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A STUDY ON CHEMICAL INTERACTIONS BETWEEN WASTE FLUID, FORMATION WATER, AND HOST ROCK DURING DEEP WELL INJECTION

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Abstract

A new disposal well was drilled in the vicinity of an injection well that had been in operation for 12 years. The drilling activities provided an opportunity to assess the fate and transport of waste products injected in the nearby well, and the impact, if any, on the host geologic formation. The origin of the fluid collected while drilling the new well and the interaction between injected waste and the formation were investigated using analyses of formation waters, waste, and formation minerals, by applying traditional graphical methods and sophisticated numerical models. This approach can be used to solve a wide range of geochemical problems related to deep well injection of waste.

Trilinear Piper diagrams, Stiff diagrams, and correlation plots show that the chemical characteristics of recovered fluid at the new well are similar to those of formation water. The concentrations of most major constituents in the fluid appear diluted when compared to formation water sampled at other locations. This could be explained by mixing with waste, which is less saline than formation water. However, the waste injected near the new well consists primarily of ammonia and sulfate, and these waste constituents are not found at concentrations elevated enough to suggest that significant mixing of formation water with waste has occurred.

To determine whether chemical interactions between injected waste and formation could explain the chemistry of fluid recovered from the new well, we simulated the chemical reaction between waste, formation water, and the formation rock by numerical modeling. Initial modeling calculations were done using a multicomponent geochemical reaction-path model to simulate fresh waste reacting with the formation. A more complex simulation coupling flow, transport, and reaction was then run using a multicomponent geochemical reactive transport model. These numerical simulations were carried out to calculate porosity changes and evaluate chemical processes resulting in mineral precipitation and dissolution. The simulations indicate that the waste injected in the vicinity of the new well is mildly reactive with the formation, and that there is a small porosity increase upon injection (approximately one to two percent) in the near-wellbore region. The simulations predict the precipitation of anhydrite, ammonium clay, and ammonium feldspar minerals. However, the precipitation of these minerals is not sufficient to account for the lower-than-expected sulfate and ammonia concentrations away from the injection well. This modeling work is preliminary in nature, and provides an example of the application of sophisticated modeling tools to problems involving deep-well injection of waste.

Introduction

A new deep disposal well (NDW-1) was drilled in 1994 within 200 m of an injection well that had been in operation for 12 years (ODW-1). One of the objectives of the new drilling activities was to assess whether waste products migrated from nearby injection well ODW-1 to the location of new well NDW-1. Another objective was to evaluate the fate of injected waste products and their effects on formation water and minerals. These data would prove useful for the planning of future deep-well injection in the area.

While drilling NDW-1, fluid samples were collected at two depth intervals correlating with the injection interval at ODW-1 (approximately 2 km below the ground surface). From previous modeling analyses, it was anticipated that the fluid samples recovered at NDW-1 would be representative of waste fluids injected at ODW-1. However, after analysis, it was found that the recovered fluid did not have the main chemical characteristics of the injected waste, although some waste degradation products were detected in small concentrations.

To evaluate the origin of the fluid from NDW-1, a geochemical investigation was carried out in two phases. First, we compared chemical analyses of formation waters (prior to waste injection) with analyses of fluid recovered from NDW-1 (before injection started in this well), and with analyses of waste injected at nearby ODW-1. We then simulated the chemical interaction between injected waste fluid and the formation water and minerals, to assess whether precipitation or dissolution of mineral phases would affect the chemical composition of fluid recovered at NDW-1. Focus was given to inorganic compounds, mostly sulfate and ammonia, which were the main components of waste injected at ODW-1.

Chemical Characterization of Formation Waters prior to Waste Injection

NDW-1 was completed in the Oakville Formation (Texas Gulf Coastal Plain), which consists mainly of poorly consolidated fine-grained sand with some shale intervals. Table 1 summarizes the general chemical composition of water samples from NDW-1 and other nearby wells in the Oakville Formation prior to waste injection (i.e., formation waters). Table 2 summarizes the composition of waste injected at ODW-1. In addition to common constituents shown in Table 1, one of the samples from NDW-1 was found to contain a low concentration of a degradation product of organic constituents injected into ODW-1. For comparison, the composition of seawater (Hem, 1989) is also included in this table. Correlation plots (Figure 1), Piper diagrams (Figure 2) and Stiff diagrams (Figure 3) were used with these data to illustrate compositional differences and possible relationships between samples.

The waters from NDW-1 and ODW-4 have a significant charge imbalance (12 and 7%, respectively) (Table 1). By correcting their sodium concentrations to bring charge balance, these waters yield sodium to chloride ratios similar to those in other formation waters (Figure 1). Compared to the samples at other wells, the water from NDW-1 appears diluted, but with otherwise similar proportions of major constituents (sodium, chloride, calcium, and magnesium) (Figures 2 and 3). However, the water from NDW-1 exhibits an increased content of sulfate, potassium, and possibly bicarbonate compared to other formation waters

for which these data are available (Table 1). This difference is not visible on the Piper and Stiff diagrams because concentrations of sulfate, potassium, and bicarbonate constitute a very small fraction of the total dissolved constituents in these waters. Note that potassium and sulfate data were not available for all samples, thus leaving some margin of uncertainty regarding the concentration trends of these constituents. Besides these differences, all formation water samples, including those from NDW-1, have similar chemical compositions.

The overall dilution of chloride and major cations, and apparently higher sulfate concentrations at NDW-1, could be the result of mixing with waste. However, if all dilution resulted from waste, sulfate and ammonia concentrations at NDW-1 would be higher than those observed. Also, the elevated potassium concentration at NDW-1 cannot be explained by mixing with waste. It could result from exchange or dissolution reactions involving minerals in the formation, such as potassium-bearing clays, which are predominant in shale beds observed in core near the sampling intervals at NDW-1.

It is possible that the higher carbonate concentration at NDW-1, compared to ODW-1, reflects some degradation of organic waste constituents. Organic carbon oxidation with sulfate reduction has been reported in the literature (e.g., Kelly and Matisoff, 1985), and we have personally observed trends of sulfate concentration decrease together with carbonate concentration (alkalinity) increase beneath landfills where groundwater was impacted by leachate and/or landfill gas. The oxidation of organic waste constituents by sulfate reduction would result in the formation of sulfide, which was reported in one of the NDW-1 samples. However, more data would be needed to confirm this hypothesis.

