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Thermodynamic and Mass Balance Analysis of Expansive Phase Precipitation in Saltstone

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Executive Summary

This report assesses the potential for future precipitation of expansive phases that could cause fracturing in saltstone. It examines the equilibrium case using The Geochemist's Workbench® reaction path model. The scenarios simulated examine the effects of different possible infiltrating fluids, different saltstone formulations, and different amounts of minerals available for reaction.

Mineralogy of the vault cement and saltstone were estimated using reported chemical compositions of each. The infiltrating fluid was assumed to be either rainwater equilibrated with vault cement or rainwater itself. The simulations assumed that minerals were homogeneously distributed in saltstone and that each pore volume of infiltration reached equilibrium with the mineral assemblage.

Fracturing that initiates in pores by expansive phase precipitation is unlikely to occur in saltstone because the maximum amount of porosity filled is 34%. If less than 100% of the saltstone minerals are available for reaction, less porosity will be lost to expansive phases. Likewise, the formulation of saltstone used will affect the amount of porosity filled by expansive phases.

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Introduction

Degradation of saltstone grout is significant to long-term performance of the saltstone waste form. In particular, degradation resulting from precipitation of expansive phases may cause fracturing of the saltstone grout that would increase advective flow and diffusion through the waste form. This would accelerate the chemical degradation of the grout and increase the flux of water contacting contaminants, resulting in quicker and potentially greater release of waste constituents to the environment.

An enormous amount of work has been done on degradation of concrete and cement by precipitation of sulfate-bearing expansive phases, but the exact mechanism is still not understood (e.g., Bournazel and Moranville, 1997; Malone et al., 1997; the entire collection of articles edited by Marchand and Skalny, 1999; Beaudoin, 2001; Tixier and Mobasher, 2003; Neville, 2004). Brown and Taylor (1999) discuss 7 mechanisms proposed in the literature and conclude that no one mechanism is likely to be responsible for all degradation. For many of these studies the primary concern with degradation is the structural integrity of the cement or concrete form. For saltstone, the structural integrity is much less of a concern than its function as a barrier to mobilization of waste constituents by infiltrating water. Thus, the primary concern is whether precipitation of expansive phases is likely to cause fracturing that provides pathways for infiltrating water to contact waste constituents.

Precipitation of expansive phases will not necessarily result in fracturing of the saltstone grout. Expansive phases that are precipitated during curing of the saltstone grout are not likely to cause fracturing because the plasticity of the grout during this time will absorb their volume. Later stage expansive phase precipitation will occur within the pore space network, because it is through this network that dissolved ions reach grout mineral phases and react to form expansive phases. Thus, there is potential for the porosity of the grout to absorb the increased mineral volume caused by expansive phase precipitation, minimizing or avoiding fracturing altogether. In their model of volumetric expansion of cementitious materials by sulfate attack, Clifton and Ponnensheim (1994) assume that no expansion, and hence no fracturing, will take place until all of the available pore space is filled with expansive phases. Tixier and Mobasher (2003) modified this by assuming that only a fraction (f) of the pore space must be filled before fracturing will ensue. This fraction varies with cement or concrete formulation. Using experimental data from other publications they estimated values of f for several cements that varied from 0.05 to 0.45 with a median of 0.3.

This report is an analysis of the potential for fracturing of the saltstone grout by late-stage expansive phase precipitation based on thermodynamic and mass balance considerations. A list of all phases and their formulas referred to in this report is presented in Table 1. Phases that are considered expansive are those that have higher molar volumes¹ than normal cement minerals. Figure 1 shows molar volumes versus number of waters of hydration for cement minerals and several hydrated CaNO_3 phases. This shows why most research has focused on ettringite with 32 waters of hydration and a molar volume of 717 cm^3 . However, there are other phases that may be considered expansive, including C_4AH_{13} , monosulfate, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

¹ Molar volume is the volume of 1 mole of a phase.

Assuming that precipitation of expansive phases can cause fracturing, the pressure of crystallization of the expansive phase must exceed the strength of the cement matrix. In the early stages of precipitation in a water saturated system, the pressure of crystallization within a void (pore or fracture) can be relieved by flow of water out of the void. Thus, the rate of crystallization versus the rate at which water can escape is an important factor. If migration of water from the void is blocked by precipitation, the crystallization rate may exceed the water loss rate and pressure within the void can increase. This suggests, as posed by Tixier and Mobasher (2003), that different cements may sustain different amounts of precipitation of expansive phases before fracturing initiates. However, a first approximation of fracturing potential is to determine the volume of expansive phases that can precipitate and its relation to porosity as the cement ages.

Table 1: Solid phases referred to in document.

Phase	Formula
Brucite	Mg(OH)_2
CSH	$\text{CaSiO}_3 \cdot \text{H}_2\text{O}$
C4AH13	$\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$
Ettringite	$\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$
Gibbsite	Al(OH)_3
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Hydrogarnet	$\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$
Hydrotalcite	$\text{Mg}_4\text{Al}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Monosulfate	$\text{Ca}_4\text{Al}_2\text{O}_7(\text{SO}_3) \cdot 12\text{H}_2\text{O}$
Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$
Portlandite	Ca(OH)_2
Quartz	SiO_2

The scope of the analysis reported here was to evaluate the equilibrium case for future precipitation of expansive phases in saltstone using thermodynamic and mass balance constraints. If large amounts of these phases precipitate and fill porosity, fracturing may occur that could accelerate the degradation of saltstone. The analysis was done by estimating the mineralogy of saltstone based on a chemical analysis and simulating the reaction of potential pore fluids with this mineralogy. This was done for several scenarios in which pore fluids migrate through the saltstone matrix. This evaluation only predicts the equilibrium reaction path for each scenario. Kinetic controls could change the reaction paths as could deactivation of the original phases by precipitated coatings.

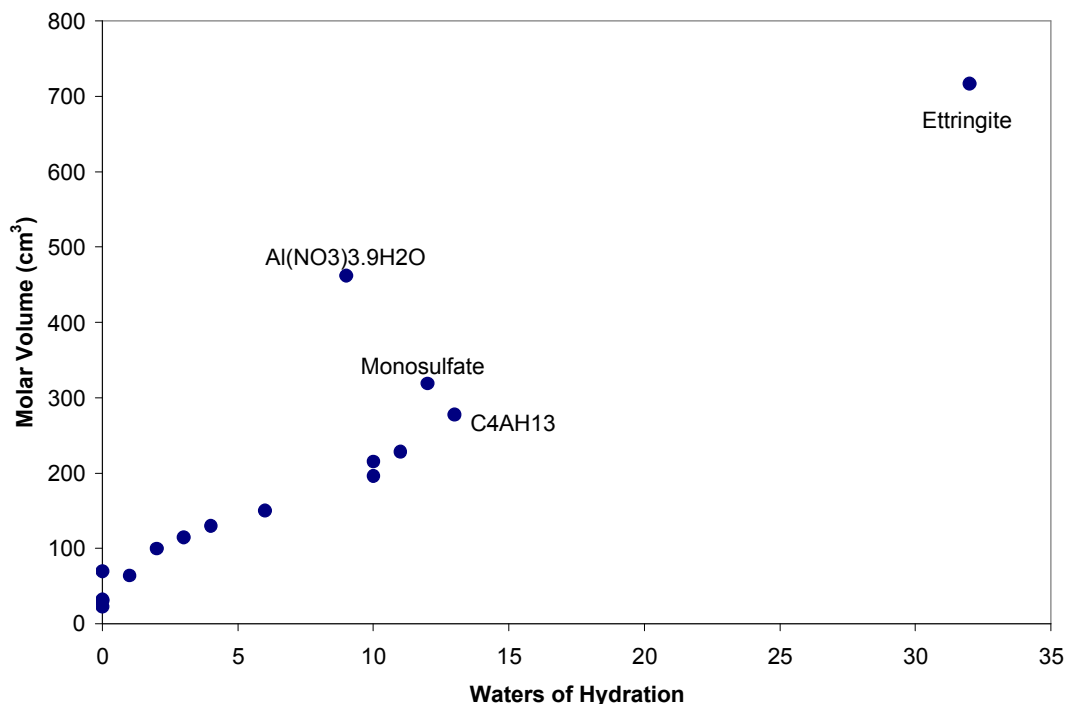


Figure 1: Molar volume vs. waters of hydration for many cement phases.

