

APPENDIX D

**EFFECTS OF CEMENTITIOUS MATERIAL
ON UNSATURATED ZONE FLOW AND TRANSPORT
(RESPONSE TO ENFE 1.04)**

Note Regarding the Status of Supporting Technical Information

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

APPENDIX D

EFFECTS OF CEMENTITIOUS MATERIAL ON UNSATURATED ZONE FLOW AND TRANSPORT (RESPONSE TO ENFE 1.04)

This report provides a response for Key Technical Issue (KTI) agreement Evolution of the Near-Field Environment (ENFE) 1.04. This agreement relates to providing additional information on the technical basis for evaluating the impact of emplaced cementitious materials on the hydrologic properties of the unsaturated zone below the repository horizon and consequent effects on radionuclide transport in this region.

D.1 KEY TECHNICAL ISSUE AGREEMENT

D.1.1 ENFE 1.04

Agreement ENFE 1.04 was reached during the U.S. Nuclear Regulatory Commission (NRC)/U.S. Department of Energy (DOE) Technical Exchange and Management Meeting on Evolution of the Near-Field Environment (Reamer 2001) held January 9 to 12, 2001, in Pleasanton, California. ENFE Subissues 1, 2, 3, and 4 were discussed at that meeting. ENFE 1.04 was discussed under Subissue 1, Effects of Coupled Thermal-Hydrologic-Chemical Processes on Seepage and Flow.

At this meeting, DOE presented material on Subissue 1: Comments on Effects of Cementitious Materials (Hardin 2001), concluding that effects of cementitious materials on performance were expected to be modest and proposing additional modeling to support this conclusion.

The wording of the agreement is as follows:

ENFE 1.04

Provide additional technical bases for the DOE's treatment of the effects of cementitious materials on hydrologic properties. The DOE will provide additional information on the effects of cementitious materials in an update to the *Unsaturated Zone Flow and Transport* PMR (TDR-NBS-HS-000002), available in FY 02. Information provided will include results of evaluation of the magnitude of potential effects on hydrologic properties and radionuclide transport characteristics of the unsaturated zone.

D.1.2 Related Key Technical Issues

ENFE 2.04 is related to this agreement in that it is concerned with trace elements and fluoride concentrations that may be introduced to the repository emplacement drifts through materials, including cement grout. ENFE 2.04 was addressed in *Technical Basis Document No. 5: In-Drift Chemical Environment*, in which the issues regarding cementitious materials were not considered because cementitious materials have been removed from the emplacement drift design (Ziegler 2003).

D.2 RELEVANCE TO REPOSITORY PERFORMANCE

Cementitious material (shotcrete) is planned for use as part of the ground support for the turnout intersections of the main access drifts and for the intersections of the exhaust drifts with the emplacement drifts. The incorporation of cementitious materials in the repository poses two concerns. The first is that the leaching of cementitious materials, particularly the shotcrete supporting the turnout intersections in the main access drifts and the intersections of the exhaust main drifts with the emplacement drifts, will affect repository performance by modifying the hydrologic properties of the surrounding rock and diverting the flow of water entering the drifts. The second concern is that an alkaline plume resulting from leaching of the cementitious material could enhance radionuclide transport to the accessible environment, either through the complexation of radionuclides or through the presence of pseudocolloids.

The original relevance of this agreement to repository performance is described in features, events, and processes (FEPs) that relate to cementitious materials in the repository. These FEPs are described and screened in a series of analysis and model reports. Revised screening summaries for these FEPs will be added to the next revision of the FEP analysis and model reports.

The original relevance of this agreement to repository performance is described in the following FEP:

- **2.1.06.01.0A, Chemical Effects of Rock Reinforcement and Cementitious Materials in the Engineered Barrier System** (BSC 2004a, Section 6.2.18)—Degradation of ground support material (cement, rock bolts, wire mesh) used for any purpose in the disposal region may affect long-term performance through both chemical and physical processes. Degradation may occur by physical, chemical, and microbial processes.

This FEP is excluded from total system performance assessment for license application because cementitious material (i.e., cement grout in ground support) is no longer part of the emplacement drift design for the engineered barrier system (BSC 2004b, Section 4.3).

The following related FEPS also consider the effects of cementitious materials:

- **2.1.09.01.0A, Chemical Characteristics of Water in Drifts** (BSC 2004a, Section 6.2.45)—When flow in the drifts is reestablished following the peak thermal period, water may have chemical characteristics influenced by the near-field host rock and engineered barrier system. Specifically, the water chemistry (pH and dissolved species in the groundwater) may be affected by interactions with cementitious materials or steel used in the disposal region. These point source contaminated waters may coalesce to form a larger volume of contaminated water. This altered groundwater is referred to as the carrier plume because dissolution and transport will occur in this altered chemical environment as contaminants move through the engineered barrier system and down into the unsaturated zone. (There is no defining limit as to what volume of contaminated water constitutes a plume.)

- **2.2.01.01.0B, Chemical Effects of Excavation/Construction in the Near-Field** (BSC 2004c, Section 6.8.2)–Excavation may result in chemical changes to the incoming groundwater and to the rock in the excavation-disturbed zone.
- **2.1.09.17.0A, Formation of Pseudocolloids (Corrosion Product) in the Engineered Barrier System** (BSC 2004d, Section 6.2.29)–Pseudocolloids are colloidal-sized assemblages (between approximately 1 nm and 1 μm in diameter) of nonradioactive material that has radionuclides bound or sorbed to it. Corrosion product pseudocolloids include iron oxyhydroxides from corrosion and degradation of the metals in the engineered barrier system and silica from degradation of cementitious materials.

These FEPs are excluded from total system performance assessment for license application because all introduced cementitious materials inside the repository are to be removed (at closure) except for ground support. These materials include all concrete structures (including inverters), as well as concrete or shotcrete used to support shafts, which is an exception to the nonremoval of ground support materials (BSC 2004b, Section 4.3). The potential effects of the cementitious material in the ground support are not significant to repository performance.

D.3 RESPONSE

There are two principal concerns relating to the incorporation of cementitious materials in the repository. The first concern is that the leaching of cementitious materials, particularly those supporting the turnouts in the main access and exhaust main drifts to the emplacement drifts, will affect repository performance by modifying the hydrologic properties of the surrounding rock and diverting groundwater flow. The second concern is that an alkaline plume could enhance radionuclide transport to the accessible environment, either through the complexation of radionuclides or through the presence of pseudocolloids. Both concerns become relevant only after the repository environment rehydrates following a period of dryout due to heating caused by radioactive decay of the emplaced waste. The dryout period is the period commencing with the boiling of water contained in the pores of the host rock mass surrounding the emplacement drifts after repository closure and ending when the affected rock mass has rehydrated.

An evaluation of the processes involved led to the following findings:

- Because the removal of all nonsupport cementitious materials from the repository is planned prior to closure, the only remaining cementitious materials would be shotcrete supports in the main access and exhaust ventilation drifts and minor quantities of grout used to secure rock bolt supports. Current plans also provide an option for tailoring the shotcrete and grout formulations to ensure that their subsequent alteration and degradation following repository closure do not adversely impact repository performance from geochemical or hydrologic perspectives.
- Both prior to and subsequent to repository closure, shotcrete and grout would be subject to degradation processes involving recrystallization and carbonation of reactive cement ingredients. Following closure, these processes would be accelerated due to increasing temperature, humidity, and CO_2 partial pressure ($p\text{CO}_2$) within the repository. Calculations indicate that, with optimal shotcrete mixes, hydrothermal recrystallization

rates would lead to substantially complete conversion of the cementitious component to silica-rich calcium silicate hydrates prior to rehydration following the repository dryout period. Upon reaction with pore water, these silica-rich phases would generate a leachate with a pH ranging between 10.1 and 10.7 but with concentrations of Ca^{2+} and dissolved silica equivalent to that of currently observed pore waters. Neutralization of the leachate by ambient CO_2 would not result in significant precipitation of calcite and would not, therefore, cause significant modification of the host-rock matrix and fracture permeability or the hydrologic regime.

- Following repository closure, gaseous CO_2 causing carbonation of the shotcrete and grout is restricted to sources within Yucca Mountain. Most will originate through pore-water evaporation due to heating of the rocks surrounding the emplacement drifts. Simple mass-balance calculations indicate that more than sufficient CO_2 would be available to carbonate all shotcrete and grout remaining in the repository. The extrapolation of a concrete carbonation model to 120°C indicates that the rates of carbonation would be so high that carbonation would instead be limited by the diffusion of CO_2 through the host-rock fractures and matrix. Calculations indicate that substantially complete carbonation would occur wherever the dryout period exceeds 1,000 years. This suggests that the shotcrete contained in the main access and exhaust drifts contiguous to the emplacement panels in the interior of the repository would be completely carbonated. However, shotcrete in the peripheral drifts would not be completely carbonated. The kinetics of carbonation by CO_2 gaseous phase diffusion into the shotcrete following rehydration would be hindered, and it is estimated that up to 5,000 more years would elapse before complete carbonation of the remaining shotcrete. Under these conditions, the carbonation reaction kinetics would be rate controlling rather than gaseous CO_2 diffusion through the repository host rocks.
- Because calculations indicate that shotcrete would be substantially altered to silica-rich calcium silicate hydrate phases, and separate calculations indicate that the shotcrete would be partially if not completely carbonated, this suggests that the competition between the two processes will result in a shotcrete degradation product that would be limited in its potential to generate an alkaline plume following rehydration.
- The rate of cementitious material recrystallization or carbonation at the elevated temperatures, humidity, and $p\text{CO}_2$ likely to be encountered in the repository during the thermal period (i.e., that period following repository closure when temperatures are significantly above those prior to emplacement) is not known with any degree of precision. Carbonation reactions are also thermodynamically less favored at elevated temperatures. Carbonation of silica-rich hydrated calcium silicates would also be slower than for portlandite or hydrated calcium silicate gels in freshly mixed cement. Therefore, carbonation at elevated temperatures could be less than predicted on the basis of extrapolated kinetic rates based on activation energies determined at ambient temperatures (assumed to be 25°C in this appendix).
- It is instructive to consider the unlikely possibility that some materials remain that would cause the generation of alkaline solutions following rehydration. The results show that the neutralization of the alkaline leachate by ambient CO_2 in the repository would be

very fast (i.e., on the order of weeks). At the slow percolation rates of pore waters in the rock matrix, all secondary precipitation of calcite is likely to occur within centimeters of the shotcrete interface. Indeed, a finite probability exists that calcite precipitation will occur primarily in situ and that no migration of an alkaline plume would take place. Thus, the issue of alkaline plumes affecting radionuclide transport would be considered extremely unlikely.

