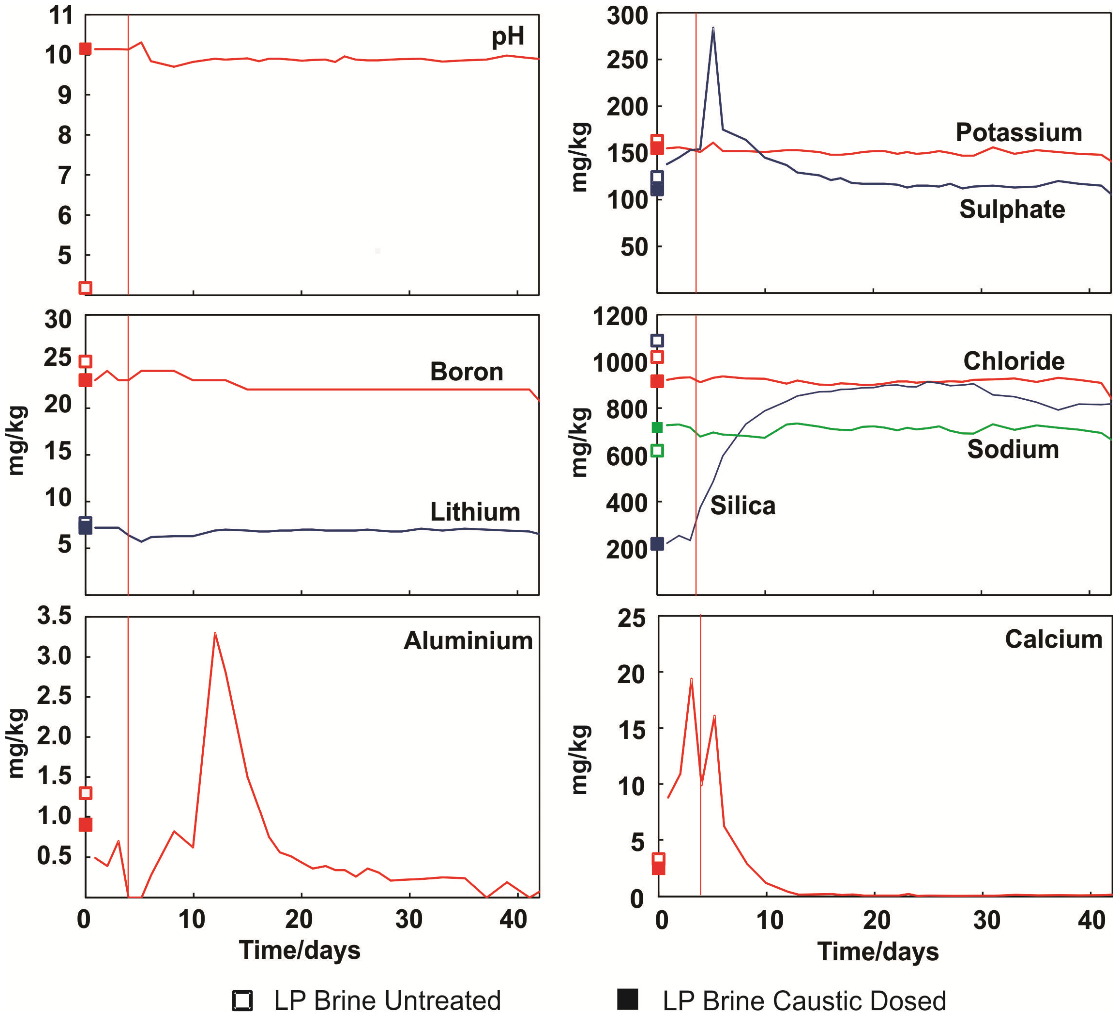

Figure 3: Chemical composition of brine (untreated and caustic-dosed) and effluent samples from the flow-through simulation. Vertical red line shows the time of the temperature shift from 25°C to 150°C.

At five days, silica concentration is much lower (375 mg/kg) than the input brine (1089 mg/kg). This is followed by a gradual increase to ~900 mg/kg by about 12 days. The explanation for the gradual increase is uncertain but could also be an experimental artefact caused by filtering of silica polymers by the rock and/or the back pressure regulator. The apparent loss of silica from the fluid over the first 12 days is not attributable to silica polymorph precipitation because of the large losses involved and yet no secondary silica polymorph was observed (see below).