Well Number ==>		NDW-1		ODW-1	ODW-2			ODW-3	ODW-4	ODW-5	Seawater
Sampling Depth (ft) ==>		6860'	7089'	6800'	5952'	6062'	6292'	~4500'	NA	5858'	
Sampling Year ==>		1994	1994	1977	1961	1961	1961	1981	1993	1975	
Parameter	Units										
pH (25 C assumed)	pH	7.5	8.2	7.0	7.25	7.31	7.42	6.6	6.8	6.7	7.8
Specific Gravity (15-25C)	None	1.0686	1.0735	1.095	1.096	1.095	1.095	1.0952	1.1	1.099	1.026
Density	mg/L	1.0677	1.0726	1.094	1.095	1.094	1.094	1.094	1.099	1.098	1.025
Total Dissolved Solids	mg/L	105699	107257	162818	156074	155234	155482	149100	213201	143961	34580
Chloride	mg/L	62993	66499	86200	95666	95039	95087	79300	101777	87900	19000
Sulfate	mg/L	683	633	-	-	-	-	19	235	43	2700
Sulfide (as HS)	mg/L	23	<1	-	-	-	-	<1	-	-	-
Alkalinity (total, as CaCO ₃)	mg/L	246	858	110	-	-	-	87	-	108	-
Total carbonates (as HCO ₃ ⁻)**	mg/L	150	523	134	153	193	238	53	230	132	142
Bromide	mg/L	<11	<11	-	-	-	-	-	-	-	67
Fluoride	mg/L	9	6	-	-	-	-	8.41	-	-	1.3
Ammonia (as N)	mg/L	22	17	-	-	-	-	16	-	-	-
Nitrate/Nitrite (as N)	mg/L	0.67	37	-	-	-	-	0.23	-	-	0.67
Sodium	mg/L	26715	28985	49000	54908	54836	55504	45800	51000	52136	10500
Potassium	mg/L	3623	4047	-	*	*	*	209	450	-	390
Calcium	mg/L	1923	2254	3200	3966	3878	3530	4610	3500	2920	410
Magnesium	mg/L	620	644	890	1355	1276	1163	1370	1100	830	1350
Iron	mg/L	<11	14	1.5	-	-	-	43	3	10	0.003
Manganese	mg/L	<2	<2	0.86	-	-	-	1.27	-	-	0.002
Silica (SiO ₂)	mg/L	<457	<459	13	15	16	27	30	-	-	6.4
Aluminum	mg/L	<21	24	-	-	-	-	1.9	-	-	0.001
Boron	mg/L	-	-	-	-	-	-	7.6	-	-	4.5
Barium	mg/L	-	-	22	88	82	48	52	-	-	0.02
Strontium	mg/L	-	-	-	-	-	-	236	-	-	8
Charge Imbalance	%	-12	-12	-1.2	0.2	0.2	0.2	2.6	-7.0	0.2	0.4

Table 1. Analyses of formation waters from well NDW-1 and other wells in the Oakville Formation. Compared to other wells, water from NDW-1 has a lower salinity, increased potassium, and slightly increased sulfate concentrations (see text). These data were used for Figures 1, 2, and 3. Table symbols are as follows: (-) not analyzed or reported; (*) the concentration of potassium is included in the reported sodium concentrations, and not reported independently; (**) total carbonate concentration is assumed equal to the total alkalinity as HCO₃⁻ unless a different value was specifically reported; (<) less than the concentration shown, which is the detection limit. Data compiled by R.G. Larkin Consulting. Seawater data from Hem (1989).

<u>General Parameters</u>	<u>Units</u>	
Specific gravity (25°C)	none	1.04
pH (25°C)	pH units	7.6
Total Dissolved Solids	mg/L	59000
Sulfate	mg/L	32000
Chloride	mg/L	3200
Ammonia (as total N)	mg/L	11000
Total carbonate (as HCO ₃ ⁻)	mg/L	18
Sodium	mg/L	2110
Potassium	mg/L	31
Calcium	mg/L	32
Magnesium	mg/L	15
Iron	mg/L	2.93
Manganese	mg/L	0.07
Silica (as SiO ₂)		11
Chemical Oxygen Demand	mg/L	20060
Total Organic Carbon	mg/L	13880
<u>Organic species</u>		
Organic acids	mg/L	3000
Cyanide (total)	mg/L	60
Methanol	mg/L	800
Other organics	mg/L	900

Table 2. Composite waste stream analysis (injectate in ODW-1). The total carbonate concentration was calculated by assuming equilibration of the waste fluid (excluding organics) with atmospheric carbon dioxide ($P_{CO_2}=10^{-3.5}$ bar).

<u>Formation Minerals</u>	<u>Weight %</u>
Quartz	65
Feldspars	25
Calcite	1
Dolomite (Fe-Rich)	2
Kalolinite	1.02
Chlorite	0.54
Illite/Mica	0.96
Montmorillonite (smectite)	3.48

Table 3. Composition of formation matrix assumed for simulations. Data provided by X-ray analysis and petrographic examination of recovered core from the Oakville Formation.