- The important question regarding the impact that the precipitation of calcite would have in sealing the host-rock matrix and fractures beneath shotcrete supports in the main access and exhaust ventilation drifts is difficult to assess. Using very conservative assumptions that all the portlandite in Type II cement of the shotcrete was available for leaching following rehydration and that calcite would precipitate within the pores and fractures immediately below the main turnoff intersection footprints, the matrix and fractures of the host rock would be filled to a depth of approximately 7 cm with calcite and to a depth of approximately 4.4 cm below the intersection of the exhaust main and the emplacement drift. If only a 1-cm thickness of rock were to be filled with calcite before it became completely impermeable and if subsequent precipitation were to take place laterally, the impermeable zone would extend an additional 8.4 m toward the emplacement drift on the main access drift side and an additional 7.1 m from the exhaust drift side. However, the standoff of the shotcreted portion of the turnout is a minimum of 60 m distance from the start of the emplacement drift. Therefore, it is unlikely that calcite precipitation would adversely affect the hydrology of the emplacement drift on the main access drift side. However, the situation would be different on the exhaust drift side, where calcite precipitation and sealing would extend laterally to within 1.5 m of the first waste package. The possibility that such sealing would occur is unlikely, however, because the shotcrete formulation can be modified to prevent the leaching of the components that would cause calcite precipitation. Furthermore, carbonation and recrystallization of the cement fraction prior to rehydration would limit leaching of calcite-forming components.
- If it is assumed that the shotcrete would be so altered that calcite precipitation adjacent to the shotcrete would not significantly modify the local hydrology, then the emplaced shotcrete is separated from the nearest waste package in the emplacement drift by a sufficiently large horizontal distance that diffusive mixing at depth of separate plumes from the leaching of shotcrete and radionuclides released by a failed waste package would not occur. However, diffusive mixing of analogous separate plumes at exhaust drift intersections is possible.
- Although the leachate from shotcrete altered by recrystallization and carbonation would be significantly alkaline, the alkalinity would be rapidly neutralized by ambient CO₂ in the vicinity of the emplaced shotcrete. The neutralized plume would differ little in composition from pore water in the repository and would, therefore, have only a minor impact on radionuclide migration, if the neutralized plume were to intersect and mix with a plume bearing radionuclides.
- Colloid generation and transport through leaching of cementitious material could take place only when the grout is young (i.e., prior to extensive hydrothermal

recrystallization and carbonation). Such processes, therefore, can occur only during the initial period following repository closure prior to dryout, when heating is close to its maximum intensity and when the likelihood of waste package failure is minimal. Furthermore, the relatively high ionic strength of the highly alkaline leachate will destabilize the mobilized calcium silicate hydrate colloidal particles, causing aggregation and adhesion. The maximum residual colloid concentration would be comparable or lower than that in the ambient environment. Thus, despite the fact that some radionuclides sorb strongly to such colloidal particles, the colloid concentration would be sufficiently low so that radionuclide sorption on the residual colloid will be of no consequence.

The information in this report is responsive to agreement ENFE 1.04 made between DOE and NRC. The report contains the information that DOE considers necessary for NRC review for closure of this agreement.

D.4 BASIS FOR THE RESPONSE

D.4.1 Background

Earlier repository designs involved the extensive use of concrete and other cementitious materials in the underground facility (Hardin 1998, p. 6-12). Of particular importance was the application of Type II expansive cement for the grouting of rock bolt supports to stabilize the emplacement drifts in order to ensure retrievability until such time as the NRC approves repository closure, the incorporation of a concrete invert structure to facilitate emplacement of the waste packages, and waste package concrete support structures.

A program was implemented to address issues relating to the presence of cementitious materials in the emplacement drifts and their impact on waste package integrity and radionuclide transport in the event of waste package failure (Younker 1996; Meike 1996; Hardin 1998; CRWMS M&O 1998). At the time, the waste package design consisted of a mild steel sacrificial (corrosion allowance) outer barrier over an inner Alloy 22 (UNS N06022) corrosion-resistant barrier. These studies uncovered several issues that increased both complexity and uncertainty in the repository design. Of particular concern were issues relating to the leaching of cementitious materials with mobilization of fluoride (CRWMS M&O 2000; Hardin 2001) and the potential production of residual CaCl_2 - MgCl_2 brines, both of which could result in enhanced corrosion of the steel outer barrier of the waste package (Hardin 1998, p. 6-12). It was determined that alkaline fluids could substantially increase outer barrier corrosion, leading to peak waste package failures at about 6,200 years (DOE 1998, p. 5-19). In addition to effects on the waste package, the extreme alkalinity of the leachate (moving as an alkaline plume) was a concern for decreasing radionuclide sorption in the unsaturated zone transport pathway because actinide sorption coefficients on tuff decreased to zero at high pH (Younker 1996, pp. 1 to 4; CRWMS M&O 1998; DOE 1998). In contrast, laboratory studies revealed that certain radionuclides (e.g., uranium and neptunium) were very strongly retarded within cementitious materials (Hardin 1998, pp. 6-42 to 6-45). Alkaline leachates may also tend to lower the activity of carbonate in solution, thereby potentially decreasing the concentration of uranyl and neptunyl carbonate complexes in solution (Hardin 1998, p. 6-36).

To address some of these concerns, a drip shield was incorporated in the design to protect the waste package from water infiltrating into the emplacement drifts, and the waste package design was modified to provide for a protective Alloy 22 outer barrier and a Stainless Steel Type 316 inner barrier (e.g., see BSC 2001).

When DOE and NRC met to discuss the status of the ENFE KTIs in January 2001, concerns regarding the introduction of cementitious materials were considered to be largely resolved. At this meeting, DOE presented material on Subissue 1: Comments on Effects of Cementitious Materials (Hardin 2001) and concluded that effects of cementitious materials on performance were expected to be modest but proposed additional modeling to support this conclusion.

Subsequently, however, a decision was made to eliminate all cementitious materials from the emplacement drifts, as reflected in *Engineered Barrier System: Physical and Chemical Environment Model* (BSC 2004e). This decision was based predominantly on the potential effects of cement on the chemistry of seepage waters and how this might affect waste package corrosion. Thus, the only aspect concerning Subissue 1 that remained to be addressed was NRC concerns regarding the presence of cementitious materials elsewhere in the repository and their potential interactions with the host rock (Hardin 2001).

A further reduction in the quantity of cementitious materials to remain in the repository after closure was affected with the requirement of *Ground Control for Non-Emplacement Drifts for LA* (BSC 2004f, Section 3.1.4.4.1) and *Subsurface Facility Description Document* (BSC 2004g, Section 3.1.1.4.13.1). This requirement specifies the removal of all noncommitted materials that could impact the long-term performance of the repository, including all concrete structures except those necessary for ground support. All concrete invert structures in all drifts and turnouts would, therefore, be removed prior to closure. Shaft concrete or shotcrete used to support shafts would also be removed. Therefore, the only significant cementitious materials remaining in the repository would be shotcrete supports and grout for rock bolt placement.

D.4.2 Cementitious Materials in the Current Repository Design

The repository incorporates introduced materials necessary for its effective functioning. Among these materials are cementitious materials, which are planned for ground support and concrete invert structures in all underground openings except the emplacement drifts. Three types of cementitious material will be used: cement grout, shotcrete, and concrete. Of these three materials, only cement grout and shotcrete are committed.

Current plans call for the removal of all cementitious materials not required for ground support. According to *Subsurface Facility Description Document* (BSC 2004g, Section 3.1.1.4.13.1):

The Subsurface Facility shall decommission, decontaminate as required, demolish, dismantle, and remove materials and equipment that cannot become permanent fixtures of the underground repository after closure in order to conform with repository long-term performance requirements that may be affected if those noncommitted materials are left underground.... Noncommitted materials are those materials excluded from the inventory of repository permanent committed materials as documented in analyses supporting Total System

Performance Assessment-License Application and shall be removed from the Subsurface Facility to prevent hydrological and geochemical conditions adverse to waste isolation.

It is, therefore, expected that almost all of the nearly 300,000 tons of concrete will be removed prior to repository closure. Therefore, for the purposes of the evaluation presented in this appendix, only the impact of shotcrete and grout requires further consideration.

The applications of the committed cementitious materials and quantities to be used are summarized in Table D-1. The information in this table is abstracted from *D&E/ PA/C IED Subsurface Facilities Committed Materials* (BSC 2004h) and *Turnout Drift Operations Configuration* (BSC 2004i), which represent current design concepts. The data contained in the table are illustrative only and may change as the design parameters are refined.

Table D-1. Summary of Committed Ground Support Cementitious Materials in Subsurface Openings of the Repository

| Subsurface Opening | Committed Material (metric tons) | |
|--|----------------------------------|----------------|
| | Cement Grout | Shotcrete |
| Emplacement Drift Turnouts | 324 | 0 |
| Turnout Intersections | 281 | 23,096 |
| Intersections (Exhaust Air Side) | 94 | 5,679 |
| Access/Exhaust Mains | 589 | 0 |
| North Construction Ramp | 110 | 11,061 |
| Exhaust Main | 32 | 0 |
| Intake/Exhaust Shaft | 0 | 0 |
| Shaft Access | 87 | 0 |
| Exhaust Raise (5 m diameter) | 0 | 0 |
| Exhaust Raise (2 m diameter) | 0 | 32 |
| Exhaust Raise Access | 5 | 0 |
| Main Slash | 40 | 0 |
| Intake Main Extension | 8 | 0 |
| Assembly/Disassembly Chambers | 15 | 0 |
| Ventilation Access | 8 | 0 |
| Intake Shaft Access | 53 | 0 |
| Observation Drift and Test Alcove | 23 | 0 |
| Exploratory Studies Facility Main Drift | 72 | 0 |
| Exploratory Studies Facility North Ramp | 124 | 12,098 |
| Exploratory Studies Facility South Ramp | 74 | 7,448 |
| TOTAL (Percentage of All Cementitious Materials) | 1,938 (3.16) | 59,413 (96.84) |

Source: BSC 2004h; BSC 2004i.

In terms of total mass, shotcrete dominates the committed cementitious materials. According to the compositions in Table D-2, grout and shotcrete contain approximately 63 and 18 wt %, respectively, of the most reactive component, cement.