Silica concentration drops slightly (to ~820 mg/kg) after the decrease in flow rate to 0.5 ml/hr at 31 days. The input brine silica concentration is 1,089 mg/kg thus there is a net loss of silica during fluid-rock interaction.

The relationship between components can point towards possible fluid-mineral interactions. Both Ca and SO_4 reach their highest concentrations (after the temperature shift) at the same time, suggesting an anhydrite control on their concentrations. CO_2 analyses are unavailable but it is likely that calcite would have saturated quite rapidly thereby contributing another source of Ca. There is a somewhat antithetic relationship between Al and SiO_2 however, this only becomes apparent post-12 days. It is during the early period before 12 days that Ca reaches its maximum. This is strong evidence for the delayed initiation of the precipitation of a Ca aluminosilicate phase which then rapidly brings Al and Ca concentrations down to low levels. We believe the rate of change for the non-conservative element concentrations to be gradual because there is considerable surface area of rock to react with relative to the instantaneous fluid/rock ratio.

2.3.2 SEM Examination

SEM-EDS analysis was performed at Auckland University School of Engineering. Figure 4 shows SEM photomicrographs of reacted diorite. The rock fragments are covered with well-formed rosettes about 8 µm in diameter of a platy phase (Figure 4a, b, c, d). EDS analysis of this phase was difficult because the rosettes are small and the platelets are partially transparent to the electron beam. The best results are obtained from analyses of rosettes on quartz. These show that the phase is a Ca-aluminosilicate. Without a diagnostic crystal form or micro X-ray diffraction, it is impossible to be certain what mineral this is (if it is indeed a naturally occurring phase) but based on the chemistry, the temperature of the experiment and the crystal form, the most likely candidate would be a zeolite; however, a Ca-rich clay mineral cannot be ruled out. The Ca-aluminosilicate phase does not discriminate on substrate and can be found on all original minerals including hornblende, oligoclase, quartz, and magnetite.