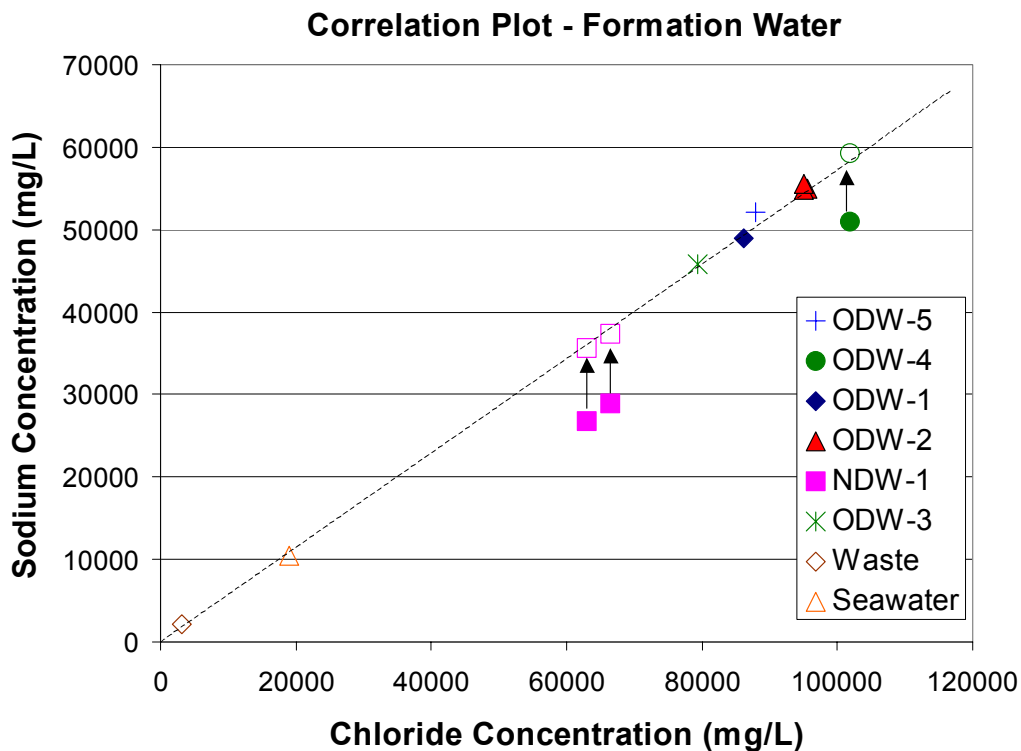


Figure 1. Correlation between sodium and chloride concentrations in Oakville Formation waters (prior to injection), fluid from NDW-1 after injection in nearby well (Table 1), liquid waste, and seawater. The dashed line represents waters with identical sodium-to-chloride ratios but various degrees of evaporative concentration (or dilution) with respect to each other. Arrows show corrections to sodium concentrations needed to bring NDW-1 and OWD-4 analyses in charge balance. After such correction, these waters exhibit a sodium-to-chloride ratio similar to that in other formation waters, supporting a similar origin. Waters from NDW-1 are the most diluted compared to other formation waters.

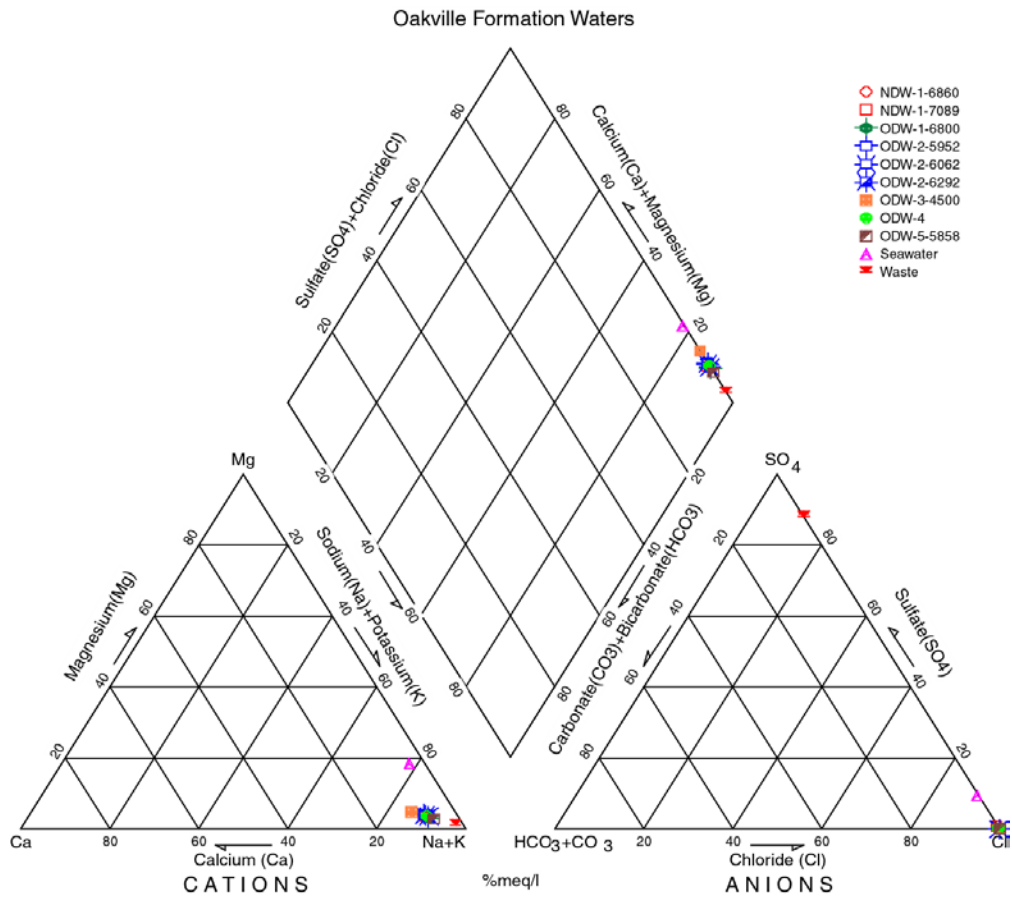


Figure 2. Piper diagram comparing the compositions of native formation waters prior to injection, fluid from NDW-1 after injection in nearby well, liquid waste, and seawater. All formation-water samples, including NDW-1, fall near each other and thus appear to be of similar origin.