The Model

The reaction path model used for all simulations was The Geochemist's Workbench (Bethke, 2002), referred to hereafter as GWB. In this study the module used is a geochemical program that combines thermodynamic and mass balance relations to calculate fluid rock interactions. GWB is capable of incorporating kinetic relations as well, but the lack of these for cement systems precludes their use here. Thus, the end point of each calculation is thermodynamic equilibrium.

Additions to the Thermodynamic Database

Cement mineralogy is unique, involving many hydrated phases that rarely occur geologically, and thus databases associated with geochemical modeling programs typically do not include thermodynamic data for these minerals. Additions were made to the thermodynamic database as listed in Table 2. The references in Table 2 provided an initial log K value that in most cases had to be recalculated in terms of the basis species in the GWB model. The log K value for the phase CSH depends upon the Ca/Si ratio in the hydrated cement (Harris et al., 2002; Park and Batchelor, 2002). Here the Ca/Si ratio was assumed to be low, Ca/Si=0.5, because of the low amount of portlandite relative to fly ash and slag used in saltstone.

Table 2: Cement phases added to thermodynamic database. Log K refers to 25°C.

Phase Name	Formula	log K	Reference
Ca-carboaluminate	$\text{Ca}_2\text{Al}_2\text{O}_4(\text{CO}_3) \cdot 11\text{H}_2\text{O}$	34.76	Reardon (1990)
CSH	$\text{CaSiO}_3 \cdot \text{H}_2\text{O}$	15.15	Park and Batchelor (2002)
C4AH13	$\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$	100.77	Reardon (1990)
Ettringite	$\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$	57.15	Reardon (1990)
Hydrogarnet	$\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$	80.55	Bennett et al. (1992)
Hydrotalcite	$\text{Mg}_4\text{Al}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	73.78	Bennett et al. (1992)
Monosulfate	$\text{Ca}_4\text{Al}_2\text{O}_7(\text{SO}_3) \cdot 12\text{H}_2\text{O}$	73.42	Reardon and Dewaele (1990)
Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$	47.22	HSC Database

The initial mineral matrix of saltstone was estimated from a normative calculation based on the chemical analysis of hydrated cement given in Table WSRC-RP-92-1360, Table D.3.2. This assumes that all components in the salt feed solution except sodium, potassium, and nitrate react to form solid hydrated phases. The normative calculation parses constituents in a chemical analysis of saltstone (Table D.3-2 in WSRC RP-92-1360) into stoichiometric phases typical of cement. For example, the saltstone calculation assumes all iron is in hematite, all magnesium in hydrotalcite, and all sulfur in gypsum. After parsing these and the required co-constituents it is assumed that remaining calcium is in CSH, and quartz and gibbsite account for any remaining silica and aluminum. For the vault cement a chemical analysis of Class H cement from Malek et al. (1985) was used. This has considerably more calcium relative to silica, magnesium, and iron than does the saltstone. Thus, the minerals used in the normative calculation were CSH, ettringite, hydrogarnet, and portlandite.

Table 3: Estimated matrix mineral volumes of vault cement and saltstone from normative calculations.

Phase	Vault Cement (cm ³)	Saltstone (cm ³)
CSH	414	426
Ettringite	301	-
Gibbsite	-	90
Hematite	-	8
Hydrogarnet	71	-
Hydrotalcite	-	148
Gypsum	-	10
Portlandite	388	-
Quartz	-	51

Conceptual Model

The conceptual model used in the simulations was a constant composition fluid passing through a volume of solid matrix (Figure 2). Each pore volume of fluid replaced the previous volume with no fluid mixing. Reaction of each pore volume of fluid with the solid matrix resulted in dissolution and precipitation reactions. The volume of minerals for each volume of pore fluid

passing through the matrix was recorded. From this a net mineral volume and porosity loss was calculated at the end of a reaction path.

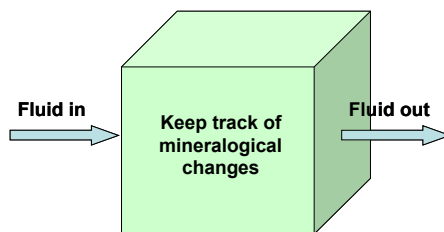


Figure 2: General conceptual model of simulations.

For the main set of simulations it was assumed that water that reaches saltstone had to pass through and react with the vault cement as shown in Figure 3. This water can then react with the saltstone. The volume of saltstone used in each simulation is the volume that holds 1 pore volume of fluid, assuming the estimated mineral volumes and a fractional porosity of 0.46 (Langton, 1984). This gives a total saltstone volume of 2172 cm³. The estimated mineral volumes from normative calculations for both the vault cement and saltstone are shown in Table 3. Composition of the water that initially reacts with the vault cement (Table 4) is from a 1988 analysis of rainfall in Santee National Forest reported by Strom and Kaback (1992).

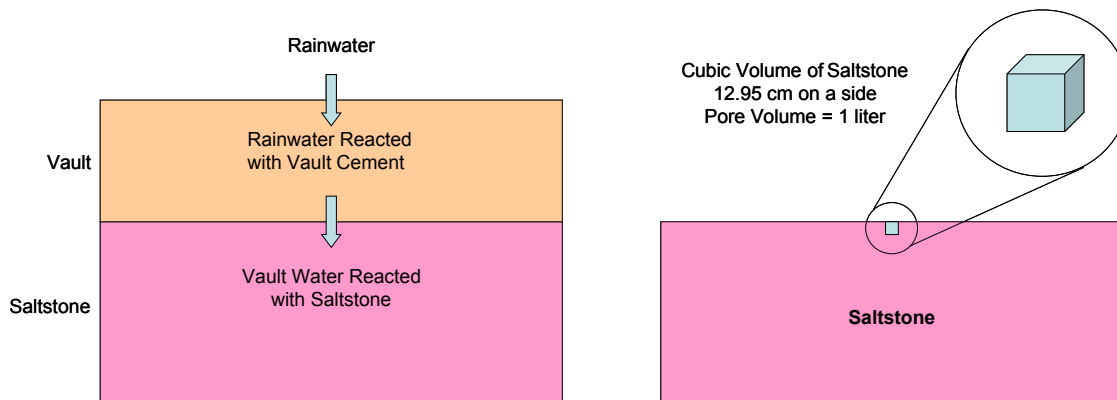


Figure 3: Conceptual model of water passing from vault cement into saltstone.

Table 4: Composition of rainfall used to react with vault cement (Strom and Kaback, 1992)

Constituent	Concentration
pH	4.53
Ca ⁺² (mg/L)	0.10
Mg ⁺²	0.03
Na ⁺	0.21
SO ₄ ⁻²	1.57
Cl ⁻	0.37

Simulation Scenarios

The primary scenarios were run according to the Conceptual Model section with the exception that hematite and monosulfate were not included in the saltstone minerals available to react with pore fluid. Their inclusion rendered the model unstable and unable to calculate results. Also, no thermodynamic data for hydrated ferric iron phases was found, and thus reaction of hematite was moot. This is not considered an issue because of the small volume of hematite in the initial saltstone. Its reaction would not result in a significant volume change relative to the other phases. The absence of monosulfate is a conservative assumption. A possible path to precipitation of ettringite is the dissolution of monosulfate. In the absence of monosulfate, gibbsite reacts to ettringite. The net volume change for the monosulfate path is about 1/3 that of the gibbsite path. Thus, ettringite precipitated from gibbsite fills more porosity than ettringite precipitated from monosulfate. Hence, the absence of hematite and monosulfate does not affect conclusions drawn from the simulations.

In any model of fluid-rock interactions an issue is the amount of total mineral mass that is available for reaction. In general, passing pore fluids do not contact the entire mineral mass of a rock either because of flow heterogeneities or because minerals get coated with reaction products, making them unavailable for reaction. To account for this, simulations were run in which 10%, 50% and 100% of the saltstone matrix was available for reaction. Rainwater reacting with saltstone minerals was also simulated. In addition, two simulations were done with alternative initial cement chemical compositions. Table 5 lists the 6 scenarios.