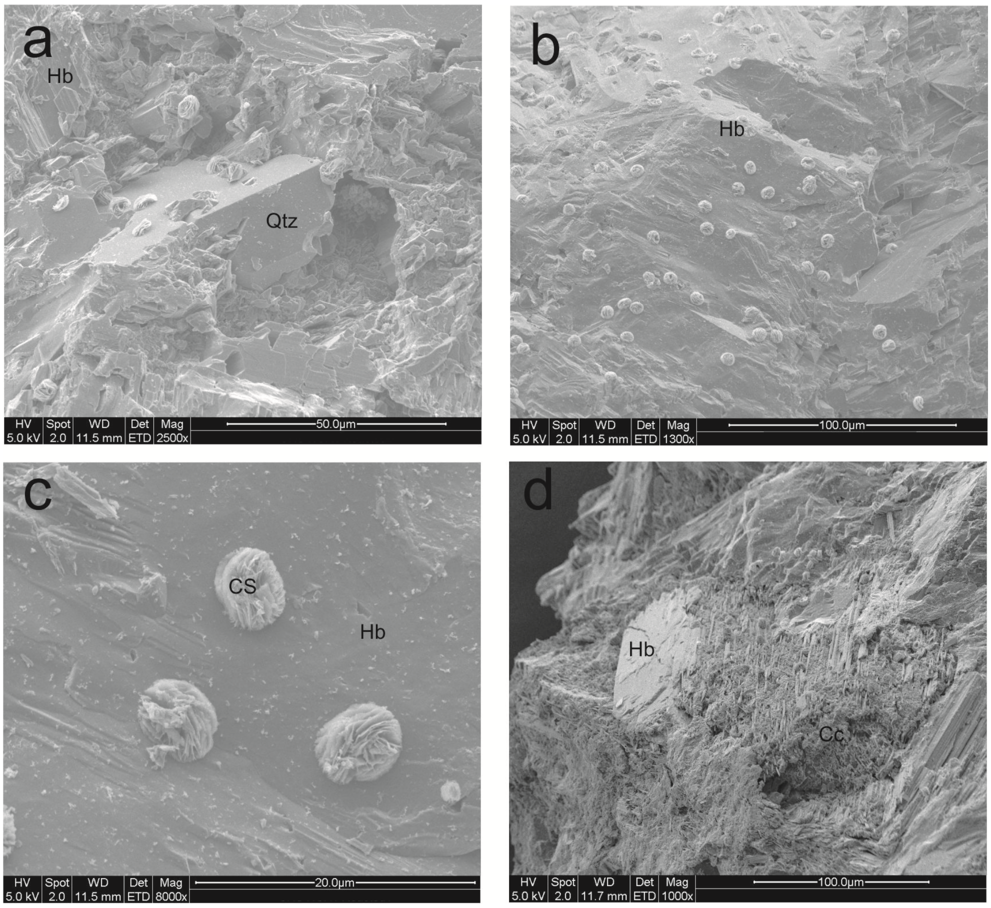

Figure 4: SEM photomicrographs of reacted diorite: a) quartz (Qtz) with associated rosettes of the Ca-silicate phase; b) and c) rosettes of the Ca-silicate phase on hornblende; d) highly altered hornblende crystal that has been converted to calcite and the Ca-silicate phase.

Figure 4a shows the Ca-aluminosilicate on quartz. The quartz is euhedral and could be newly precipitated during the experiment. Quartz in the original rock was interstitial and would unlikely be euhedral; however, there is the possibility that what is observed in SEM is vein quartz and not precipitated in the experiment. Nevertheless, it is enticing to conjecture that quartz was precipitating during the experiment. The fluid was supersaturated with respect to quartz as the pH dropped to about 9.3 on heating from room temperature to 150°C.

There is evidence of substantial alteration of hornblende. In Figure 4d a hornblende crystal shows extensive alteration and conversion to a mixture of calcite and the Ca-aluminosilicate phase. There are remnant needles of hornblende sticking up through the secondary minerals. This texture could not be derived from the original rock as these needles would be too delicate to survive the crushing and sieving of the diorite. The origin of the CO_2 to form the calcite is unknown but must have derived from the original rock as the brine was low in CO_2 (<20 mg/kg).

In summary, SEM examination shows dissolution of oligoclase and alteration of the hornblende to a mixture of calcite and Ca-silicate. The fate of the Mg and Fe released from hornblende is unknown as no other new phases were identified. It is possible that the amount released was below detection limit in the effluent. Fe may have been oxidised to form hematite but this mineral was not observed in SEM examination. There is a possibility that quartz was precipitating but this is more speculative.

3. GEOCHEMICAL MODELLING OF BRINE-DIORITE INTERACTION

3.1 Modelling Method

Geochemist's Workbench® (GWB Version 9.0) was used to model the interaction of a hypothetical rock of dioritic composition with either untreated and caustic-dosed re-injection brine, as well as, untreated and caustic-dosed bypass brine (atmospherically-flashed brine). The GWB thermodynamic database does not have any provision for solid solutions and therefore plagioclase and hornblende could not be used. Albite and anorthite at a ratio of 5:1 were employed to simulate oligoclase ($An_{10\text{-}30}$). The amphibole mineral pargasite ($NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$) was substituted for hornblende. Remaining minerals included quartz (5%), pyrite (substituting for magnetite at 5%), and anhydrite (1%). The model temperature of both reactants and fluid is 150°C.

The composition of the brine was calculated based on the chemical analysis of a real separated water and steam sample re-combined and its pH shifted to 10.5 at 25°C using GWB. The model type used is a flush model with mineral precipitation. This simulates the changes in a rock as fluid is reacted with it. The fluid is then removed and further fresh fluid is reacted. This is done in small incremental steps (1/100 total reaction progress in this model). This is the best model for the simulation of brine flowing through a reservoir rock. The volume of rock used in the simulation is 1 cm^3. This is reacted with ~12 kg of re-injection brine giving a maximum fluid rock ratio of approximately 12,000:1. Note that in a flush simulation, newly precipitated minerals remain with the original phases. They are free to react with the incoming fresh fluid.

Eight scenarios were considered (Table 1). These cover situations where re-injection brine or bypass fluids are both untreated and treated and are re-injected. Also considered is whether the stable silica polymorph that precipitates is amorphous silica or quartz.