Oakville Formation Waters

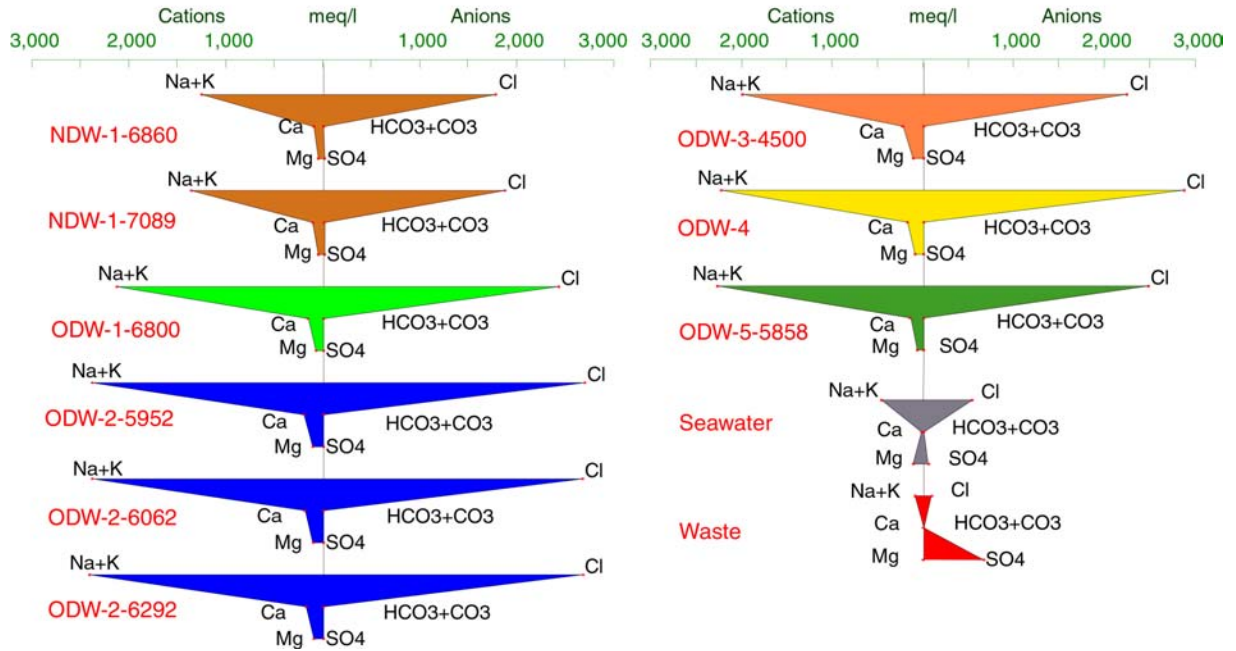


Figure 3. Stiff diagrams comparing the composition of native formation waters prior to injection, fluid from NDW-1 after injection in nearby well, liquid waste, and seawater. Figures depicting similar shapes, regardless of size, indicate waters with similar proportions of constituents. Samples from NDW-1 appear diluted compared to the other formation water samples, but have otherwise similar proportions of constituents (i.e., similar diagram shape).

Simulation of Chemical Interaction between Native Fluid, Waste, and Host Rock

Simulations of the chemical reaction of waste, formation water, and formation minerals were performed to evaluate the extent of waste-water-rock interaction resulting from injection. One goal was to calculate changes in formation porosity to help assess long-term injection efficiency. Another goal was to assess whether mineral precipitation/dissolution reactions might explain the lower-than-expected sulfate and ammonia concentrations and increased potassium level at well NDW-1. This work was performed in two stages. First, simple speciation computations and multicomponent reaction-path simulations were run to help define the general chemical system, the type of controlling primary mineral phases, and any potential secondary minerals that could form as a result of reaction with waste constituents. Using this information, a more sophisticated multicomponent reactive transport simulation was then run to predict the evolution of the modeled system under hydrological and chemical conditions more representative of actual field conditions.

These simulations were run using thermodynamic data from various literature sources. The main original database was the *SOLTHERM* database (Reed and Palandri, 1998), with references therein, including data for ammonium minerals from Daniels (1992) and many data derived using SUPCRT92 (Johnson et al., 1992) with modifications as follows. For silicate minerals, equilibrium constants were adjusted for consistency with the thermodynamic properties of aqueous silica reported by Gunnarsson and Arnorsson (2000). Consistent feldspar thermodynamic data were taken from Arnorsson and Stefansson (1999). Equilibrium constants for illite and smectites were recomputed (courtesy J. Apps, LBNL) using data from Kulik and Aja (1997). These are also consistent with the silica data reported by Gunnarsson and Arnorsson (2000).

Initial Speciation and Reaction Path Simulations

The composition of the initial formation water input into simulations was taken as the analysis of water originally recovered from well ODW-1 before waste injection began (Table 1). The composition of reactant liquid waste (Table 2) and the initial formation mineralogy (Table 3) were also available from measurements. Note that organic species were assumed to be non-reactive and were omitted from simulations. The presence of organic acids could affect the modeled system chemistry, particularly pH. These effects were tested in limited simulations and appear to be small, although a more significant effect cannot be ruled out at this time.

The measured temperature within the injection interval is around 65°C, and waste is heated up to this temperature before being injected. Therefore, to perform realistic simulations, the formation water and waste (25°C analyses) were numerically heated from 25 to 65°C before reacting them together. The SOLVEQ code (Reed, 1982; Spycher and Reed 1992) was used to compute the pH and chemical speciation of these fluids at 65°C, from the 25°C analyses (Reed and Spycher, 1984). At 65°C, the recalculated pH of formation water was 6.9, and that of the waste was 6.5, compared to values of 7.0 and 7.6, respectively, at 25°C (Tables 1 and 3).

Because concentrations of aluminum, potassium, and sulfate in the formation water (native fluid in OWD-1) were unknown, these were calculated by assuming equilibrium with illite, potassium feldspar, and barite at 65°C, respectively. This yielded concentrations of 0.006 ppm Al, 421 ppm K, and 45 ppm SO₄. Sulfate and potassium concentrations computed in this

way are in line with other formation water analyses (Table 1). Because the solution was supersaturated with respect to calcite (likely as the result of CO₂ loss during sampling; see Palandri and Reed, 2001), this mineral was brought to exact saturation with the native fluid at 65°C by adjusting the bicarbonate concentration to 40 ppm, within the expected typical large uncertainty of analytical values for this constituent. The adjustment of the bicarbonate concentration brought iron dolomite close to exact saturation, and, for this reason, a slight adjustment to the measured iron concentration (from 1.5 to 1.8 ppm) was made to allow this mineral to saturate exactly. Note that for simplicity, iron dolomite was treated as a pure end-member (ferrodolomite). In reality, an ankerite phase is likely to prevail, with a composition intermediate between dolomite and ferrodolomite.

Using these adjusted compositions, the computed equilibration temperatures for a few other minerals observed in the formation are close to measured downhole temperatures around 65°C (Figure 4). Note, however, that smectites are undersaturated and chlorite supersaturated by approximately 1.5 log(Q/K) units at the temperature of interest (Figure 4), likely the result of poorly constrained thermodynamic data for these minerals. Also note that quartz is undersaturated at the formation temperature, possibly the result of silica loss by removal of precipitates when filtering samples for analysis (e.g., Palandri and Reed, 2001). These authors have shown that corrections for such silica deficiency, for CO₂ loss, and for downhole pressure (~220 bar in our case) effect on thermodynamic data significantly improves the clustering of log(Q/K) curves near the formation temperature on plots such as Figure 4. However, because of the preliminary nature of the simulations presented here, these corrections were not attempted.