Table 5: Different scenarios simulated using The Geochemist's Workbench®.

Scenario	Initial Saltstone Composition	Reactive Fluid
1	WSRC (1992) Hydrated, 10% minerals available	Rainwater equilibrated with vault cement
2	WSRC (1992) Hydrated, 50% minerals available	Rainwater equilibrated with vault cement
3	WSRC (1992) Hydrated, 100% minerals available	Rainwater equilibrated with vault cement
4	WSRC (1992) Hydrated, 100% minerals available	Rainwater
5	WSRC (1992) Pre-Hydrated, 100% minerals available	Rainwater equilibrated with vault cement
6	Harbour et al. (2006) Material Compositions; Dixon et al. (2008) Formulation, 100% mineral available	Rainwater equilibrated with vault cement

Results

All of the scenarios involve reaction of an infiltrating fluid with saltstone minerals. Some minerals dissolve, others precipitate during the simulations. The Geochemist's Workbench® has the option to eliminate various mineral phases from consideration. This allows phases to be eliminated that are known to be impossible or unlikely. In these simulations all phases but those

typical of cement systems were eliminated from consideration. Otherwise many phases that are unreasonable and normally found only in high temperature systems will precipitate. In preliminary runs in which high temperature phases were suppressed, the resulting mineralogy includes zeolite and clay minerals. These can form at low temperatures (25°C) but more often precipitate during hydrothermal alteration of rocks at somewhat elevated temperature. In addition, they are rarely mentioned in cement literature. Hence, consideration of these was eliminated leaving only phases common to cement systems shown in Table 6. It should be noted that even if the zeolite and clay minerals precipitate, the volume of mineral precipitation is well below the volume of pore space.

Table 6: Phases allowed to precipitate in GWB Modeling

Allowed Phases	
Brucite	Hydrogarnet
C4AH13	Hydrotalcite
CSH	Kaolinite
Ettringite	Monosulfate
Gibbsite	Quartz
Gypsum	C4AH13

The results of the reaction path simulations are shown as plots of mineral volumes ($\log \text{cm}^3$) versus the pore volumes of fluid passing through the simulated volume of saltstone. This provides important information on the timing of precipitation or dissolution of minerals relative to one another. Pore volumes passing through a volume of saltstone can be related to time if hydraulic conductivity, fluid driving force, and the volume of the system are specified. To estimate this for an entire vault of saltstone grout would also require an understanding or assumption of how hydraulic conductivity changes as dissolution/precipitation reactions occur. For example, if expansive phases fill porosity without causing fracturing, then hydraulic conductivity will decrease. On the other hand, once fracturing begins, hydraulic conductivity is likely to increase. The pore volumes to time relationship is specifically avoided here for these reasons and because it is considered less important to this analysis than the total volumes of minerals precipitated and dissolved.

Scenario 1

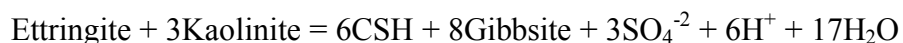
In this scenario rainwater equilibrates with vault cement and the resulting fluid migrates through the saltstone volume reacting with 10% of the saltstone matrix that is available for reaction. Equilibration of the vault cement with rainwater produces a low ionic strength (0.04molal) solution of the composition given in Table 7.

Table 7: Composition of water entering saltstone (equilibration of vault cement with rainwater).

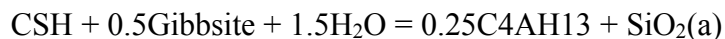
Constituent	Concentration (molal)
OH^-	2.4E-2 (pH=12.38)
Ca^{+2}	1.7E-2
Na^+	9.1E-6
Cl^-	9.6E-5
SO_4^{-2}	5.1E-5

When this solution reacts with saltstone, the ionic strength remains low. Thus, the default ion interaction model, an extended Debye-Hückel model called B-dot, was used rather than high ionic strength models such as the Pitzer (1973) model. However, the B-dot model gave unreasonably high concentrations of dissolved silica because of the inclusion of two polymeric species, $\text{H}_4(\text{H}_2\text{SiO}_4)_4^{-4}$ and $\text{H}_6(\text{H}_2\text{SiO}_4)_4^{-2}$. These were removed from the database leaving the aqueous silica species $\text{SiO}_2(\text{aq})$, H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{-2}$. This resulted in quartz solubility at high pH consistent with literature values. This approach is reasonable given the results of saltstone pore fluid analyses reported in Langton (1987) in which the highest silica concentration was 2,280 mg/L.

The results of the reaction path are presented in Figure 4. In the figure, volumes of minerals precipitated or dissolved are shown as the reacting fluid passes through the saltstone matrix. Ettringite is oversaturated in the initial pore water and is present before any infiltration is reacted. For the initial several pore volumes of infiltrate, ettringite is lost to reaction with kaolinite:



This reaction results in a net mineral volume loss of 377 cm³ per mole of ettringite lost or 2.2 cm³ lost for the model system. The volume of ettringite remains stable for the duration of the simulation – 1000 pore volumes. Following early formation of CSH, it begins dissolving and continues to dissolve for the remainder of the simulation. Another potentially expansive phase, C4AH13, is produced early in the simulation by reaction of CSH and gibbsite:



This reaction produces a net mineral volume loss of 43 cm³ per mole of C4AH13 formed because of the ratio of CSH and gibbsite dissolved to C4AH13 precipitated. A total of 19 cm³ of C4AH13 precipitates before it begins to slowly dissolve as successive pore pass through the system.

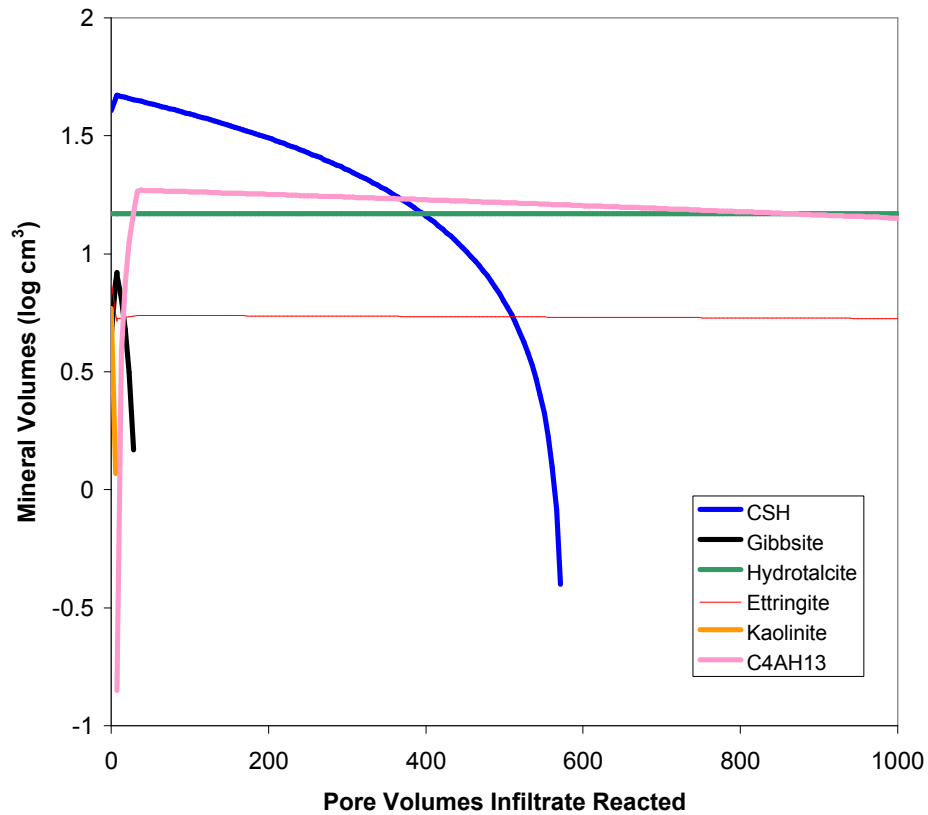


Figure 4: Results of Scenario 1 (10% of mineral matrix available for reaction).