It is important to note that because the modelling does not use any kinetic parameters, all species and minerals are necessarily in thermodynamic equilibrium at all times. The initial starting assemblage of pargasite/ plagioclase/pyrite/quartz/anhydrite is not in thermo-dynamic equilibrium with the starting fluid at 150°C and thus is converted into an assemblage of laumontite/ saponite(clay)/calcite/quartz at the beginning of the model. This may not seem realistic; however, at high water/rock ratios, it would be expected that fractures in the aquifer would be lined with similar secondary phases. These minerals would be those with which the brine is reacting.

Table 1: Eight scenarios simulating the interaction between hypothetical diorite and treated and un-treated re-injection brine and bypass fluid.

Scenario	Fluid	pH dosing	Silica Polymorph
1	Brine+Condensate	10.5	Quartz
2	Brine+Condensate	none	Quartz
3	Brine+Condensate	10.5	Am. Silica
4	Brine+Condensate	none	Am. Silica
5	Bypass	10.5	Quartz
6	Bypass	none	Quartz
7	Bypass	10.5	Am. Silica
8	Bypass	none	Am. Silica

3.2 Results

Figure 5 shows an example of a reaction path between the hypothetical diorite and caustic-dosed brine with quartz as the stable silica polymorph. During the initial kilogram of H_2O reacted only calcite and quartz are precipitated in small amounts, after which laumontite destabilises and begins to dissolve. At the same time K-feldspar begins to precipitate. There is a brief period of albite precipitation but this dissolves again as reaction progresses. A switch from Ca-bearing saponite to Na-bearing saponite occurs just below 5 kg of H_2O reacted. Although this seems unlikely in nature, it could be reflected in a gradual change in the Na:Ca ratio in a stable clay mineral phase. After 5 kg of H_2O reacted (5000:1 water/rock ratio) the only mineral precipitating is quartz and the final stable assemblage of K-feldspar/quartz/calcite/saponite is reached. The volume increase at a water/rock ratio of 5000:1 is approximately 200% while at a water/rock ratio of 12,000:1, it is ~260% (due to continued quartz precipitation).

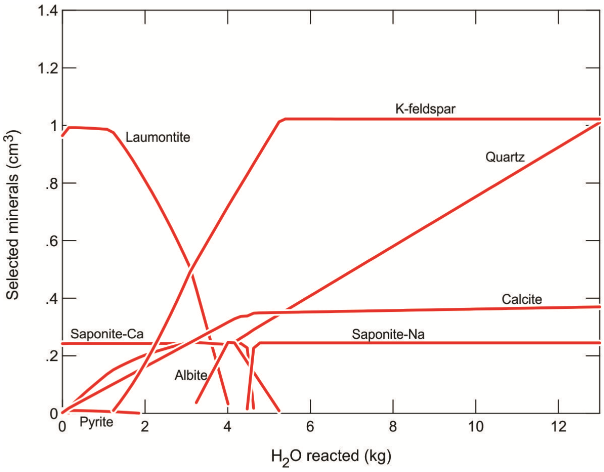

Figure 5: Modelling results for the interaction between 1 cm^3 of diorite with caustic-dosed combined brine at 150°C with quartz as the stable silica polymorph.

The modelling results of the eight scenarios listed in Table 1 show that for models where quartz is the stable silica polymorph:

1. the final stable assemblage is quartz/K-feldspar/clay ± calcite or quartz/ muscovite/clay;
2. quartz is saturated throughout because the pH is insufficiently high enough to keep it undersaturated;
3. this results in continuous volume increases due to the precipitation of quartz.

For models where amorphous silica is the stable silica polymorph with the exception of the untreated bypass fluid scenario:

1. the final stable assemblage is clinoptilolite/talc ± calcite for all models;
2. amorphous silica remains undersaturated throughout because the pH is sufficiently high to keep it in equilibrium;
3. there is considerable volume gain with increasing water/rock ratio but this ceases once the stable assemblage is reached.

For the untreated bypass fluid model with amorphous silica as the stable silica polymorph:

1. the stable assemblage is clinoptilolite/talc/ amorphous silica;
2. saturation with respect to amorphous silica is reached at a fluid/rock ratio of ~3000:1;
3. this results in continuous volume increase due to the precipitation of amorphous silica.