The reaction of waste with the formation water and minerals was then carried out in two stages using the CHILLER code (Reed, 1982; Spycher and Reed 1992). First, the formation mineral assemblage (Table 3) was numerically titrated into the formation water (ODW-1, Table 1) until the calculated proportion of water and minerals was consistent with the observed porosity of the formation (approximately 28% by volume). Then, the resulting water/mineral assemblage was reacted with waste fluid by simulating infusion of liquid waste into the formation. This pseudo-flowthrough simulation involved incrementally mixing and reacting a finite amount of liquid waste with the formation mineral/water assemblage, and subsequently fractionating (i.e., removing) the resulting fluid by an amount suitable to accommodate for additional infusion of waste fluid. For this simulation, the mixing increment of waste fluid was taken as 10% of the initial pore-fluid volume. After infusing a total waste fluid amount equal to 10 pore-fluid volumes, the mixing increment was increased to a full pore-fluid volume for the rest of the simulation. The model therefore simulates fresh liquid waste infusing through a given volume of formation (e.g. a “box”), and calculates resulting porosity and other chemical changes within that “box”.

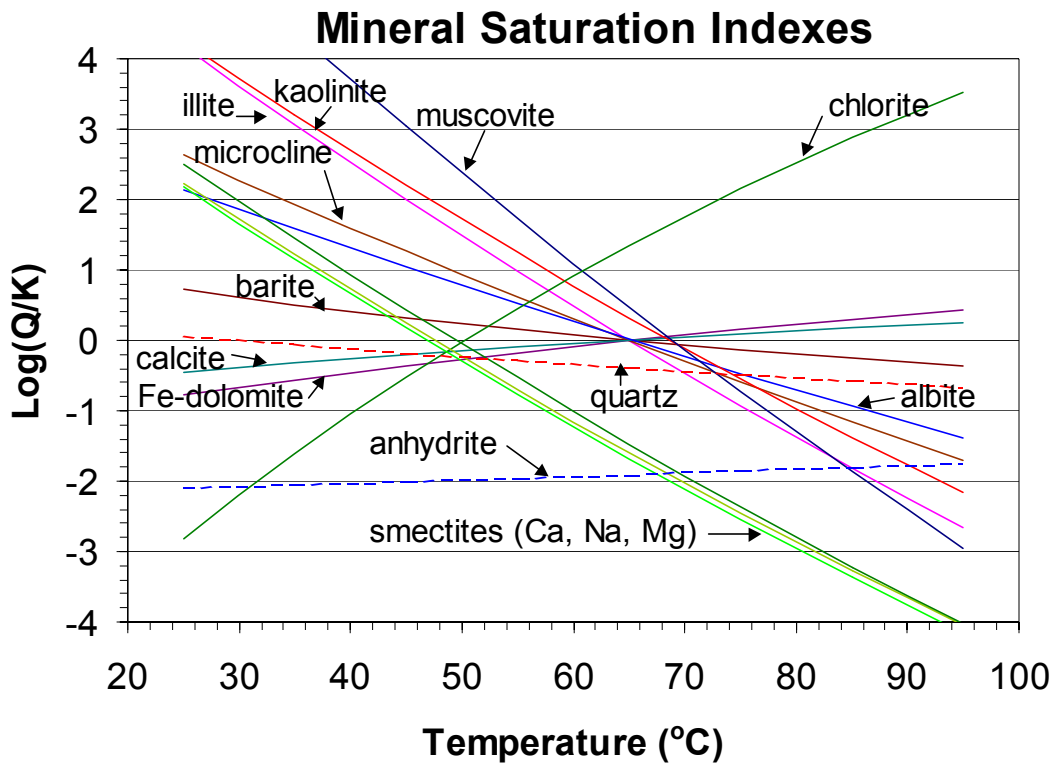


Figure 4. Saturation indexes for typical formation minerals and anhydrite using the water analysis from well OWD-1 (prior to injection) (Table 1) somewhat modified (see text) to bring equilibrium with illite, microcline, barite, iron-dolomite and calcite at 65°C (the approximate downhole temperature). Anhydrite is shown for information because it precipitates upon waste injection. Equilibration temperatures are defined at $\text{log}(Q/K) = 0$.

This modeling exercise represents a crude but very useful approximation of the real system. It is also limited, in our case, by the assumption of thermodynamic equilibrium. Nevertheless, it is an important step in the development of more sophisticated reactive transport simulations such as those presented later. The assumption of equilibrium provides a useful limiting case and allows for evaluating the relative stability of a multitude of potentially important secondary minerals. The modeling simplifications also enable a quick evaluation of reactions within a large chemical system, the number of which can then be narrowed down for further evaluations using more computationally intensive reactive transport simulations.

Several important observations were made from this initial simplified simulation. Sulfate and total ammonia (here reported as ammonium) concentrations quickly rise, as expected, because of the elevated concentrations of these constituents in the injected waste (Figure 5a). The concentrations of other aqueous species decrease as a result of dilution because the waste (Table 2) is more dilute than the formation water (Table 1). Chloride, which is unreactive here, best illustrates this trend (Figure 5a). Anhydrite (calcium sulfate) quickly forms because of the added sulfate from the waste (Figure 5b), but redissolves shortly thereafter because of

the dilution effect on calcium concentrations and additional calcium depletion caused by calcite (calcium carbonate) precipitation. Eventually, anhydrite precipitates again as calcite dissolves due to further mixing with mildly acidic waste (calculated pH of 6.5 at 65°C). Note that the difference between the measured formation water pH value of 7 at 25°C and the initial value of 6.4 in this simulation results from the reequilibration at 65°C with formation minerals prior to reaction with waste.

Another interesting observation from this simulation is the precipitation of ammonium silicates upon reaction with injected waste. Ammonium illite and, to a lesser extent, buddingtonite (ammonium feldspar) are predicted to form (Figure 5b), although not in amounts sufficient to significantly decrease the elevated concentration of ammonia in solution. Albite and kaolinite completely dissolve, and some annite (an iron mica) precipitates. Other formation minerals are not affected significantly by waste injection, and potassium concentrations remain below initial ambient concentrations. The overall effect of injection is a slight increase in porosity (Figure 5d). Consequently, the formation water evolves from a composition similar to that of the original fluid (OWD-1) to a composition similar to waste, with some reactivity but not enough mineral precipitation to keep sulfate and ammonia concentrations from increasing.