Scenario 2

This scenario was the same as Scenario 2 except that 50% of the saltstone minerals were made available for reaction. The results are shown in Figure 5. Allowing 50% of the minerals to react has the effect of stretching the reactions out over the x-axis and allowing a larger volume of minerals to precipitate. Ettringite dissolution ceased and C4AH13 began to precipitate at 28 pore volumes, rather than at 7 pore volumes as was the case when only 10% of the original minerals were allowed to react. A total of 97 cm³ of C4AH13 precipitated before it began to slowly dissolve.

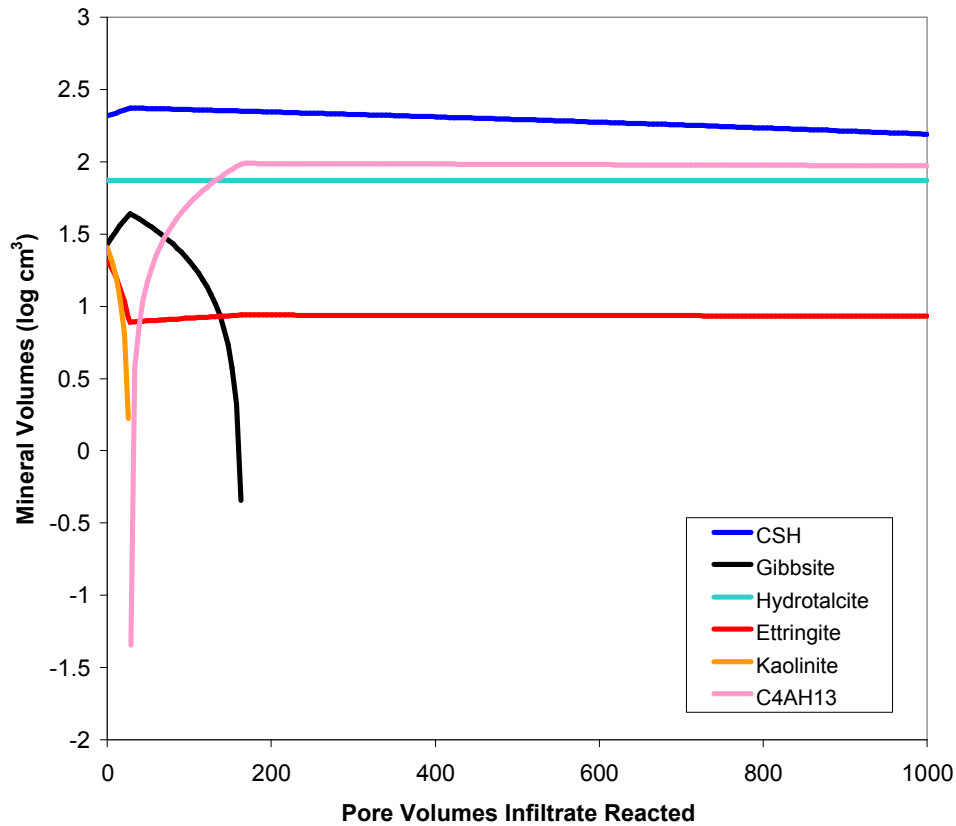


Figure 5: Results of Scenario 2 (50% of mineral matrix available for reaction).

Scenario 3

This scenario was the same as Scenario 3 except that 100% of the saltstone minerals were made available for reaction. The results are shown in Figure 6. This has the effect of further stretching the reaction path along the x-axis and allowing a larger volume of minerals to precipitate. Hence, ettringite stopped dissolving and C4AH13 began precipitating at 55 pore volumes, and 196 cm³ of C4AH13 were precipitated at its maximum volume at 339 pore volumes. The volume of ettringite increased less than 2 cm³ from its minimum at 339 pore volumes through the end of the simulation at 1000 pore volumes.

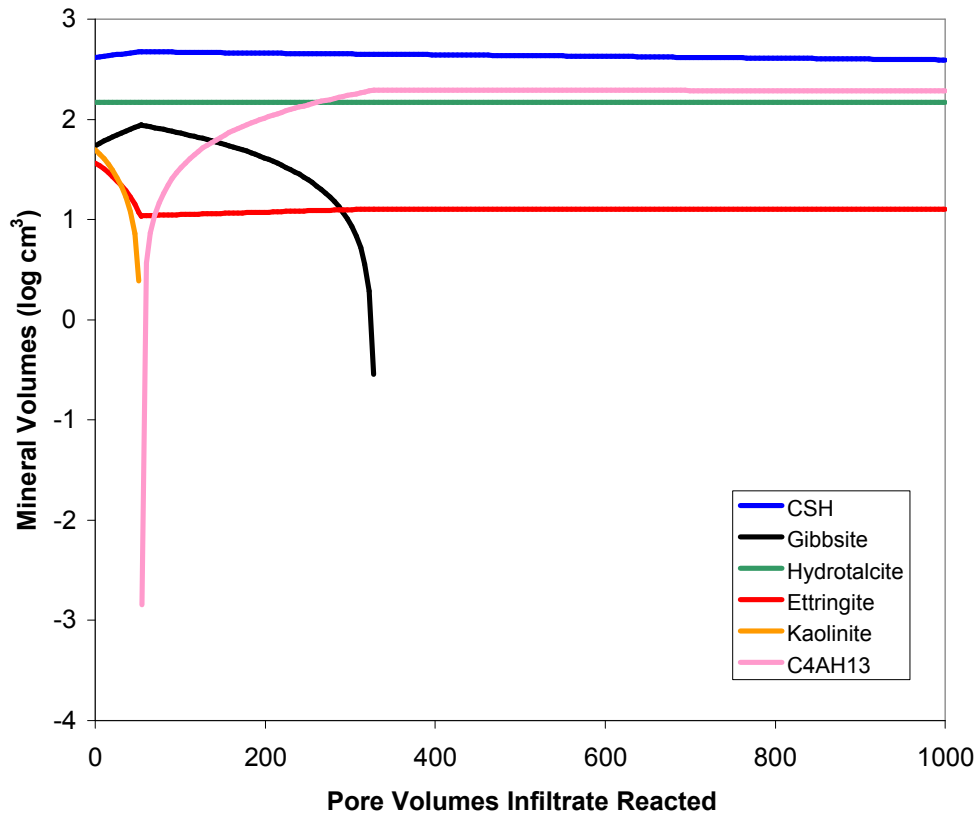
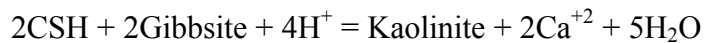


Figure 6: Results of Scenario 3 (100% of mineral matrix available for reaction).

Scenario 4

This scenario follows the advective conceptual model of Figure 3, but assumes the fluid reacting with saltstone is rainwater. This evaluates the case where infiltrating pore water reacts very little with the vault cement. This could occur if flow through the vault cement was limited to a few fractures or the kinetics of reaction with the vault cement were very slow. Though the infiltrating rainwater would have to pass through a layer of soil before reaching the vault cement, it is assumed here that the difference in composition of rainwater and soil water will make little difference in the final reaction path. The reaction path for this scenario (Figure 7) is different from those of Scenarios 2-4 because the reacting water is far from equilibrium with the saltstone matrix. In this scenario ettringite dissolves from the beginning and is exhausted by 72 pore volumes of reacted rainwater. The only solid phase that precipitates within 1000 pore volumes is kaolinite by the reaction of CSH and gibbsite:



Thus, in this scenario there is a considerable net mineral volume loss throughout the simulation.