Table D-2. Components of Cementitious Materials

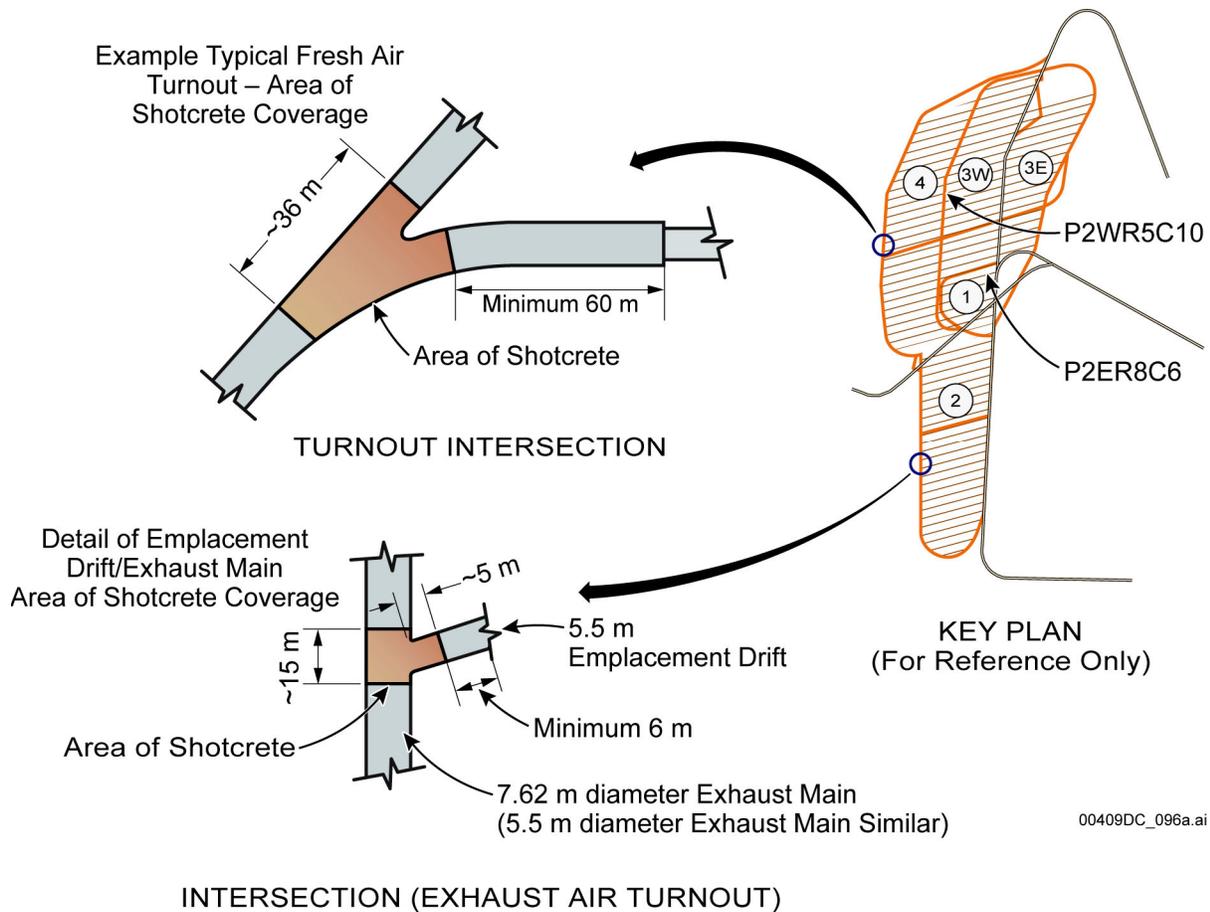
| Component | Grout (kg/m ³) | Shotcrete (kg/m ³) |
|-----------------------|----------------------------|--------------------------------|
| Cement, Unspecified | 1,228 | – |
| Cement, Type II | – | 437 |
| Water | 546 | 186 |
| Coarse Aggregate | – | 534 |
| Fine Aggregate | – | 1,203 |
| Silica Fume | 136 | 30 |
| Super-Plasticizer | 27 | – |
| Polyhead | – | 4.5 |
| Shotcrete Accelerator | – | 1.5 |
| Steel Fiber | – | 39 |

Source: BSC 2004h.

NOTE: Shotcrete also contains 0.09 kg/m³ of Micro Air.

It should be noted that the cement compositions specified in Table D-2 are less than optimal in terms of their reactivity and tendency to generate alkaline plumes upon leaching (DTN: LL020805523125.002). *Ground Control for Non-Emplacement Drifts for LA* (BSC 2004f, Section 6.5.4.2) suggests that a low pH grout and shotcrete and concrete mix will be developed with lesser amounts of Portland cement and silica fume, or, alternatively, other types of grouts and cements that are not of the Portland type could be used. For the purposes of the evaluation presented in this appendix, it will be conservatively assumed that Type II Portland cement will be used because this is the cement used in shotcrete. The issue of cement formulation is discussed further in Section D.4.4.

The cementitious materials most likely to affect repository performance are those associated with the intersections of emplacement drifts with the main access and exhaust drifts. Two types of intersections are specified: (1) the fresh-air side, where a 61-m-radius rail turnout from the 7.62-m-diameter circular main access drift transitions into the horseshoe-shaped 7-m-high by 8-m-wide turnout drift and (2) the exhaust-air side of the emplacement drift and the exhaust main drift intersection (Figure D-1). At these intersections, a 10-cm-thick layer of shotcrete will be applied over the backs of each drift to just below the springline on each side. In total, (1) approximately 36 m of the combined fresh-air main and horseshoe-shaped 7-m-high by 8-m-wide turnout drifts will be shotcreted, and (2) 15 m of the exhaust main and approximately 5 m of the turnout to the emplacement drift will be shotcreted for each emplacement drift. The quantities of shotcrete in each case are estimated to be 161 and 53 MT, respectively, for each turnout (BSC 2004h). Because the emplacement drift centerlines are 81 m apart, and the drifts subtend an angle of 70° to the main drifts over much of the repository, the emplacement drift centerlines will intersect the main drifts with a spacing of 86 m. If 36 m of shotcrete were applied to the main access drift at each intersection with an emplacement drift, then 42% of main access drift contiguous with the emplacement panels would be shotcreted. Similarly, with approximately 15 m of shotcrete applied at 86 m intervals to the exhaust main drifts, 17% of these drifts would be shotcreted contiguous to the emplacement panels. Each emplacement drift turnout will also contain 0.45 MT of grout for rock bolt placement.



Source: BSC 2003a.

Figure D-1. Schematic of the Current Planned Locations Where Cementitious Material Will Be Used in the Repository Intersections and Turnouts

In the following discussion, scientific and technical bases are presented that assess the impact of the shotcrete support structures and rock-bolt grout on repository performance, particularly in relation to potential modifications to the hydrology and the effect of cementitious leachates on radionuclide migration.

D.4.3 Environment to Which Cementitious Materials Would Be Exposed Following Repository Closure

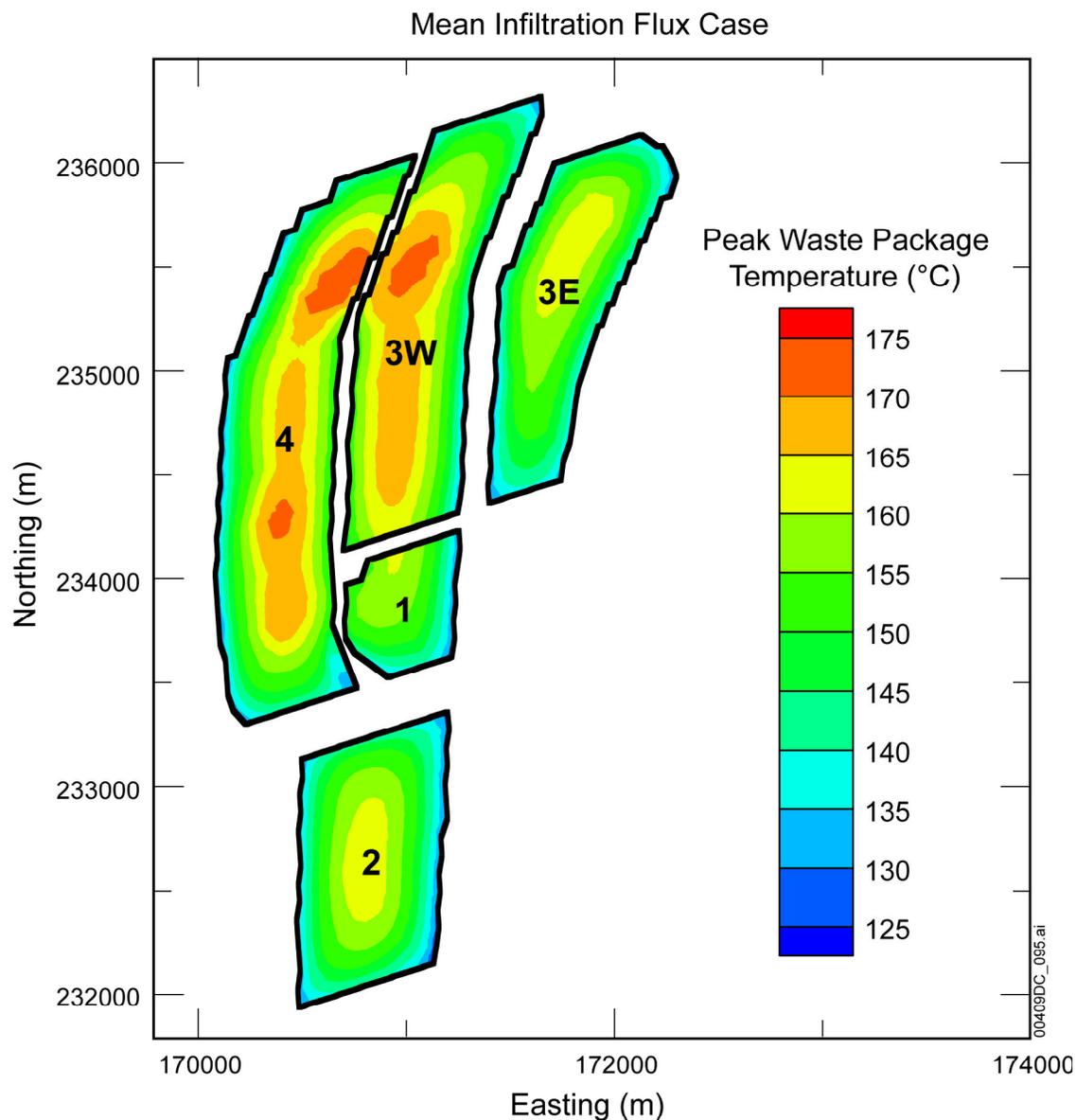
Upon closure of the repository, the cementitious materials would have aged for a period that could be as long as 100 years, depending on when they were installed during construction, the time required to load the repository, and the duration of the monitoring and performance confirmation period, during which retrievability would have to be maintained. During that time, cementitious materials would be subject to drying and carbonation under thermally driven ventilation, but the maximum temperature excursion to which these materials would be exposed is expected to be modest. The maximum temperatures would occur at the exhaust side of the emplacement drifts and should not exceed 85°C.