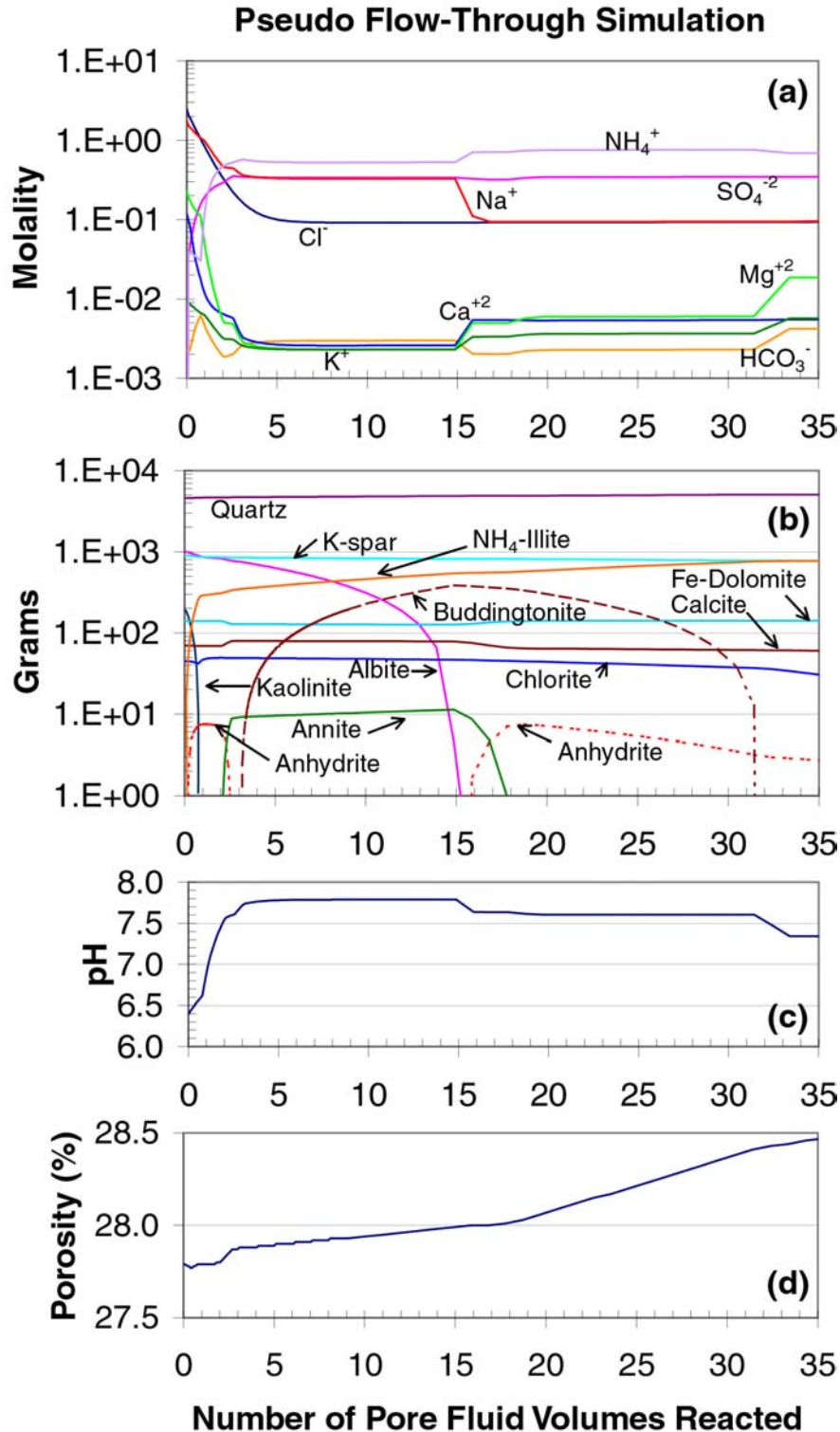


Figure 5. Reaction path simulation results: (a) dissolved species (total aqueous concentrations), (b) minerals, (c) pH, and (d) porosity. The interaction between waste, formation fluid, and formation minerals is simulated as a “box” of initial formation minerals and fluid (1 kg fluid and near 27.8% porosity) infused with liquid waste in successive increments (see text). Local equilibrium is assumed. Precipitating secondary minerals include mostly anhydrite with some ammonium illite, ammonium feldspar (buddingtonite), and annite. Conceptually, the well head is to the right side of the graph.

Reactive Transport Simulation

The computations described above were supplemented with a simulation of coupled flow, transport, and reaction using the TOUGHREACT code (Xu and Pruess, 2001; Xu et al., 2001). This simulation was kept as simple as possible, with the goal of focusing primarily on the evaluation of waste-formation reactions around the disposal well, and less so on exact long-term transport predictions.

Waste injection was modeled as a one-dimensional radial flow problem (i.e., injection from a single well into a horizontal homogenous and confined geologic formation). A variable mass flux was applied at the well head (averaging approximately 16 kg/s, with fluctuations between 2 and 19 kg/s), corresponding to the actual injection flow rates recorded during the investigated time period (1982 to 1994). The outer model boundary was set to a constant pressure representative of regional conditions (around 21.9 MPa), and was located at a distance far enough from the injection well (10 km) to avoid boundary effects in the area of interest (i.e., at distances < 1,000 m). The temperature of the formation and of the injected fluid was maintained at 65°C, consistent with values measured in the field. The permeability of the formation (around $1.8 \cdot 10^{-13} \text{ m}^2$) was estimated from field pumping tests. Injection was simulated for a period of 12 years corresponding to the time between the start of injection activities at well ODW-1 and the drilling of well NDW-1.

The same primary formation minerals were used as previously (albite, K-feldspar, quartz, chlorite, kaolinite, Fe-dolomite, calcite, illite, and smectites). Potential secondary minerals were selected on the basis of the results of the CHILLER reaction path simulation described earlier, and included anhydrite, barite, ammonium illite, buddingtonite, and annite. Muscovite and amorphous silica were also considered but never formed. Anhydrite, calcite and barite were set to react at equilibrium because the reaction rate of these minerals is typically quite fast. The other minerals were set to react under kinetic constraints using effective reaction rates calculated from published rate constants and geometric surface areas estimated from a grain size around 10 microns. The implemented rate law was that derived from transition state theory (Lasaga, 1981) yielding an affinity-dependent formulation (e.g., Aagaard and Helgeson, 1982; Steefel and Lasaga, 1994). The same thermodynamic data were used as in the previous CHILLER simulation.