4. INTERPRETATION

4.1 Comparison between Experimental and Modelling Results

The experimental results provide information on what would occur during the initial stages of caustic-dosed brine re-injection. The heating of the pH 10.15 experimental brine to 150°C results in a decrease in *in situ* pH to ~9.2. At the same time the pK_1 of H_4SiO_4 decreases to about this value. This ensures that quartz is supersaturated throughout the experiment. In the geochemical models, if the brine becomes supersaturated with respect to a phase, it will directly precipitate, i.e., kinetic barriers are not considered. This contrasts with the experimental approach in which intrinsic kinetic factors are expected to be active.

In a previous experimental simulation at 150°C, using re-injection brine from a New Zealand power station, amorphous silica was observed as the sole precipitated phase in the greywacke substrate. This fluid was acid-dosed which should inhibit silica precipitation, but it was concluded that neutralisation of the acid by rock minerals resulted in an increase in pH and the precipitation of amorphous silica. Quartz was not the silica polymorph to form even though it was more highly supersaturated in the fluid. This is attributed to kinetic inhibition of quartz precipitation at such a low temperature (150°C). In the current experiment, amorphous silica was not observed. This is consistent with it being undersaturated at the high pH value involved (9.2). In this way, experimental results probably reflect the real situation more closely than the geochemical modelling, at least in the short term.

The experimental approach only simulates fluid-rock interaction at the earliest stages of re-injection as the integrated fluid-rock ratio is necessarily low in an experiment of only six weeks. It would be impractical to conduct a continuous flow fluid-rock interaction experiment for years. Geochemical modelling provides information on the longer term effects of re-injection but cannot, at least at the present, incorporate all the hydrodynamic and kinetic effects. A combination of the results from the two approaches can provide a more comprehensive interpretation.

The geochemical models show that the starting mineral assemblage of the diorite is highly out of equilibrium with both brine and bypass fluid at 150°C. Without kinetics taken into account, the result is the conversion of the starting assemblage to a more stable one consisting of secondary phases. In the experiment, SEM results show the dissolution of primary minerals and the precipitation of a Ca-aluminosilicate phase along with calcite. This Ca-aluminosilicate phase is conjectured to be a zeolite but it is also possible that it is a Ca-rich clay mineral. Nevertheless, the models predict that the stable phases at low water/rock ratio will be Ca-rich phases such as Ca-clinoptilolite, Ca-saponite and calcite. This is consistent with the experimental results. Thus, the experiment suggests that during the initial stages of re-injection of caustic-dosed brine there will be considerable dissolution of primary phases. This is due to the high pH of the fluid. As long as the pH can be maintained by the influx of fresh fluid, this process will continue. This will eventually lead to fracture networks lined with secondary phases.

As further caustic-dosed fluid passes through these fractures, armouring effects will prevent further interaction with the primary mineral phases and pH reduction will not occur. As a result the secondary minerals will become unstable and will further react with the brine to form the other secondary phases found in the models at higher water/rock ratio (in most models at about 3000:1). Note that the geochemical models assume 100% access of the fluid to 1 cm^3 of diorite, however, in reality; this access is only through fracture networks. As a result, the generation of these later secondary phases could be expected at much lower water/rock ratios (due to armouring).

4.2 Inferred Effects on Permeability

At the initial stages of caustic-dosed brine re-injection, primary mineral dissolution could increase permeability until the point that secondary mineral surface area greatly reduces the access of the fluid to the unstable primary phases. At this point, the fluid will begin to react with the secondary phases to form further alteration minerals. Eventually the secondary phases will equilibrate with the fluid and a final stable assemblage will be formed. Once the mineral assemblage equilibrates with the fluid, further mineral precipitation will occur only because the fluid is supersaturated with respect to some secondary phase. Quartz constitutes this phase in both treated and untreated models (where quartz is assumed to be the stable silica polymorph) while amorphous silica is encountered in the untreated bypass model (where amorphous silica is assumed to be the stable silica polymorph). The overall result is, however, that permeability will decrease as water/rock ratio increases. In contrast, the three other models where amorphous silica is the stable polymorph, this mineral remains undersaturated and mineral precipitation ceases at high water/rock ratio. If hydrodynamic and armouring effects are considered, caustic-dosing may be at least partially operative at maintaining permeability.

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