After repository closure, ambient temperatures would rise rapidly, and cementitious materials would be exposed to environmental conditions controlled by repository design parameters. The duration and magnitude of the postclosure temperature excursion, the corresponding relative humidity, and the $p\text{CO}_2$ changes to which cementitious materials would be exposed are discussed in the following sections.

Modeled predictions regarding thermal-hydrologic processes within the repository configuration following closure can be found in *Multiscale Thermohydrologic Model* (BSC 2004j, pp. 80 to 82, 95, 116 to 136). Figure D-2 shows that, for a mean infiltration flux case and representative pwr1-2 waste package (BSC 2004j, Table 6.3-10), the peak temperatures adjacent to the main access and exhaust main drifts would range between 130°C and 160°C, although waste packages in a small region adjacent to the northwest margin of Panel 3W could exceed 170°C.

The base-case temperatures of waste packages adjacent to the main access and exhaust main drifts are predicted to fall below the boiling point between 200 and 1,200 years after closure, with the temporal distribution correlating closely with the temperature distribution shown in Figure D-2. This waste package temperature distribution is used as a basis for estimating the maximum temperatures expected in the adjacent main access and exhaust drifts in the repository. The small region of the exhaust main drift adjacent to the northwest margin of Panel 3W in Figure D-2 would be expected to remain above the boiling temperature for the longest time (1,200 years). The evolution of relative humidity would be variable, depending on locality within the repository. At position P2ER8C6 (Figure D-1), adjacent to the main access drift (see BSC 2004j, Figures 6.3-1 and 6.3-7d), the relative humidity would range from a low of 17% after closure for 60 years to approximately 90% after closure for 2,000 years. In location P2WR5C10 (Figure D-1), near the hottest region of the exhaust main drifts, noted above (BSC 2004j, Figures 6.3-1 and 6.3-9d), the relative humidity would fall to about 15% after 40 years and recover to about 90% after 2,000 years, a time when the region occupied by the emplacement drifts would have rehydrated and when leaching of cementitious materials would become operative.

The excursion of $p\text{CO}_2$ during a period of 7,000 years has been modeled in the region surrounding the emplacement drifts (BSC 2004k, Figure 6.4-16). Carbon dioxide would evolve from evaporating pore waters during heating of the rock matrix adjacent to the emplacement drifts and, to a substantially smaller extent, during calcite dissolution as a result of the increasing ambient $p\text{CO}_2$ (BSC 2004l). The initial phase of dryout of the host rocks surrounding the emplacement drifts would cause the generation of a steam atmosphere. The steam would dilute the concentration of CO_2 in the vapor phase in the emplacement drifts, causing it to fall to very low values between closure and eventual rehydration. According to *Drift-Scale Coupled Processes (DST and THC Seepage) Models* (BSC 2004l, Figure 6.5-8), CO_2 partial pressures at the rock in fractures adjacent to the emplacement drift would range from between ambient (1,000 ppmV) and as low as 1 ppmV during that period. The steam, together with the CO_2 , would be displaced outward where the steam would condense, causing a differential enrichment of CO_2 in the residual vapor phase and an increase in the $p\text{CO}_2$ in the main access and exhaust main drifts of the repository. Mountain-scale simulations of the repository between 200 and 7,000 years (BSC 2004k) show that the emplacement and main drifts could be exposed to log $p\text{CO}_2$ values of -2.5 (3,200 ppmV) over the first 3,000 years, declining slowly thereafter.



Source: BSC 2004j, Figure 6.3-3.

NOTE: The Pwr1-2 waste package contains waste from a pressurized water reactor and has a higher initial heat generation rate than most other waste packages (BSC 2004j, Table 6.3-10).

Figure D-2. Contour Map of Peak Waste Package Temperature for the Pwr1-2 Waste Package Plotted over the Repository Area for the Mean Infiltration Flux Case

The cited CO₂ partial pressures reflect model results obtained in two dimensions simulating a cross section through Yucca Mountain perpendicular to the axes of the emplacement drifts (BSC 2004k). A zero-flux condition was specified parallel to the emplacement drift axes. This, however, is the direction that CO₂ would migrate if CO₂ were to be sequestered through carbonation of the cementitious materials in main access and exhaust drifts.

The information extracted from *Drift-Scale Coupled Processes (DST and THC Seepage) Models* (BSC 2004I) is not part of any modeling activity that specifically addresses the environment to which cementitious materials in the main access and exhaust main drifts are exposed. The extracted data are, therefore, approximate. Uncertainties in the temperature, relative humidity, CO₂ partial pressure, and hydrology associated with end effects relating to the positioning of waste packages within the emplacement drifts are not addressed. The shedding of pore-water condensate above the emplacement drifts could result in increased concentrations of condensate percolating into and around the main access and exhaust main drifts. Despite these limitations, the data described approximately bound the conditions under which cementitious materials are exposed and provide a basis for estimating their behavior during and following the thermal period.

D.4.4 Fate of the Cementitious Materials

The primary processes that must be addressed to understand the fate of cementitious materials in the repository and their impact on repository performance include the following:

- Dehydration
- Hydrothermal recrystallization
- Carbonation
- Formation and migration of hyperalkaline plumes
- Calcite precipitation and permeability modification in unsaturated zone host rocks
- Colloid generation and transport.

These processes are reviewed in relation to repository performance in the following sections.

The chemistry of cementitious materials is an important aspect of the following reviews. For convenience, a shorthand notation commonly used to describe the composition of cementitious phases will be used in the following sections. The notation for the components described is C = CaO; S = SiO₂; H = H₂O; A = Al₂O₃; F = Fe₂O₃; \bar{C} = CO₂; and \bar{S} = SO₃.

Principal constituents of Type II cement used in the formulation of shotcrete are listed below. The chemical composition of Type II Portland cement (Tennis 1999) is 21.1 wt % SiO₂, 4.5 wt % Al₂O₃, 3.4 wt % Fe₂O₃, 63.8 wt % CaO, 2.2 wt % MgO, and 2.7 wt % SO₃. The potential compound composition of Type II Portland cement (Tennis 1999) is 0.54 wt % Na₂O(eq.), 56 wt % C₃S, 19 wt % C₂S, 6 wt % C₃A, and 10 wt % C₄AF.

Portland cement is created by calcining a specified mixture of limestone and clay in a rotary kiln at 1,450°C (Neville 1996). The resulting clinker is then ground to a mean particle size of about 30 μm. The anhydrous cement is composed dominantly of C₂S, C₃S, C₃A, and minor C₄AF, the relative proportions of these phases being a function of the initial feed and the potential application of the cement product. The phases comprising Portland cement are highly reactive with water. Upon mixing with water, therefore, several secondary phases rapidly form that result in creation of a hardened paste. Most prominent of these secondary phases is a colloidal C-S-H gel of indeterminate composition (C:S approximately 1.7:1), which forms from the C₂S and C₃S with concomitant production of secondary CH according to Equations D-1 and D-2 (Nelson 1990):



Using these data, the initial concentration of CH in shotcrete cement can be calculated. This information is presented in Section D.4.4.3.

D.4.4.1 Dehydration

Upon closure of the repository, the cementitious materials will have aged for a period that could be as long as 100 years depending on when they were installed during construction, the time required to load the repository, and the duration of the monitoring and performance confirmation period, during which retrievability must be maintained. The Portland cement fraction would initially have contained excess water over that required to hydrate the component phases of the cement. According to Meike (1997), a small portion of this water is expected to be lost due to bleeding during hydration of concrete. Some of this water will have evaporated prior to closure, despite the relatively high ambient relative humidity. The remainder will evaporate during the period up to 1,200 years after the temperature of the shotcrete exceeds the boiling point of water (approximately 96°C), leading to minor enhancement of condensate concentrations above and below the main access and exhaust main drifts. Using the data in Table D-2, it can be shown that young cement in the shotcrete would initially contain 30 wt % of water, but a thermally modified cement would, according to Meike (1997, Table 5), contain only 18 wt % water. Thus, the cement would release 48 wt % of the initial water content before and during the thermal period following closure. This is equivalent to 3.7 wt % of the shotcrete being lost through bleeding or evaporation of water, roughly equivalent to the amount of water released by a corresponding mass of devitrified tuff, which initially contains about 4.2 wt % of water (see Table D-3). However, the quantity of committed cementitious materials is trivial in relation to the total mass of rock that would be desiccated during the thermal period. Therefore, it can be concluded that the excess of water over that required to form the hydrated phases in the cement component of grout or shotcrete would not impact the hydrology of the unsaturated zone within Yucca Mountain.