Results of this TOUGHREACT simulation are shown as a function of distance from the modeled well head after 2 and 12 years of continuous injection (Figures 6 and 7, respectively). The dilution front, as shown by chloride concentrations, is predicted to move approximately 200 m after 2 years (Figure 6a) and 500 m after 12 years (Figure 7a). The profiles of sulfate and ammonia concentrations show a similar rate of expansion (Figures 6a and 7a). A zone of anhydrite precipitation and calcite dissolution is predicted to form and migrate away from the well head, to approximately 20 m after 2 years (Figure 6b) and 80 m after 12 years (Figure 7b). Anhydrite does not form close to the well head because calcium concentrations are too small (only 32 mg/L calcium in waste) or farther away, where calcite precipitation competes for calcium. Ammonium illite and kaolinite progressively precipitate near the well head as feldspars dissolve (Figures 6b and 7b). As predicted in the previous CHILLER simulation, the precipitation of anhydrite and ammonium illite does not significantly affect the concentrations of sulfate and ammonia in solution. The pH within the waste plume (Figure 6c and 7c) remains lower than previously predicted (Figure 4c) by up to around one pH unit, because the kinetic constraints in the present TOUGHREACT simulation reduce the buffering effect of formation minerals reacting with waste. The porosity near the well is predicted to

increase from the initial value of 28% to 28.8% after 2 years and 29.7%, after 12 years (Figure 6d and 7d). The porosity barely decreases in the area of anhydrite precipitation because of simultaneous calcite dissolution. In general, this TOUGHREACT simulation displays trends consistent with earlier CHILLER results, showing mild reactivity and porosity change (after 12 years at the location where NDW-1 was drilled, at approximately 200 m from the simulated injection well), and an increase in concentrations of sulfate, ammonia, and bicarbonate, but a decrease in the concentrations of all other constituents.

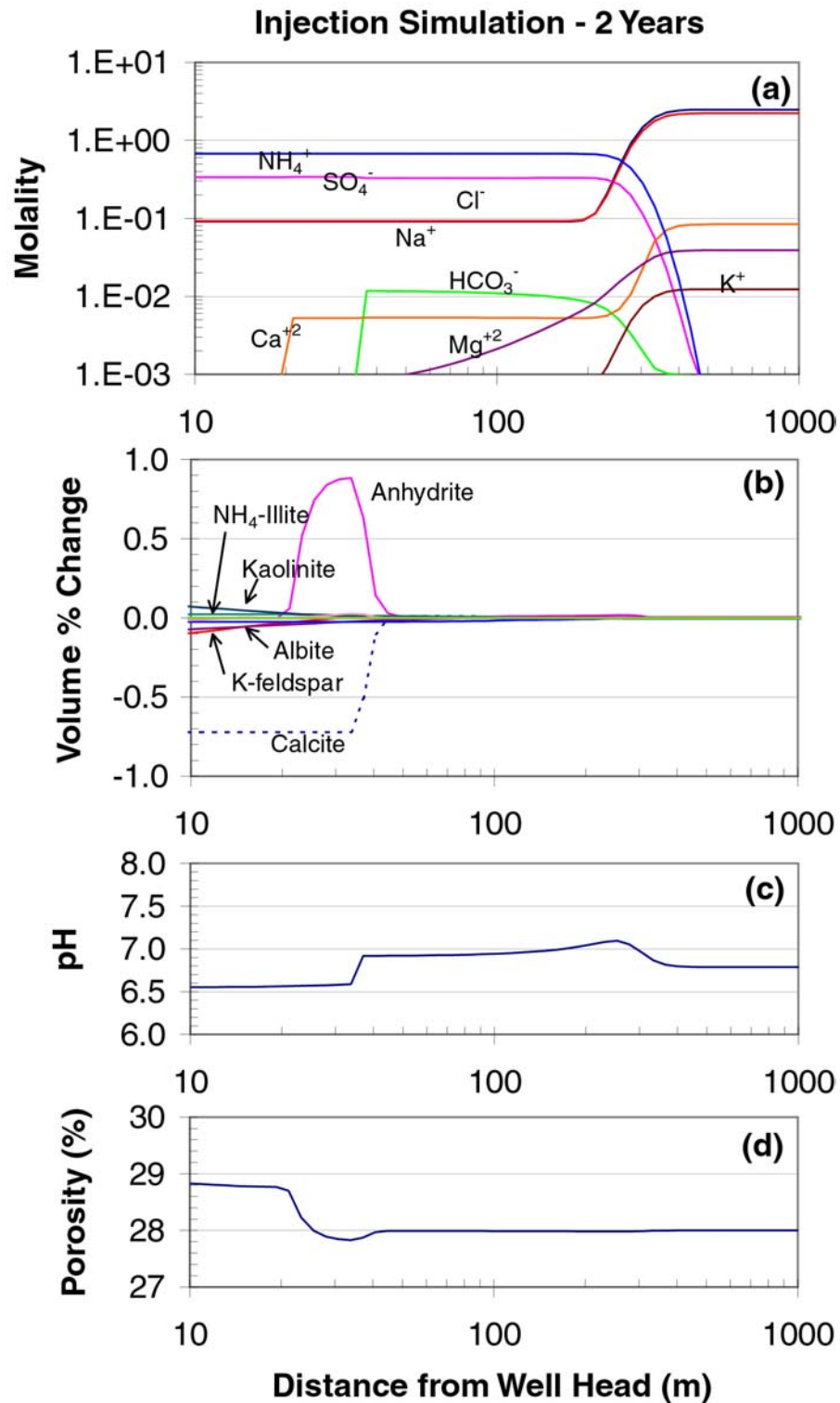


Figure 6. Reactive transport simulation results after 2 years of injection at ODW-1: (a) dissolved species (total aqueous concentrations), (b) minerals, (c) pH, and (d) porosity. The interaction between waste fluid, formation water, and formation minerals is simulated as a 1-D radial flow problem, coupling the effects of flow, transport, and reaction. Silicate minerals are reacting under kinetic constraints. Anhydrite is the dominant secondary mineral, precipitating as a front moving away from the well (negligible porosity decrease).