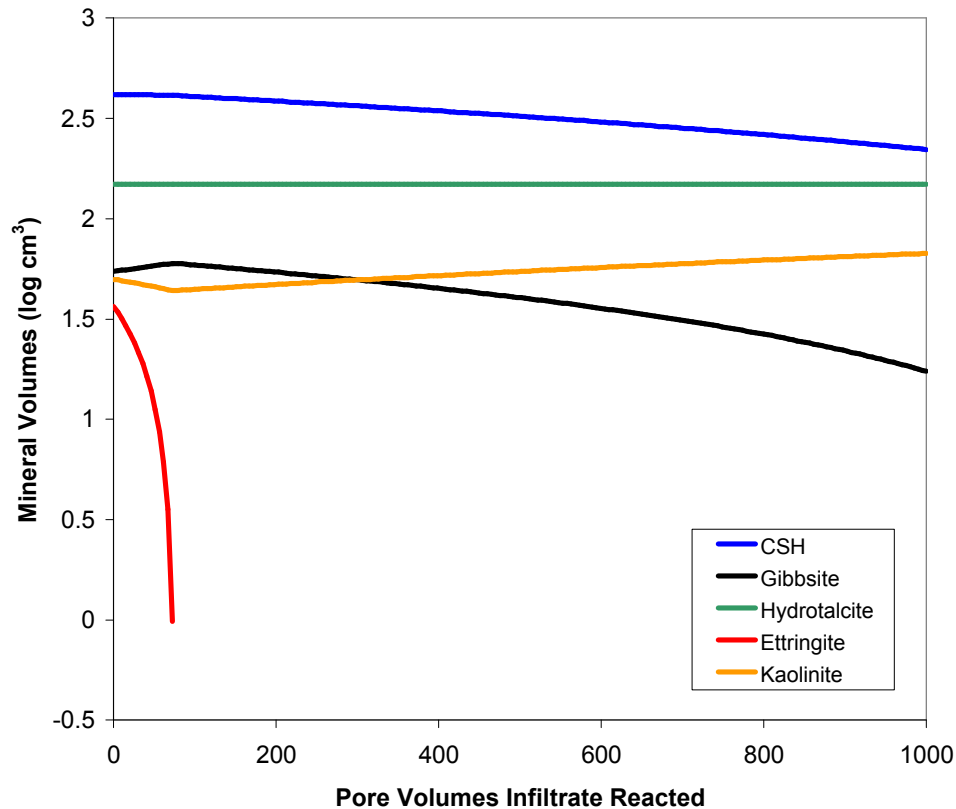


Figure 7: Mineral volumes during a reaction path in which rainwater is reacted with 100% of the matrix minerals (Scenario 4).

Alternative Saltstone Formulations

In scenarios 5 and 6 alternate saltstone formulations were used to evaluate their effect on precipitation of expansive phases. In scenario 5 the chemical composition of the saltstone is that presented in Table 3.2.2 of WSRC (1992) as the pre-hydrated cement composition. This assumes that hydroxide and water are the only components of the salt feed solution used to make saltstone that contribute to the saltstone mineralogy. In scenario 6, the compositions of the raw saltstone ingredients, portland cement, fly ash, and slag are from Harbour (2006). These were combined with the DDA simulant salt feed composition presented in Dixon et al. (2008). All aluminum and carbonate in the salt feed were assumed to contribute to the saltstone mineralogy. A water to dry ingredient weight ratio of 60 to 40 was used to determine the final composition of this saltstone formulation. The mineralogy of these compared to that of the formulation used in scenarios 1-4 is shown in Table 8. It should be noted that the mineralogy at zero pore volumes of infiltrate reacted in the results of the simulations does not exactly match the mineralogy shown in Table 8. This is because there is an initial equilibration of the normative mineral assemblage input into The Geochemist's Workbench®.

Table 8: Saltstone mineralogy of scenarios 5 and 6 compared to scenarios 1-4. Units are cm³ mineral per 1 liter pore volume.

Mineral	Scenarios 1-4 (cm³)	Scenario 5 (cm³)	Scenario 6 (cm³)
CSH	426	629	472
Hydrotalcite	148	206	173
Gypsum	10	23	24
Kaolinite			238
Gibbsite	90	114	-
Quartz	51	189	76
Hematite	8	13	108
Ca-Carboaluminate	-	-	83

Scenario 5

The simulation results for scenario 5 are shown in Figure 8. In this scenario the reacting fluid was rainwater equilibrated with vault cement and 100% of the minerals were available for reaction. Thus, it is comparable to scenario 3 (Figure 6). The two main differences involve ettringite and C4AH13. In scenario 5 ettringite dissolves initially, but re-precipitates after 495 pore volumes of infiltrate have reacted. The maximum volume of ettringite after this point is 2.2 cm³, much lower than the final volume of ettringite in scenario 3, 72 cm³. C4AH13 precipitates much later than in scenario 3, beginning at 495 pore volumes reacted and producing a maximum volume of 233 cm³. This is a larger volume than the 196 cm³ of C4AH13 produced in scenario 3. Another important reaction is precipitation of CSH through 495 pore volumes. This occurs by the fluid reacting with quartz until it is exhausted and then continues by reaction of the fluid with kaolinite. Once the kaolinite is exhausted, CSH stops precipitating and the expansive phases C4AH13 and ettringite begin to precipitate. Though it is not an expansive phase, the early precipitation of CSH through 495 pore volumes accounts for most of the increase in mineral volume during this period.

The simulation results for scenario 6 are shown in Figure 9. In this scenario the reacting fluid was rainwater equilibrated with vault cement and 100% of the minerals were available for reaction. Thus, it is also comparable to scenario 3. Again, ettringite is completely dissolved early in the simulation, but reappears in this scenario at 487 pore volumes reacted. The maximum volume that precipitates after reappearance is 3 cm³. C4AH13 also begins to precipitate at 487 pore volumes reacted, and a maximum volume of 318 cm³ is produced. As in scenario 5, early precipitation of CSH accounts for most of the early increase in mineral volume. This reaction stops at 487 pore volumes in scenario 6.

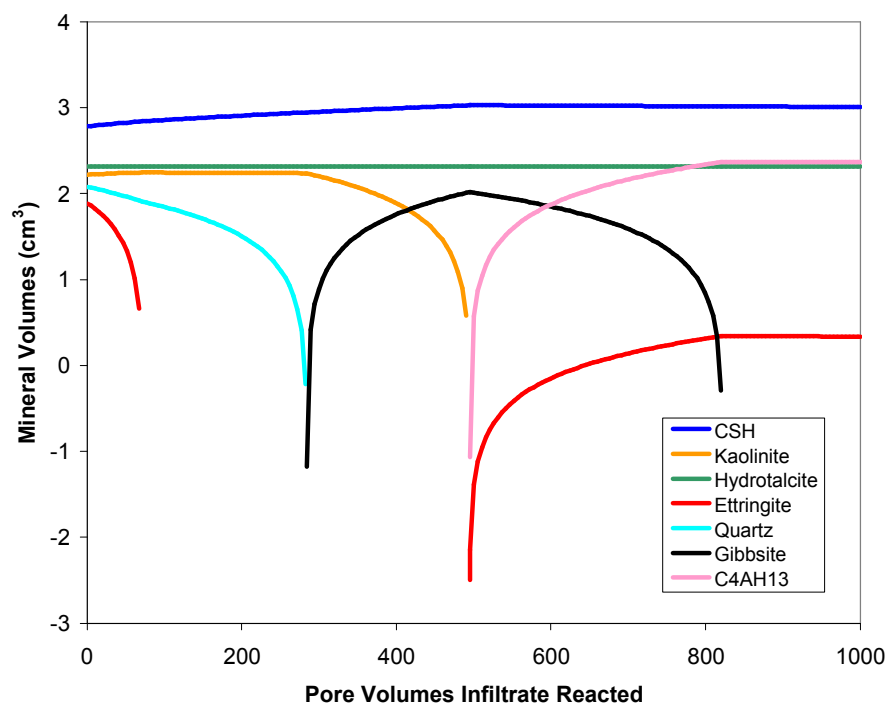


Figure 8: Results of scenario 5 (100% of the minerals available for reaction).