Table D-3. Parameters Used to Calculate the Transient Diffusion of CO₂ toward Carbonating Cementitious Material following Repository Closure

| Parameter | Units | Value | Source |
|--|-------------------------|-------------------------|----------------------------------|
| Diffusion coefficient of CO ₂ in air at ambient temperatures ^a | m ² /s | 1.39 × 10 ⁻⁵ | Lackner et al. 1999. |
| Molecular weight Ca(OH) ₂ | g/mol | 74.09 | Lide 2000, p. 4-50. |
| Density of portlandite | g/cm ³ | 2.26 | Calculation from Table D-2. |
| Density of shotcrete | kg/m ³ | 2,425 | Calculation from Table D-2. |
| Average concentration of portlandite in shotcrete | mol/m ³ | 1,821 | Calculated, this appendix. |
| Saturated bulk density of tuff | g/cm ³ | 2,410 | BSC 2003b, Section 8.2.4.3. |
| Fracture tortuosity coefficient, τ | – | 0.5 | Liu et al. 2003. |
| Fracture porosity, φ | – | 0.01 | Assumed. |
| Matrix porosity | – | 0.164 | Liu et al. 2003. |
| Saturation | – | 0.61 | Liu et al. 2003. |
| Total gas-phase porosity | – | 0.174 | Assumed. |
| Water content in rock | kg/m ³ | 100 | Calculated from Liu et al. 2003. |
| Water content of rock | vol % | 4.15 | Calculated, this appendix. |
| HCO ₃ ⁻ concentration in pore water | mg/L | 110 | Yang et al. 1996. |
| CO ₂ in pore water | mol/m ³ rock | 0.1792 | Calculated, this appendix. |
| CO ₂ concentration pores and fractures | mol/m ³ | 0.5149 | Calculated, this appendix. |

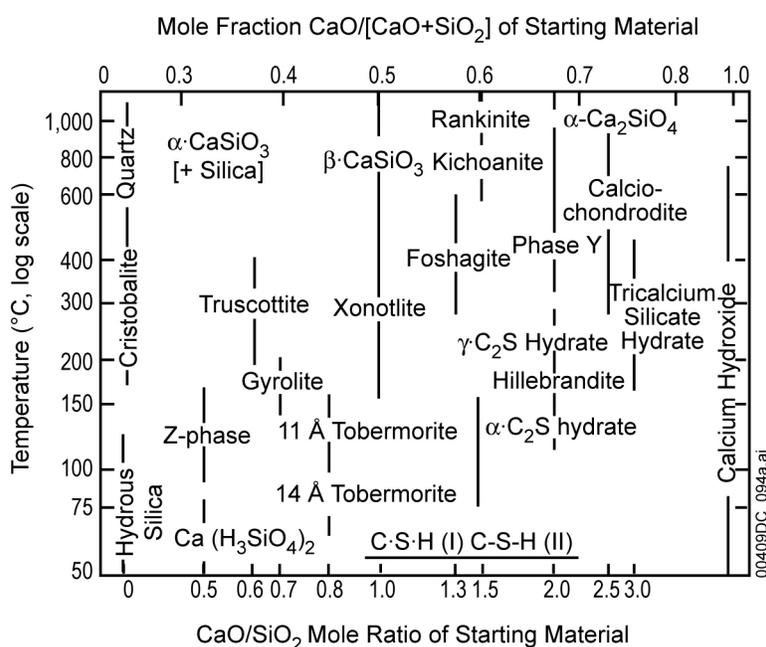
NOTE: ^aAmbient temperature is assumed to be 25°C for the purposes of this appendix.

Water released through bleeding, rather than evaporation, would initially be highly alkaline, containing dissolved sodium and potassium hydroxides in addition to calcium hydroxide (DTN: LL020805523125.002; Rothstein et al. 2002; Wieland et al. 2004, p. 120). The quantity of alkali present (as Na₂O(eq.)) in Type II Portland cement is about 0.5 wt % (Tennis 1999). If all such alkali were to be released in the initial seeps, it would immediately react with gaseous CO₂ in the host-rock fractures, producing sodium and potassium bicarbonate (DTN: LL030211423125.005). The quantity of alkali metal bicarbonate produced would be about 2.3 kg per metric ton of shotcrete. Sodium bicarbonate is highly soluble and would dissolve in the pore waters following rehydration of the repository.

D.4.4.2 Hydrothermal Recrystallization

After repository closure, the cementitious materials will be subject to recrystallization and carbonation, especially during the dryout period when temperatures, *p*CO₂, and humidity are significantly elevated. In this section, the implications of recrystallization of the cementitious component of shotcrete are considered. Carbonation is dealt with separately in Section D.4.4.3. Hydrothermal recrystallization of cementitious materials would have important consequences regarding the leachability of alkaline components with rehydration of the host rocks following the dryout period. The cementitious materials would become progressively less soluble, leaching would be curtailed, the alkalinity of leachate plumes would be less severe and less probable, and modifications to the permeability of the host rocks due to alkaline plume neutralization and calcite precipitation would be attenuated.

The hydrothermal alteration of cementitious materials proceeds in several stages. The original principal constituents (C-S-H gel, portlandite (CH), initially formed C-S-H crystalline silicates and silica fume) alter to a variety of secondary hydrated calcium silicates, the specific phases depending on the duration, temperature, and C/(S+C) mole fraction (Figure D-3) (Nelson 1990; Neville 1996) and overall composition of the cement. (The dashes in C-S-H represent the lack of fixed stoichiometry in this gel phase.) The two most reactive phases are CH and C-S-H gel. Most, if not all, of the available CH could initially transform into calcite because of its high reactivity. The initial formation of CH can be avoided, however, by the addition of sufficient silica fume so that no residual C is available to form CH. Silica fume additions have the added advantage of inhibiting permeability degradation during alteration under hydrothermal conditions at elevated temperatures (Nelson 1990, Chapter 9). Thus, some of the uncertainties associated with CH reactivity are expected to be mitigated with appropriate attention to the cement formulation used.



Source: Nelson 1990, Figure 9-2.

Figure D-3. Formation Conditions for Various Calcium Silicates

The C-S-H gel would carbonate more slowly, and, therefore, it could recrystallize to secondary calcium silicates before extensive carbonation, particularly within the interior of large monolithic concrete structures. Experimental evidence in the published literature indicates that recrystallization of the C-S-H gel is very rapid at elevated temperatures (e.g., see Shaw et al. 2000; Shaw et al. 2002). Shaw et al. (2002) show that C-S-H gel with the composition of gyrolite will recrystallize at 200°C within hours, and, at temperatures of 100°C to 160°C (typical of postclosure repository conditions during the dryout period), recrystallization would take place in a matter of weeks. Therefore, all gel materials are expected to have been transformed to secondary hydrated calcium silicates long before rehydration of the repository. Because of the amorphous nature of silica fume and the high reactivity of portlandite, it can likewise be presumed that all portlandite would react with silica fume additives within a similar time frame, provided that sufficient silica fume would be available to neutralize the portlandite.

Over a longer time period, the recrystallized components of the cement would further react with the minerals contained within the aggregate, causing progressive silication with further phase transitions in the cement and aggregate. Experimental studies have been conducted to evaluate the hydrothermal alteration of cementitious materials representative of those originally selected for emplacement in the repository. Exploratory Studies Facility invert concrete samples (autoclaved at 200°C in 0.003 mol/L NaHCO₃ solution for 8 months) indicated the minor formation of such C-S-H phases as scawtite, tobermorite, and xonotlite, together with clays with 2:1 layer smectitic and 1:1 layer serpentinitic structures (Hardin 1998, p. 6-38, Figure 6-38) (see Table D-4 for chemical formulas). A subsequent study showed that Type K cements, with a water-to-cement ratio of 0.35 and autoclaved in a steam atmosphere at 177°C for 8 hours, yielded major secondary phases: hydroxyllellstadite and katoite with varying concentrations of portlandite and calcite, together with minor ettringite (DTN: LL020805523125.002). Autoclaving for 16 hours gave essentially identical results, indicating that the brief time period of 8 to 16 hours is sufficient to convert most of the portlandite to C-S-H phases.

Table D-4. CaO/(CaO + SiO₂) Ratios of Cementitious Materials

| Phase | Mineral | Chemical Formula | Cement Formula ^a | C/(S+C) |
|--|--|--|--|---------|
| Shotcrete Components (Multiphase Mixtures) | Type II Cement | – | – | 0.76 |
| | Type II Cement + Silica Fume | – | – | 0.71 |
| | Type II Cement + Silica Fume + Fine Aggregate ^a | – | – | 0.23 |
| CaO-SiO ₂ Binary | Portlandite | Ca(OH) ₂ | CH | 1.00 |
| | Hillebrandite | Ca ₆ Si ₃ O ₉ (OH) ₆ | C ₆ S ₃ H ₃ | 0.67 |
| | Tobermorite | Ca ₅ Si ₆ O ₁₆ (OH) ₂ ·4(H ₂ O) | C ₅ S ₆ H ₅ | 0.45 |
| | Gyrolite | Ca ₁₆ Si ₂₄ O ₆₀ (OH) ₈ ·14H ₂ O | C ₁₆ S ₂₄ H ₁₈ | 0.40 |
| | Cristobalite(alpha) | SiO ₂ | S | 0.00 |
| Other Cement Phases | Ettringite | Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26(H ₂ O) | C ₆ AS ₃ H ₃₂ | – |
| | Hydroxyllellstadite | Ca ₅ (SiO ₄ ,SO ₄) ₃ (OH,Cl,F) | C ₅ S ₃ OH _{0.5} | 0.77 |
| | Katoite | Ca ₃ Al ₂ (SiO ₄) _{1.5} (OH) ₆ | C ₃ A ₂ S _{1.5} OH ₃ | 0.50 |
| | Scawtite | Ca ₇ Si ₆ (CO ₃)O ₁₈ ·2(H ₂ O) | C ₇ S ₆ H ₂ | 0.54 |
| | Xonotlite | Ca ₆ Si ₆ O ₁₇ (OH) ₂ | C ₆ S ₆ H | 0.50 |

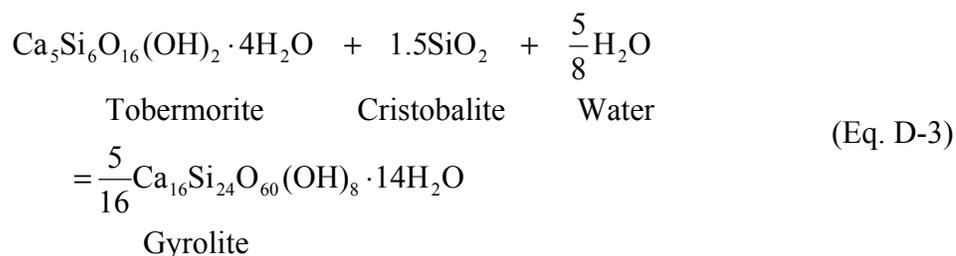
Source: Gaines et al. 1997 (chemical and cement formulas); DTN: LB0408CMATUZFT.002 (C/(S+C) values).

NOTE: ^aTtpmn and Ttpul (Peterman and Cloke 2002).