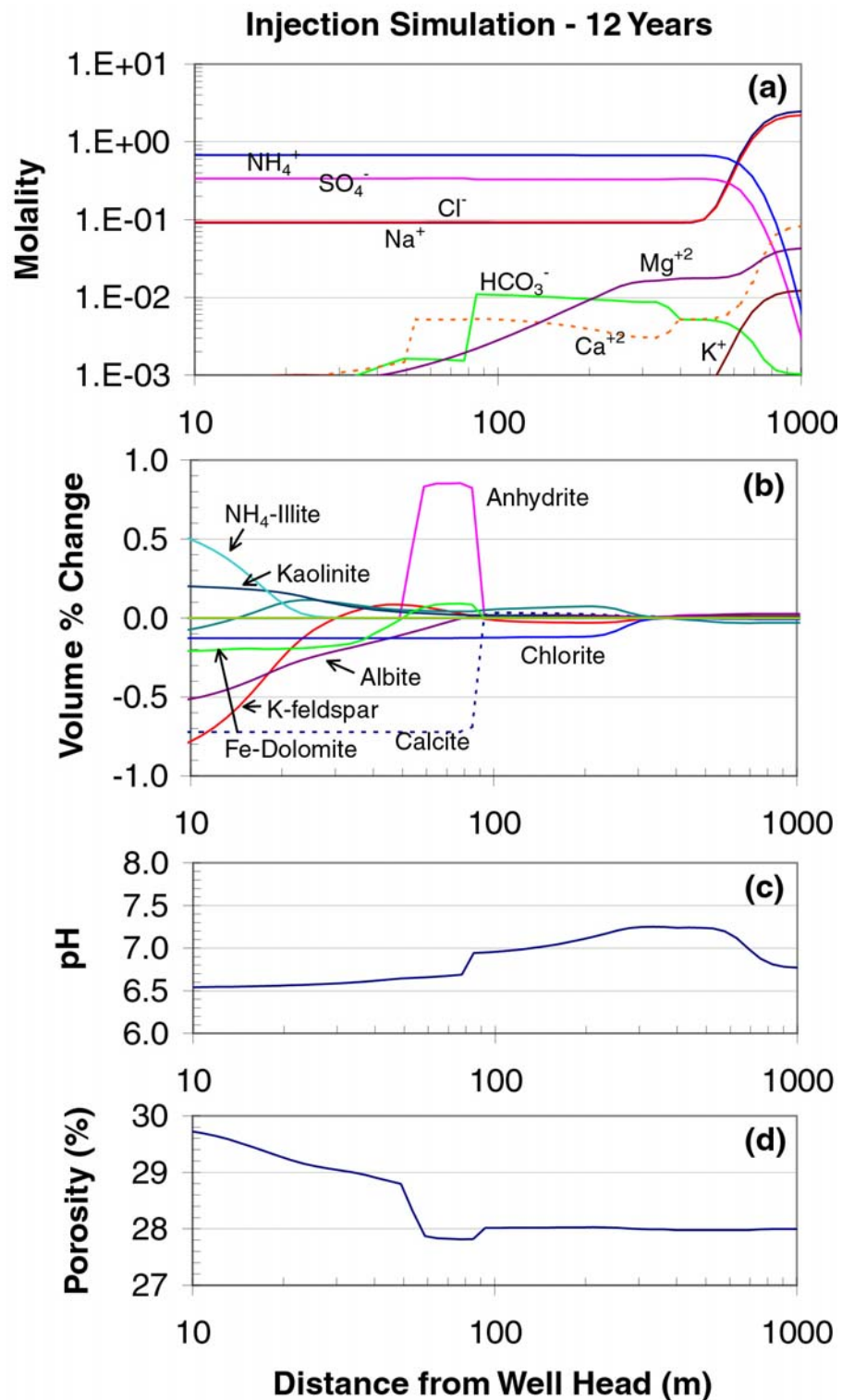


Figure 7. Reactive transport simulation results after 12 years of injection: (a) dissolved species (total aqueous concentrations), (b) minerals, (c) pH, and (d) porosity. The interaction between waste, formation water, and formation minerals is simulated as a 1-D radial flow problem, coupling the effects of flow, transport, and reaction. Silicate minerals are reacting under kinetic constraints. Near the well head, ammonium illite and kaolinite form at the expense of feldspar dissolution, and all calcite initially present dissolves (overall porosity increase with time).

Discussion and Conclusions

The composition of fluid from NDW-1 is similar to formation water unaffected by waste. However, the presence of small concentrations of a waste degradation product, slightly increased sulfate concentrations, apparent dilution, and possibly higher alkalinity compared to other formation waters, all suggest that some mixing with waste has occurred. The waste appears to be, at least theoretically, not very reactive with formation water and minerals.

If significant mixing with waste had occurred, one would expect elevated sulfate and ammonia concentrations at NDW-1. Sulfate and ammonium minerals were predicted to form. However, the precipitation of these minerals was not predicted to significantly reduce the elevated concentrations of sulfate and ammonia in the waste plume. It could be that the precipitation of sulfate and ammonium minerals was underpredicted by the models. It cannot be ruled out, at this time, that other important sulfate and ammonium solid phases form in the real system and significantly deplete sulfate and ammonium in solution. Another possible explanation for the observed dilution without elevated sulfate and ammonia concentrations may be that these species were retarded by mechanisms other than mineral precipitation (e.g., sorption and cation exchange for NH_4^+ , and sulfate reduction to sulfide). It may also be that dilution is caused by mixing with other less saline waters, either naturally or by introduction through the drilling/sampling process. Given the fact that the sampled intervals at NDW-1 coincide closely with injection intervals at ODW-1, and judging from the reactive transport simulation, which shows that migration occurred several hundred meters away from the injection well after 12 years, we would expect that NDW-1 was located within the bulk of the waste plume from ODW-1.

It must be recognized that the modeling work presented in this study is preliminary and subject to many uncertainties. Most notably, the effect of reactions involving organic acids present in the injected waste warrants further investigation. The consideration of organic species was not within the scope of this study, although the modeling tools could accommodate these species, their degradation, and potential interactions between such species. Uncertainties regarding kinetic and thermodynamic data must also be acknowledged, because these data are crucial to the outcome of simulations such as those presented here. Also, the potential formation of other sulfate and ammonium minerals should be further investigated. Thus, the simulation results presented here should not be interpreted without keeping in mind these uncertainties.

Finally, this study illustrates how geochemical modeling and more traditional graphical methods can be applied to problems related to deep-well injection of waste. Simple graphical analyses provide useful characterization tools. Geochemical simulators are more complex, but are powerful tools in helping to solve a wide range of problems, such as the assessment of chemical reactions between waste and host rock, waste compatibility and mixing studies, formation damage and reduced porosity, and the precipitation of scale in injection wells (and its prevention).

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