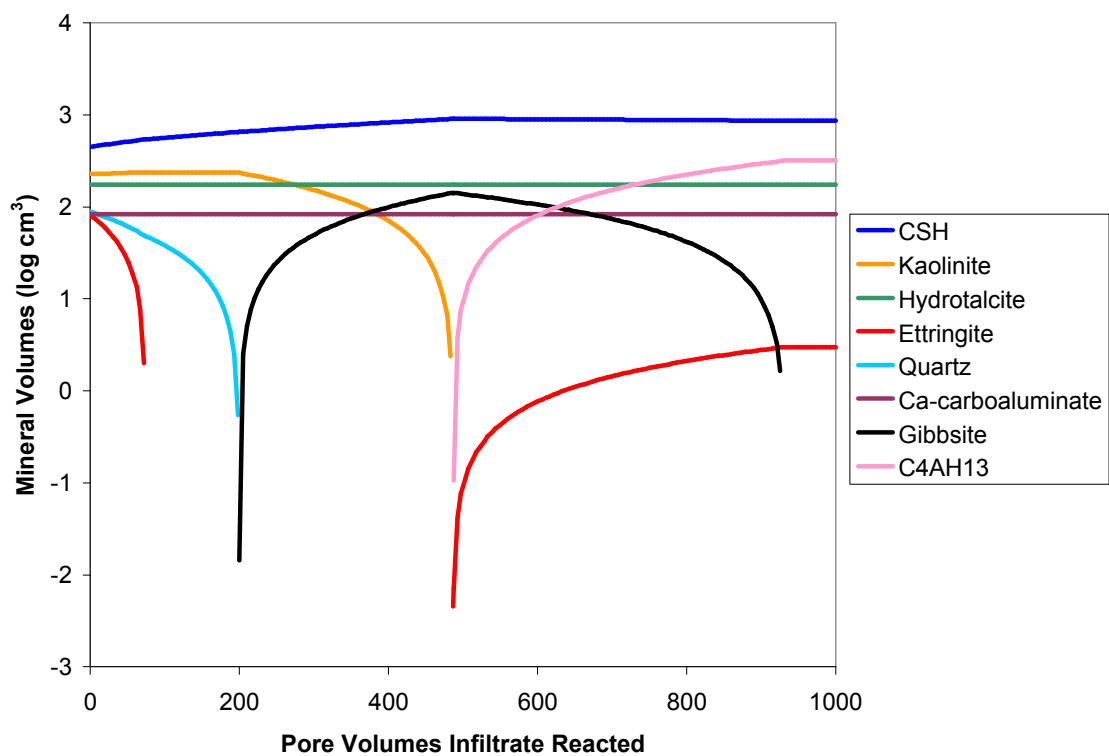


Figure 9: Results of Scenario 6 (100% of mineral matrix available for reaction).

Discussion

The most likely fluid compositions that may enter saltstone advectively are water that has equilibrated with the vault cement, soil water (groundwater), or rainwater. It is assumed here that soil water will not cause any reactions that are significantly different than rainwater. In all of these scenarios there is a net loss of ettringite from the initial saltstone mineral composition. As long as there is silica in the system available for reaction, it will react with these infiltrates and any ettringite to produce CSH. In these simulations the silica is present as kaolinite and the reaction is:

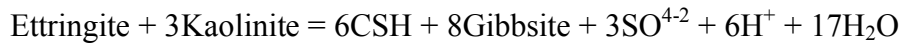


Figure 10 is a sulfate activity-pH diagram showing the stability of ettringite and monosulfate in the presence of silica (quartz in this case). For ettringite to be stable at a pH of 12 requires sulfate activity be greater than 10, higher than possible in saltstone. The initial precipitation of ettringite during hydration does not lead to degradation because it does not cause fractures to develop. In these simulations there is little late stage ettringite precipitation that could cause fracturing and degradation of the saltstone. There is precipitation of the less expansive phase C4AH13 that may cause a loss of porosity. This is discussed below.

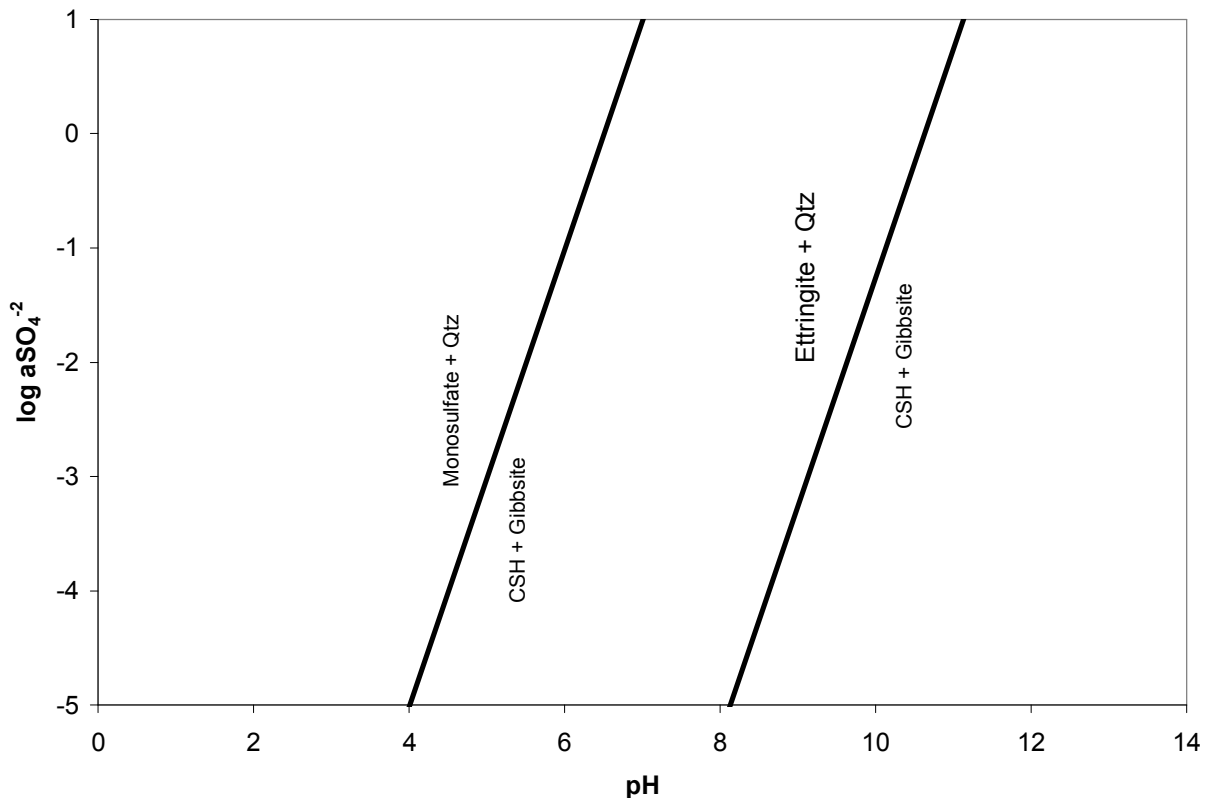


Figure 10: Stability of monosulfate and ettringite in the presence of silica as a function of sulfate activity and pH.

The other mechanism by which constituents that form expansive phases – calcium, aluminum, sulfate, and carbonate – could enter the saltstone matrix is diffusion from the vault walls or surrounding soil. However, diffusion of these constituents into saltstone is unlikely because the necessary concentration gradients are unlikely to develop. It is assumed here that most of the calcium, aluminum, sulfate, and carbonate present in the initial fluid used to mix the saltstone and vault cements are precipitated during cement hydration (WSRC, 1992). If this is the case, their concentrations in the equilibrium pore fluids of the vault wall and the saltstone itself should be similar and no diffusion from the vault wall into the saltstone should occur. If this is not the case, then aluminum, sulfate, and carbonate will diffuse out of saltstone, rather than into saltstone, because the concentrations of these in the initial salt feed water used to make saltstone is very high. The equilibrium activity of calcium in the vault wall pore fluid could be higher than that in saltstone and calcium might diffuse into saltstone. Even were that to happen, the amount of ettringite that would precipitate would be limited by the sulfate concentration of the saltstone pore fluid. The highest sulfate concentration expected in the initial salt feed to saltstone is 0.08 molal. Thus, if all of the sulfate in a 1 liter pore volume reacted with calcium diffusing into saltstone, 19 cm³ of ettringite could be precipitated. This would fill only 2% of the porosity. Thus, scenarios in which constituents diffuse into the saltstone grout causing expansive phase precipitation were considered unlikely and were not addressed by numerical simulations.