The most important issue regarding repository performance concerns the longer-term reaction of the secondary hydrated calcium silicates with the fine aggregate of the shotcrete formulation (see Table D-4). The fine aggregate will be finely pulverized devitrified tuff, a silica-rich volcanic rock (Peterman and Cloke 2002) consisting mainly of cristobalite and alkali feldspars. This silica-rich material will react progressively with the cement component to form more rich silica phases, whose aqueous solubility with respect to Ca²⁺ is drastically lower than cementitious mineral assemblages containing portlandite (see Section D.4.4.4.4).

The silication process can be schematically represented as a series of steps representing two-phase assemblages in a water-saturated binary component system, CaO-SiO₂ (+H₂O), as represented in Figure D-3. Over the temperature range of the postclosure repository environment with temperatures ranging up to 160°C, the sequence of phase assemblages with progressively increasing silica content would be portlandite-hillebrandite, hillebrandite-tobermorite-14A, tobermorite-14A-gyrolite, and gyrolite-cristobalite(alpha). The chemical formulas and C/(C+S) mole ratios of these phases and that of the CS components of the shotcrete are summarized in Table D-4.

Calculations show that if the Type II cement component of the current shotcrete formulation were to react completely with all silica fume and all of the fine aggregate, there would be insufficient free silica available to generate the most silica-rich gyrolite-cristobalite(alpha) assemblage. Therefore, the most silica-rich phase assemblage that could possibly form with the current shotcrete formulation would be tobermorite-14A-gyrolite, generated according to the following equation:

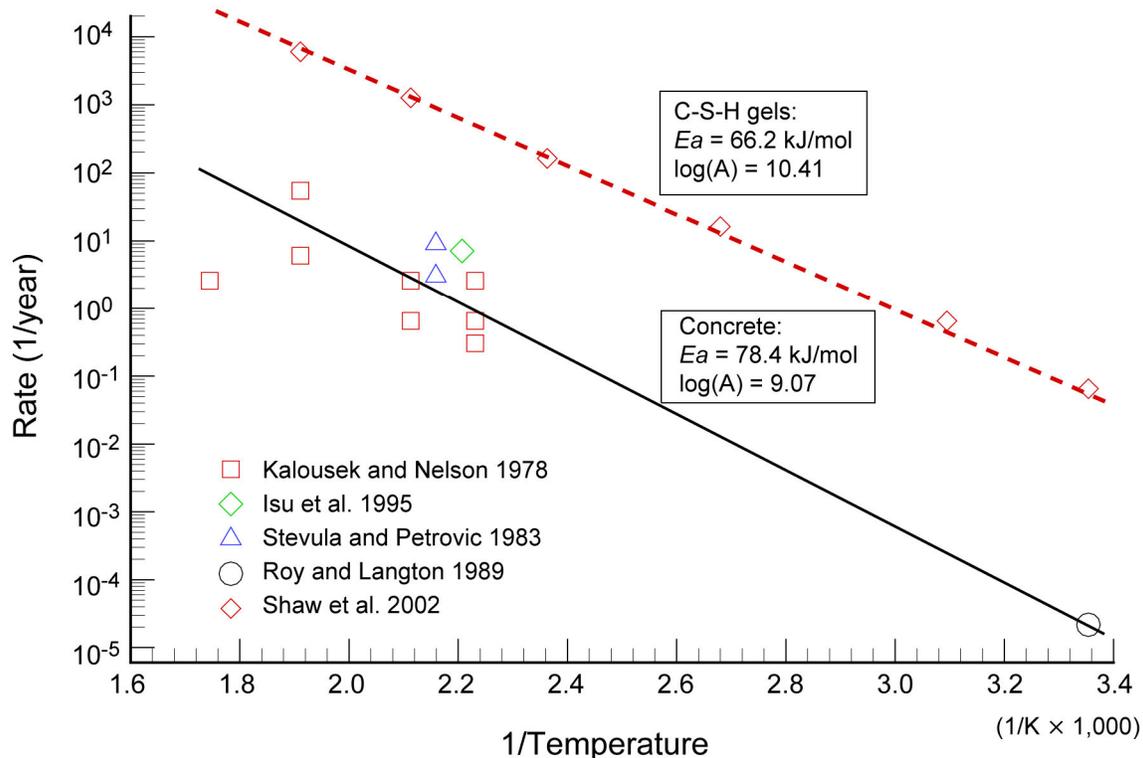


The anticipated kinetics of reactions leading to the formation of this mineral assemblage from the original shotcrete constituents is of critical importance, because this will allow an estimate of the time required for substantially complete shotcrete alteration under repository conditions.

The hydrothermal recrystallization of cement is a complex process that involves many chemical, mineralogical, and microstructural factors, including matrix mineralogy, particle size, porosity; aggregate type, grading, and proportioning (Roy and Langton 1989, p. 1). The recrystallization occurs with concomitant degradation of the physical properties of the cementitious material. Information is available in the literature regarding the formation of gyrolite from tobermorite in some laboratory experiments performed under hydrothermal conditions at elevated temperatures (Kalousek and Nelson 1978; Stevula and Petrovic 1983). At the room temperature, the transformation of tobermorite is very slow and has not been observed in laboratory experiments. For the low temperature scenario, the weathering rate of ancient Roman concrete dating to approximately 2,300 years ago was used as a basis for estimating reaction rates (Roy and Langton 1989).

Certain assumptions were made regarding the mineral mass fraction to derive the kinetic rates of gyrolite formation. This is necessary in the calculation of the kinetic rates, because available data concerning the mass fractions of mineral phases in the literature are qualitative. Specifically, the reactants tobermorite and cristobalite are assigned a unit mass fraction, which remains constant through the investigated time period. The gyrolite product is assumed to be present with a 0.05 mass fraction. This value was arbitrarily chosen to represent low concentrations generally observed in experiments. In addition, ancient Roman concrete is

considered to have been subject to alteration for 2,300 years at an ambient temperature assumed to be 25°C for this appendix. The temperatures of laboratory runs range from 175°C to 300°C. Experiments differed in duration, ranging from 8 hours to 60 days. All were conducted in a steam atmosphere, and, therefore, reactions were catalyzed by the presence of water vapor at elevated pressures. The calculated kinetic rate (1/yr) as a function of temperature is shown in Figure D-4.



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Source: DTN: LB0408CMATUZFT.001.

Figure D-4. Interaction of Cement with Siliceous Aggregate to Form Tobermorite-14A-Gyrolite Assemblages, Based on Laboratory Experiments and Ancient Concrete Weathering

The estimated kinetic rates have large uncertainties because of the use of phase changes to measure reaction rates, and mass quantifications are, therefore, approximations. However, a comparison can be made with the rate of conversion of C-S-H gel of gyrolite composition to gyrolite in a steam atmosphere, as studied by Shaw et al. (2002). The rate of transformation determined by these investigators is also plotted in Figure D-4 for comparison. Their determination is in satisfactory agreement with the estimated rate of formation of gyrolite from tobermorite-14a in the presence of cristobalite. The rate, approximately 2 orders of magnitude higher, and lower activation energy of the gel-gyrolite transformation is consistent with theoretical expectations and provides a measure of confidence in the validity of the rate of formation of gyrolite from tobermorite and cristobalite.

The effect of temperature on reaction rates is quantified using the Arrhenius equation.

$$k = A \cdot \exp\left(-\frac{Ea}{RT}\right) \quad (\text{Eq. D-4})$$

where k is the rate coefficient (1/yr), A is a constant, Ea is the activation energy, R is the universal gas constant, and T is the temperature (in degrees Kelvin). R has the value of 8.314×10^{-3} kJ/mol·K.

The calculation yields an activation energy of 78.4 kJ/mol and a value for the constant $\ln A$ of 20.9. The kinetic rates at 100°C, 120°C, and 150°C are 0.0125, 0.0452, and 0.2476 per year, respectively.

This shows that it would take approximately 1,000 years ($\text{Ca} (1/\text{rate}) \times 10$) to produce a tobermorite-14A-gyrolite assemblage through reaction of the cement with the fine aggregate in the shotcrete at 100°C but only about 50 years at 150°C. However, at 150°C, most if not all of the residual capillary pore water would have evaporated, and reaction rates would be retarded. Because capillary water can remain under repository conditions up to about 120°C in the pores of devitrified tuff host rocks, it would be expected that a minimum time for alteration would be somewhat in excess of 200 years. The implication of this estimate is that most of the cementitious component of the shotcrete would be substantially altered to a tobermorite-14A-gyrolite assemblage prior to rehydration. This has significant consequences for carbonation rates, which would be retarded by the presence of more stable silica-rich mineral phases and have lower solubilities with respect to dissolved calcium (Section D.4.4.4.4). Alkaline plume formation subsequent to rehydration would, therefore, be negligible (Section D.4.4.5).

D.4.4.3 Carbonation

The carbonation of cementitious materials in the repository is strongly dependent on the accessibility of gaseous CO₂, and this depends, in part, on the transport of atmospheric CO₂. Prior to repository closure, it can be demonstrated that convective ventilation would be more than sufficient to permit some carbonation of the contained cementitious materials and that carbonation reaction rates would be controlled by gaseous diffusive transport within the open pores of the cementitious material. After closure and backfilling of all access drifts with crushed tuff, advective transport of atmospheric CO₂ would be restricted. Carbonation rates would for the most part be limited by internally driven gas phase thermal convection and diffusion of CO₂ in fractures released from pore waters in the tuffaceous host rocks surrounding the emplacement drifts during the dryout period. Because of the importance of carbonation in affecting the leaching behavior of cementitious materials and because the conditions before and after repository closure would differ significantly, carbonation processes before and after closure are reviewed separately.

Preclosure Conditions—Papadakis (2000) developed a model to calculate carbonation distances in cementitious materials at 25°C. This model has been used in the design of DOE-sponsored laboratory experiments to measure the extent of carbonation of cementitious materials (DTN: LL020711323125.001). The model is used in this appendix to estimate the extent of carbonation of shotcrete support applied to drifts in the repository during the monitoring and performance confirmation period 50 years prior to closure. This period would be the minimum time to which all shotcrete materials would be exposed to carbonation prior to closure.

The model is a relatively simple one in which it is assumed that the rate of carbonation is gas diffusion-controlled, with the effective diffusivity of CO₂ in the cementitious material controlled by the porosity of the carbonated zone through which the gas must migrate. The effective diffusivity is also described as an empirical function of the relative humidity, which affects the water content of the cementitious material. At high water contents, for example, there is relatively little of the pore space available through which the gas can diffuse. While CO₂ can diffuse in the aqueous phase, the diffusion coefficient is about 4 orders of magnitude slower than it is in the gas phase. The effective diffusivity also depends on the water-cement ratio of the cementitious material, because the water-cement ratio has a strong effect on the amount of capillary porosity developed in the cured cementitious material. The water referred to here is that used in preparation of the cementitious material and is not the water content of the pores of the resulting product.

The Papadakis equation is defined according to the following parameters:

- C (kilograms of cement per cubic meter)
- SF (kilograms of silica fume per cubic meter)
- W (kilograms of water per cubic meter)
- ρ_c , cement density (kilograms per cubic meter)
- ρ_{sf} , silica fume density (kilograms per cubic meter)
- ρ_w , water density (kilograms per cubic meter).

Papadakis (2000) shows that in the case of complete hydration and pozzolanic action (reaction with the silica fume), the amounts of CH, C₃S₂H₃ (C-S-H) (in kilograms per cubic meter of cement) and the total porosity of carbonated concrete is given as follows:

$$CH = 0.29 C - 1.62 SF \quad (\text{Eq. D-5})$$

$$C-S-H = 0.57 C + 2.49 SF \quad (\text{Eq. D-6})$$

$$\epsilon_c = (W - 0.267 C - 0.0278 SF)/1000 \quad (\text{Eq. D-7})$$

For one-dimensional geometry, the evolution of the carbonation depth, x_c (meters), with time, t (seconds), is given by the analytical expression:

$$x_c = \sqrt{\frac{2D_{e,CO_2} (CO_2/100)t}{0.33CH + 0.214CSH}} \quad (\text{Eq. D-8})$$

where CO₂ is the CO₂ content (percent) in the ambient air at the concrete surface and D_{e,CO_2} is the effective diffusivity of CO₂ in carbonated cement (square meters per second). The effective diffusivity also depends on the ambient relative humidity according to the following empirical equation:

$$D_{e,CO_2} = A \left[\frac{\epsilon_c}{\frac{C}{\rho_c} + \frac{SF}{\rho_{SF}} + \frac{W}{\rho_W}} \right]^a (1 - RH/100)^b \quad (\text{Eq. D-9})$$

The optimal parameter values presented by Papadakis (2000) are 6.1×10^{-6} and 3 for A and a , respectively, and 2.2 for b . The parameter values for A , a , and b given above are strictly valid for $0.38 < W/(C + 2SF) < 0.58$.

Calculations based on the Papadakis (2000) carbonation model, updated to include the effects of silica fume, can be used to estimate the extent of carbonation of cementitious materials in the repository. The material likely to be most extensively carbonated is the shotcrete applied to provide ground support in the main access and ventilation drifts. This material currently has a design thickness of 10 cm (BSC 2004f), and it is assumed that the exposed face would be most prone to carbonation. It is also assumed that the availability of atmospheric CO_2 is unlimited (i.e., pCO_2 is not rate controlling). In Table D-5, the calculated depth of carbonation is given as a function of relative humidity, pCO_2 , and temperature, which is accounted for by using an activation energy for gaseous diffusion of 27 kJ/mol in the Arrhenius equation. All calculations are carried out at pCO_2 of 3×10^{-4} bar, the accepted value for atmospheric CO_2 at 25°C. Minor pressure corrections for elevation have been omitted. The densities of cement (C) and silica fume (SF) used in the calculations are those cited by Papadakis (2000).

Table D-5. Shotcrete Carbonation Depth after 50 Years Using the Papadakis (2000) Carbonation Model

| Temperature (°C) | $W/(C+SF)$ | Relative Humidity (%) | Carbonation Depth (cm) | | |
|---------------------|------------|--------------------------|------------------------|---------------------|---------------------|
| | | | $SF(C+SF) =$ 6.4% | $SF(C+SF) =$ 15% | $SF(C+SF) =$ 25% |
| 25 | 0.40 | 5 | 2.12 | 2.64 | 3.36 |
| 25 | 0.40 | 10 | 1.99 | 2.49 | 3.16 |
| 25 | 0.40 | 20 | 1.75 | 2.19 | 2.78 |
| 25 | 0.40 | 40 | 1.28 | 1.60 | 2.03 |
| 25 | 0.40 | 60 | 0.82 | 1.02 | 1.30 |
| 25 | 0.40 | 80 | 0.38 | 0.48 | 0.61 |
| 25 | 0.40 | 98 | 0.03 | 0.04 | 0.05 |
| 40 | 0.40 | 60 | 1.06 | 1.33 | 1.68 |
| 50 | 0.40 | 60 | 1.24 | 1.56 | 1.98 |
| 60 | 0.40 | 60 | 1.45 | 1.81 | 2.30 |
| 70 | 0.40 | 60 | 1.67 | 2.09 | 2.65 |
| 80 | 0.40 | 60 | 1.91 | 2.39 | 3.03 |
| 90 | 0.40 | 60 | 2.17 | 2.71 | 3.44 |

Source: DTN: LB0408CMATUZFT.002.

It should be noted that the Papadakis model assumes transport control on the rate of carbonation. Therefore, it does not adequately capture the potential switch in the rate-controlling mechanism, which occurs at low relative humidity. Because the rate of gas diffusion increases with increasing gas saturation (because decreasing relative humidity results in lower liquid

saturation), the Papadakis model will always predict the highest carbonation rates at the lowest relative humidity. However, carbonation rates should decrease at very low relative humidity, but the model does not capture this. Although at relative humidities approaching 100% the model predicts that the carbonation rate falls to zero, carbonation continues at a much slower rate, dictated by the diffusion of CO₂ through the liquid aqueous phase. The values given here, therefore, should be considered as maximum values for the very low relative humidity values.

The calculated depths of shotcrete carbonation are predicted to vary by over 2 orders of magnitude depending primarily on relative humidity. The possibility exists that the higher rates of carbonation could not be sustained because advective mass transport of CO₂ through the repository access drifts might be rate controlling. A simple mass-balance calculation demonstrates that this is not the case. In the following calculation, it is assumed that the shotcrete represents a substantial fraction of the reactive cementitious material in the repository and that only the exposed face of the shotcrete becomes carbonated at the maximum rate given in Table D-6 (i.e., 3.4 cm depth after 50 years). An approximation is also made that the carbonation rate is linear with time and that the volume fraction of the shotcrete due to portlandite is converted to calcite (CaCO₃). Elevation corrections for atmospheric pCO₂ are ignored. The approach assumes that all CO₂ is provided by the atmosphere through advective flow of air exclusively through the main access drift and that the air mass velocity in this drift determines whether such a velocity would be realistic in relation to natural convection. Values used in the calculation are given in Table D-6.

Table D-6. Parameters Used to Calculate Main Access Drift Velocity Required to Satisfy Shotcrete Carbonation Rates

| Parameter | Units | Value | Reference |
|--|--------------------|--------|-----------------------------|
| Carbonation depth | cm | 3.4 | This appendix. |
| Carbonation time | years | 50 | Assumed. |
| Fraction of shotcrete due to portlandite | – | 0.056 | This appendix. |
| Density of calcite | g/cm ³ | 2.710 | Calculation from Table D-2. |
| Molecular weight of calcite | g/mol | 100.09 | Lide 2000, p. 4-50. |
| Density of portlandite | g/cm ³ | 2.26 | Calculation from Table D-2. |
| Density of shotcrete | g/cm ³ | 2.425 | Calculation from Table D-2. |
| Area of shotcrete associated with each emplacement drift | m ² | 885 | BSC 2004h. |
| Number of emplacement drifts | – | 106 | BSC 2004h. |
| CO ₂ concentration in carbonated shotcrete | mol/m ³ | 1,821 | This appendix. |
| Access drift diameter | m | 7.62 | BSC 2004h. |

Source: DTN: LB0408CMATUZFT.002.

A calculation using the parameters given in Table D-6 shows that the air velocity in the main access drift required to satisfy maximum shotcrete carbonation rates is 5.17×10^{-3} m/s. This velocity is about 200 times slower than current forced ventilation rates in the Exploratory Studies Facility main drift. Therefore, forced ventilation rates prior to repository closure would be unlikely to control the rate of shotcrete carbonation.

Postclosure Conditions—Permanent closure of the repository is expected after approximately 100 years of atmospheric ventilation (BSC 2004m). Current plans are to backfill all access and ventilation drifts with pneumatically emplaced crushed tuff. Under these conditions, access of atmospheric CO₂ could be restricted. A simple application of Fick's first law of diffusion (see below) shows that the diffusive flux of atmospheric CO₂ to the repository through the fractures of the undisturbed host rock would be so small that such a mechanism would not account for any further carbonation of cementitious materials. It is also not clear whether sufficient CO₂ would be available within the repository host rocks to permit continued unrestricted carbonation of cementitious materials.

Given the quantity of cementitious materials remaining in the repository after closure, the quantity of CO₂ required for complete carbonation of the portlandite generated initially with shotcrete can be compared with what could be made available from the host rocks surrounding the repository. Table D-7 lists the parameters used in this calculation. The calculation ignores the presence of grout, which contributes only a minor quantity of Portland cement to the planned total inventory. It should also be emphasized that the calculation is simplistic in that it ignores CO₂ contributions due to calcite dissolution, aqueous phase equilibrium with respect to ambient *p*CO₂ in the coexisting gas phase, and kinetic and mass transfer constraints involved in degassing of matrix pore waters.

Table D-7. Parameters Used to Calculate the Availability of CO₂ within Yucca Mountain Pore Waters to Carbonate All Cementitious Materials within the Repository

| Parameter | Units | Value | Reference |
|--|-------------------------|-------------------------|----------------------------------|
| Type II cement in shotcrete | wt % | 17.95 | BSC 2004h. |
| Ca(OH) ₂ generated in Type II cement | wt % | 31 | Calculated, this appendix. |
| Molecular weight Ca(OH) ₂ | g/mol | 74.09 | Lide 2000, p. 4-50. |
| Concentration of portlandite in shotcrete | mol/m ³ | 1,821 | Calculated, this appendix. |
| Density of shotcrete | kg/m ³ | 2,425 | Calculated from Table D-2. |
| Mass of shotcrete | tons | 159,413 | From Table D-1. |
| CO ₂ required to react with Ca(OH) ₂ | mol | 4.461 × 10 ⁷ | Calculated, this appendix. |
| Matrix porosity | – | 0.164 | Liu et al. 2003. |
| Saturation | – | 0.61 | Liu et al. 2003. |
| Water content in rock | kg/m ³ | 100 | Calculated from Liu et al. 2003. |
| HCO ₃ [–] concentration in pore water | mg/L | 110 | DTN: GS951108312271.006. |
| Rock volume above repository horizon | km ³ | 2.23 | BSC 2004h. |
| CO ₂ in pore water | mol/m ³ rock | 0.1792 | Calculated, this appendix. |
| Total CO ₂ in pore water | mol | 4.001 × 10 ⁸ | Calculated, this appendix. |

Source: DTN: LB0408CMATUZFT.002.