There has been a considerable amount of work on expansive reactions in cement (e.g., Bournazel and Moranville, 1997; Malone et al., 1997; the entire collection of articles edited by Marchand and Skalny, 1999; Beaudoin, 2001; Tixier and Mobasher, 2003; Neville, 2004). However, there is no consensus as to how much precipitation of expansive phases can be tolerated by cement before fracturing ensues. This is because it depends on the specific cement, the rate of precipitation, and even the location of precipitation within the matrix of the cement. In addition, as shown here, the amount of expansive phases that can precipitate depends strongly on the amount of minerals available for reaction.

Glasser (1999) argues quite effectively that precipitation of high molar volume phases does not necessarily result in expansion of cement. He makes the point that the volume of water used in precipitation of ettringite is large. One mole of ettringite has a volume of 717 cm³, but the reaction to produce it from dissolved components uses 26 moles of water. This water, at 25°C and 1 bar pressure, had a volume of 468 cm³ in the pore space in which the ettringite precipitated. Therefore, the net volume increase is 249 cm³ when a mole of ettringite precipitates from solution, rather than 717 cm³. If it precipitates from a reaction involving an existing mineral, the volume lost by reaction of this mineral must also be accounted for.

Another factor to consider when evaluating cement degradation by expansive phases is that the net volume change when expansive phases precipitate depends on the specific reactions. As an example, Table 9 shows the net volume increase for different pathways of 1 mole of ettringite precipitation, including the water lost, but neglecting the volumes of dissolved species. The highest net volume increase occurs when ettringite is precipitated from all dissolved species. In contrast, when ettringite is precipitated by reaction of dissolved aluminum and sulfate with CSH, there is a net mineral volume loss. The actual reaction path may be very difficult to determine, because truly quantitative analyses of the solid phases involved is difficult. Hence,

Table 9: Molar volume change for 5 reactions that precipitate ettringite (includes volumes of mineral phases and water, but not dissolved constituents).

Reactant Phases	Molar Volume Increase (cm ³)
$12\text{OH}^- + 6\text{Ca}^{+2} + 2\text{Al}^{+3} + 3\text{SO}_4^{-2} + 26\text{H}_2\text{O} = \text{Ettringite}$	249
$6\text{CSH} + 2\text{Al}^{+3} + 3\text{SO}_4^{-2} + 26\text{H}_2\text{O} = \text{Ettringite} + \text{Quartz}$	2
$6\text{CSH} + 2\text{Al}^{+3} + 3\text{SO}_4^{-2} + 26\text{H}_2\text{O} = \text{Ettringite} + \text{SiO}_2(\text{aq})$	-134
$2\text{Gibbsite} + 6\text{OH}^- + 6\text{Ca}^{+2} + 3\text{SO}_4^{-2} + 26\text{H}_2\text{O} = \text{Ettringite}$	185
$3\text{Gypsum} + 12\text{OH}^- + 3\text{Ca}^{+2} + 2\text{Al}^{+3} + 20\text{H}_2\text{O} = \text{Ettringite}$	133

a complete analysis of fracturing potential requires consideration of many factors, some of which may never be known with certainty. However, the low volume increases predicted here for reactions in saltstone are unlikely to be the cause of future fracturing, if fracturing is caused by the stress exerted by filling porosity.

For this initial analysis of expansive phase precipitation in saltstone, the most important result is the changes in mineral volume during reaction of the saltstone with the infiltrating fluid. This is presented in Figure 11 as the percent change in porosity for each scenario.

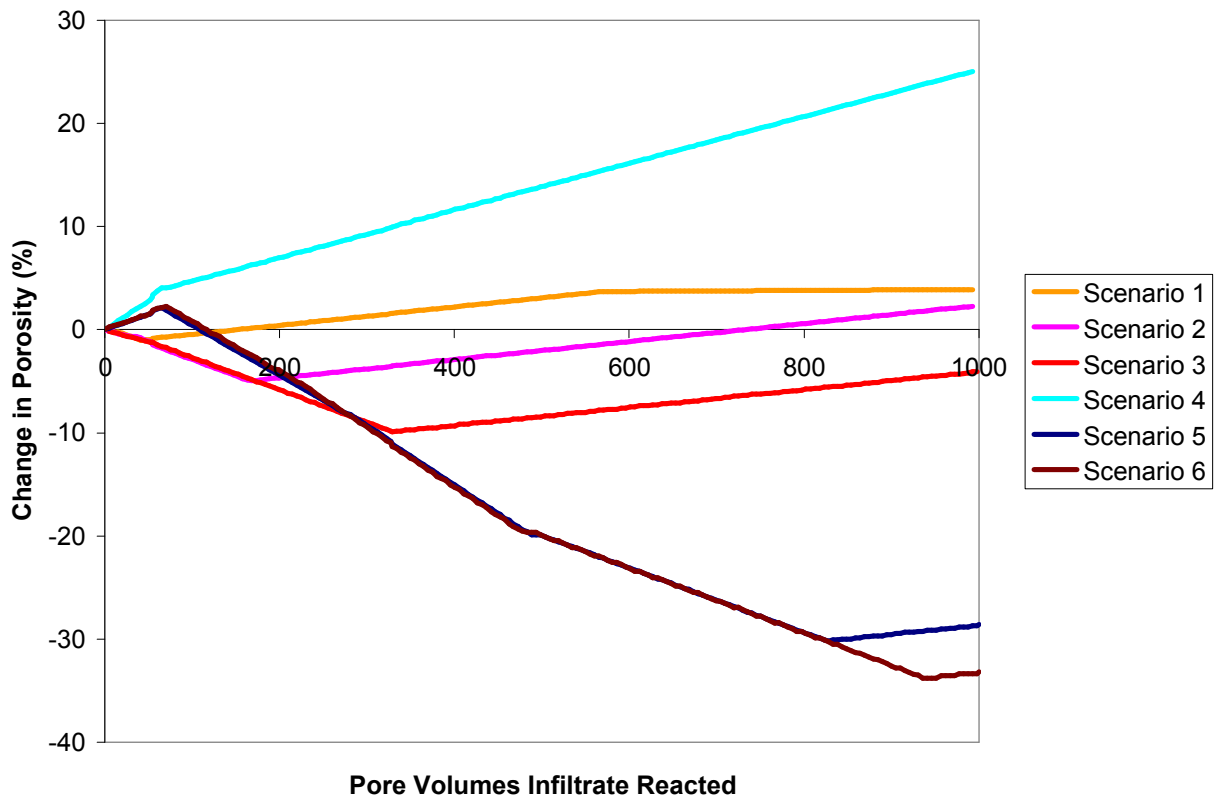


Figure 11: Change in saltstone porosity during simulations, negative values mean porosity was filled.

The results of scenarios 1, 2, and 3 demonstrate that the amount of minerals available to react with infiltrating pore fluid is very important to the amount of porosity lost by expansive phase precipitation. The maximum amount, about 10%, is lost when 100% of the saltstone minerals are available for reaction. Scenario 4 compared to scenario 3 shows that the infiltrating fluid also makes a difference. If the fluid is far from saturated with vault cement minerals, like the rainwater in scenario 4, dissolution of saltstone minerals occurs rather than precipitation of expansive phases. Comparison of the results of scenarios 3, 5, and 6 illustrates that the saltstone formulation is also important to the precipitation of expansive phases. The initial porosity increase in scenarios 5 and 6 is caused by dissolution of ettringite. This is followed by porosity decrease caused by the precipitation of CSH until all of the kaolinite has reacted to gibbsite, and no additional silica is available for reaction. From this point on, porosity decrease is caused by precipitation of the expansive phases ettringite and C4AH13. The maximum porosity loss in scenarios 5 and 6 is 30% for scenario 5 and 34% for scenario 6. The difference in the mineralogy of the formulations appears to be that the formulation used in scenarios 1-4 has much less kaolinite relative to hydrotalcite and CSH than formulations used in scenarios 5 and 6.

The results of the simulations reported here show that the maximum porosity loss for these saltstone formulations and compositions of infiltration is 34%. It should also be noted that these simulations only consider porosity loss due to mineral precipitation. A more thorough analysis of fracture potential due to mineral precipitation should also consider the loss of water from the fluid during mineral precipitation. For example, most of the 34% loss of porosity in scenario 6 is from precipitation of C4AH13. The increase in mineral volume of the reaction



is 213 cm³ per mole of C4AH13 formed. However, there is a total volume loss of 38 cm³ if water that is transferred from the fluid into the C4AH13 is considered. This could be important if there is a component of hydraulic pressure required to initiate fractures by expansive phase precipitation.

Uncertainties

- The mineralogy of the vault cement will evolve with time producing a somewhat different composition pore fluid with time. In scenarios that used infiltration equilibrated with vault cement a constant composition fluid was used to react with saltstone. The change in mineralogy of the vault cement with time would likely produce a fluid with a lower pH and a lower Ca⁺² concentration. Precipitation of expansive phases from reactions involving this fluid is less likely.
- This analysis is for the equilibrium case only. If kinetics cause different phases to precipitate at different times, the reaction paths could be different. Likewise, if original minerals become coated by precipitating phases, they may become unreactive and reaction paths could change. Kinetic controls or coating of solid phases could change reaction paths to cause precipitation of either more or less expansive phases, depending upon which reactions are kinetically controlled or which solid phases are coated. Useful

simulation of these controls is not possible without additional experimental information. Nevertheless, the equilibrium case provides the starting point for any analysis of potential fracturing due to expansive phases.

- The fraction (f) of porosity that must be filled by expansive phases before fracturing can ensue is unknown. If it is ≥ 0.30 – the median value of several cements estimated by Tixier and Mobasher (2003) – then fracturing due to expansive phase precipitation is unlikely given the conditions stated in this analysis. It should be noted that the low values of f estimated by Tixier and Mobasher (2003) were for a sulfate resistant cement that showed very little volumetric expansion despite the low f value.
- The long-term behavior of gel-like phases is unknown. CSH and silica may exist primarily as gels. The long-term behavior of these gels is uncertain and could affect the reaction paths.
- This analysis assumes that the minerals in saltstone are homogeneously distributed. A heterogeneous distribution could result in more porosity being filled in some areas and less in others.

Conclusions

The following conclusions were reached. They should be viewed in light of the uncertainties associated with fracturing by expansive phases and should recognize that this analysis only considers fracturing that initiates in pores where an increase in stress caused by expansive phase precipitation exceeds the strength of the pore walls.

- Given the volume of pore space that remains in all of the scenarios and the slow infiltration of water, fracturing of saltstone by expansive phases is not probable, assuming equilibrium is maintained. The maximum porosity loss during any scenario was 34%, slightly above the estimates by Tixier and Mobasher (2003) for the percent of porosity that must be filled before fracturing ensues (median = 30%).
- The total volume changes depend proportionally on the amount of minerals available for reaction. The amount of minerals available in saltstone is not well constrained.
- If ettringite or other expansive phases precipitate, it does not necessarily result in fracturing. The total volume change must be sufficient to cause fracturing. The amount of porosity loss that saltstone can sustain before fracturing ensues is unknown.
- If there is a component of hydraulic pressure to initiating a fracture, the loss of water from the pore fluid by incorporation into expansive phases must be considered.

References Cited

- Beaudoin, J.J., 2001. Dimensional changes, in Handbook of Analytical Techniques in Concrete Science and Technology, V.S. Ramachandran and J.J. Beaudoin, eds. William Andrew Publishing/Noyes, p. 368-402.
- Bennett, D.G., D. Read, M. Atkins, and F.P. Glasser, 1992. A thermodynamic model for blended cements. II: Cement hydrate phases; thermodynamic values and modelling studies. Journal of Nuclear Materials, 190, 315-325.
- Bethke, C.M., 2002. The Geochemist's Workbench®. University of Illinois, Champaign IL, 224 p.
- Bournazel, J.P. and M. Moranville, 1997. Durability of concrete: The crossroads between chemistry and mechanics. Cement and Concrete Research, 27, 1543-1552.
- Brown, P.W. and H.F.W. Taylor, 1999. The Role of Ettringite in External Sulfate Attack, in Materials Science of Concrete: Sulfate Attack Mechanisms, Marchand, J. and J.P. Skalny, eds., The American Ceramic Society, Westerville OH, 73-98.
- Clifton, J.R. and J.M. Ponniersheim, 1994. Sulfate Attack of Cementitious Materials: Volumetric Relations and Expansions. NISTIR 5390. National Institute of Standards and Technology, Gaithersburg, MD 20899.
- Dixon, K.L., M.A. Phifer, and J.R. Harbour, 2008. Task Technical and QA Plan: Saltstone Grout and Vault Concrete Sample Preparation and Testing. WSRC-TR-2008-00037. Washington Savannah River Company, Aiken, SC.
- Glasser, F.P., 1999. Reactions Between Cement Paste Components and Sulfate Ions, in Materials Science of Concrete: Sulfate Attack Mechanisms, Marchand, J. and J.P. Skalny, eds., The American Ceramic Society, Westerville OH, 99-122.
- Harbour, J.R., E.K. Hansen, T.B. Edwards, V.J. Williams, R.E. Eibling, D.R. Best, and D.M. Missimer, 2006. Characterization of Slag, Fly Ash, and Portland Cement for Saltstone. WSRC-TR-2006-00067, Rev. 0. Washington Savannah River Company, Aiken, SC.
- Harris, A.W., M.C. Manning, W.M. Tearle, and C.J. Tweed, 2002. Testing of models of the dissolution of cements – leaching of synthetic CSH gels. Cement and Concrete Research, 32, 731-746.
- HSC Database, HSC Chemistry for Windows, Version 3.0. Outokumpu Research, Finland.
- Langton, C.A., 1984. Physical Properties of Saltstone: A Savannah River Plant Waste Form. DP-MS-84-112. E.I. du Pont de Nemours and Company, Aiken SC.

- Langton, C.A., 1987. Analysis of Saltstone Pore Solutions PSU Progress Report IV. DPST-87-530, E.I. du Pont de Nemours and Company, Aiken SC.
- Malek, R.I.A., D.M. Roy, M.W. Barnes, and C.A. Langton, 1985. Slag Cement – Low-level Waste Forms at the Savannah River Plant. DP-MS-85-9, E.I. du Pont de Nemours and Company, Aiken SC.
- Malone, P.G., T.S. Poole, L.D. Wakeley, and J.P. Burkes, 1997. Salt related expansion reactions in Portland-cement-based wasteforms. *Journal of Hazardous Materials*, 52, 237-246.
- Marchand, J. and J.P. Skalny, eds., 1999. *Materials Science of Concrete: Sulfate Attack Mechanisms*. The American Ceramic Society, Westerville OH, 371 p.
- Neville, A., 2004. The confused world of sulfate attack on concrete. *Cement and Concrete Research*, 34, 1275-1296.
- Park, J-Y. and B. Batchelor, 2002. General chemical equilibrium model for stabilized/solidified wastes. *Journal of Environmental Engineering*, 128, 653-661.
- Pitzer, K.S., 1973. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *The Journal of Physical Chemistry*, 77, 268-277.
- Reardon, E.J., 1990. An ion interaction-model for the determination of chemical-equilibria in cement water-systems. *Cement and Concrete Research*, 20, 175-192.
- Reardon, E.J. and P. Dewaele, 1990. Chemical model for the carbonation of a grout/water slurry. *Journal of the American Ceramics Society*, 73, 1681-190.
- Strom, R.N. and D.S. Kaback, 1992. Groundwater Geochemistry of the Savannah River Site and Vicinity (U). WSRC-RP-92-450, Westinghouse Savannah River Company, Aiken SC.
- Tixier, R. and B. Mobasher, 2003. Modeling of damage in cement-based materials subjected to external sulfate attack. II: Comparison with experiments. *Journal of Materials in Civil Engineering*, 15, 314-322.
- WSRC-RP-92-1360, 1992, Radiological Performance assessment for the Z-Area Saltstone Disposal Facility, Westinghouse Savannah River Company, Aiken SC.