The results of this calculation, summarized in Table D-7, show that there would be an order of magnitude excess of CO₂ available to carbonate all of the cementitious materials. However, removal of all CO₂ from the pore waters to satisfy the requirements of carbonation would be impossible, as noted above, because thermodynamic back reactions would prevent complete stripping. The availability of CO₂ would be primarily dependent on CO₂ released by evaporation of pore water adjacent to the emplacement drifts. The extent to which CO₂ would be retained by

the pore waters and condensate elsewhere in the repository would depend on the depression of $p\text{CO}_2$ in the gaseous phase due to carbonation.

The maximum potential diffusive fluxes possible within the repository and whether they could limit the carbonation of cementitious materials can be gained through evaluation of the case of diffusion through a semi-infinite medium to a sink for the diffusing material. Crank (1975) gives an analytical solution for this case, where the initial concentration, C_0 , of the diffusing substance is uniform throughout, and the interface is maintained at a concentration, C_1 . The solution is:

$$C - C_1 / C_0 - C_1 = \text{erf}(x/2\sqrt{Dt}) \quad (\text{Eq. D-10})$$

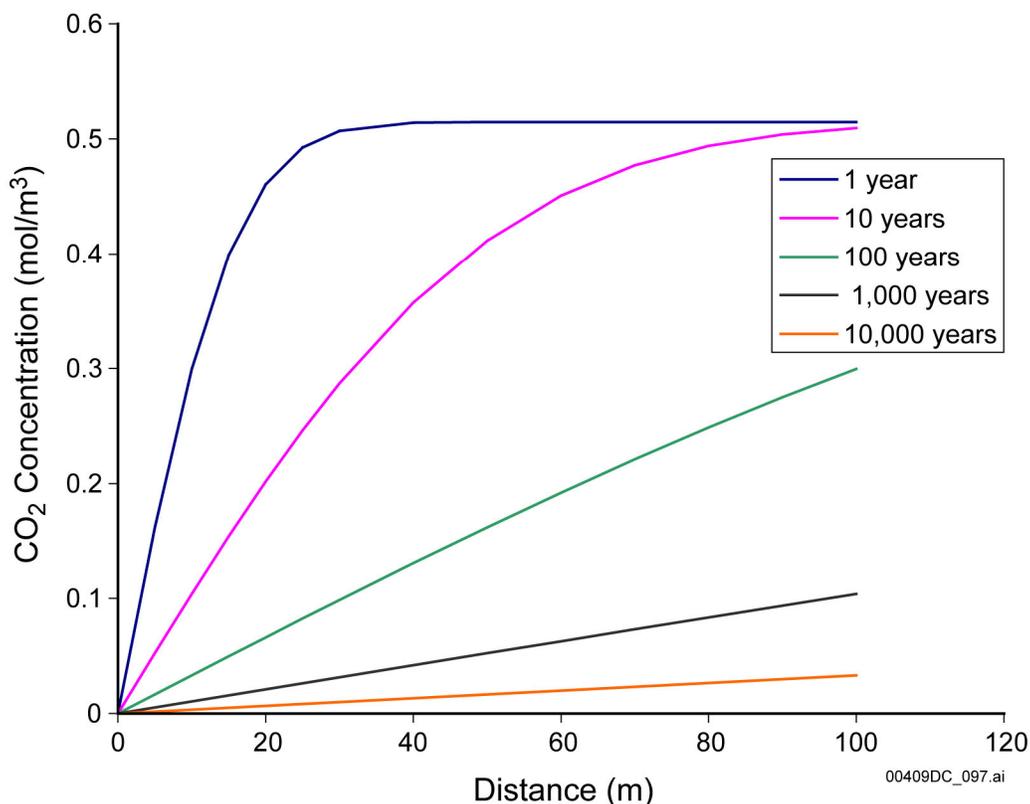
For the special case where the surface concentration is zero, the total amount of diffusing substance, which has left the medium, is given by:

$$M_t = 2C_0 \sqrt{Dt/\pi} \quad (\text{Eq. D-11})$$

Equation D-10 permits calculation of the linear distribution of CO_2 in the fractures of the rock as a function of time, and Equation D-11 permits calculation of the depth to which concrete has been carbonated at various times following repository closure, assuming that carbonation is not rate controlling.

The capacity of the pore water to contain CO_2 exceeds that of the air in the fractures and unsaturated rock pores by a factor of 65, assuming the average bicarbonate concentration in pore waters is approximately 110 mg/L (Yang et al. 1996; DTN: GS951108312271.006) and the volume of aqueous phase per unit volume of rock exceeds the volume of air in the fractures by a factor of approximately 3.5. Thus, the preponderance of CO_2 is present initially in the pore water and not in the gas phase. It is assumed that 50% of all bicarbonate in the pore water is made available in the gas phase as CO_2 and that all pore and fracture space is occupied by the CO_2 , the pore water having evaporated during the thermal period. The resulting concentration of CO_2 in the gaseous phase is 0.515 mol/m^3 ($\log(p\text{CO}_2)$ value of -2.0 , or $p\text{CO}_2$ value of approximately 9,350 ppmV). This value is somewhat higher than the average concentration of CO_2 in the gaseous phase under dryout conditions. Therefore, the diffusion rates, calculated below, represent an upper limit. Table D-3 summarizes the parameters used in the calculation.

Figure D-5 shows the linear distance of host rock affected by the uptake of CO_2 by shotcrete, assuming one-dimensional geometry. In cylindrical or spherical coordinates, the distances are compressed in comparison, but, because of the complex nature of the geometry of the repository, representations in higher dimensions are not justified in this simple analysis.



Source: DTN: LB0408CMATUZFT.002.

Figure D-5. Effective Distribution of CO₂ as a Function of Time and Distance from Carbonating Cementitious Material

Table D-8 shows that if the carbonation rate of cementitious materials were fast in relation to the diffusion of CO₂ through the rock fractures, all shotcrete would be completely carbonated before 1,000 years had elapsed, assuming that carbonation proceeds from both sides of the shotcrete that is 10 cm thick.

Table D-8. Depth to which Cementitious Material Would Be Carbonated, Assuming the Diffusive CO₂ Flux Would Be Rate Controlling

| Time (years) | Carbonation Depth (cm) |
|--------------|------------------------|
| 1 | 0.267 |
| 10 | 0.843 |
| 100 | 2.67 |
| 200 | 3.31 |
| 1,000 | 8.43 |
| 10,000 | 26.7 |

Source: DTN: LB0408CMATUZFT.002.

The results summarized above are limited by the assumptions inherent in the calculations. Thus, it is assumed that the reaction rate is limited by the flux of CO₂, that the CO₂ diffusion coefficient at elevated temperatures is the same as that at 25°C, and that CO₂ equilibrium

between the aqueous (pore water) and gaseous (fracture) phase is always maintained. It should also be emphasized that the above analysis takes into account mass transport by gaseous phase diffusion alone. Advective transport through convection could also be operative. However, thermal-hydrologic-chemical modeling (BSC 2004h) suggests that CO₂ advective transport in the gaseous phase would be retarded by interaction with the aqueous phase, where pore waters or condensate exist beyond the region of dryout and would, therefore, be coupled with pore water percolation.

The above evaluation showing that the carbonation of shotcrete would be essentially complete within 1,000 years after repository closure presumes that the carbonation rate is not rate limiting. The extrapolation of the Papadakis model (Papadakis 2000) to temperatures in the vicinity of the boiling point of water allows a preliminary estimate to be made regarding the possibility that the carbonation rate could be sufficiently slow that the shotcrete would not be completely carbonated prior to rehydration. The calculations presented in Table D-9 show that the shotcrete formulated with Type II cement with 6.4 wt % silica fume would be completely carbonated in just over 100 years at a relative humidity of 80%. Extrapolation of the model to higher temperatures indicates even more rapid rates of carbonation. However, for reasons stated elsewhere in this section, the Papadakis model does not account for either boiling or dryout. The boiling of the aqueous phase in the pores of the cement would enhance gaseous phase diffusion of CO₂ into the cement, thus greatly accelerating carbonation in the presence of residual capillary water. Current estimates indicate that residual capillary water would persist to a temperature of about 120°C. The presence of dissolved (calcium or magnesium) chlorides in the shotcrete could stabilize the aqueous phase at still higher temperatures and enhance carbonation rates even further. In contrast, declining relative humidity with increasing temperature could inhibit carbonation because of the elimination of residual capillary or absorbed water that would otherwise act as a catalyst.

Table D-9. Shotcrete Carbonation Depth following Closure using the Papadakis (2000) Carbonation Model

| Time (years) | Relative Humidity (%) | Carbonation Depth (cm) | | | |
|--------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| | | 90°C | 100°C | 120°C | 140°C |
| 50 | 40 | 10.70 | (12.06) | (15.05) | Out of modeling bounds |
| | 60 | 6.85 | 7.72 | (11.76) | (11.76) |
| | 80 | 3.19 | 3.60 | 5.49 | 5.49 |
| | 98 | 0.25 | (0.29) | (0.36) | (0.44) |
| 100 | 40 | 15.10 | Out of modeling bounds | Out of modeling bounds | Out of modeling bounds |
| | 60 | 9.68 | 10.92 | (13.62) | (16.64) |
| | 80 | 4.52 | 5.09 | 6.35 | 7.76 |
| | 98 | 0.36 | (0.40) | (0.50) | (0.62) |

Source: DTN: LB0408CMATUZFT.002.

NOTE: Numbers in parentheses are estimates for conditions outside the bounds of the Papadakis (2000) model. See text for discussion. $p\text{CO}_2 = 0.30\%$ or 3,000 ppmV.

Carbonation of all shotcrete is also constrained for the following reasons: (1) as the temperature rises in the repository, the C-H-S gel phase rapidly crystallizes (Shaw et al. 2002), which would

retard carbonation by back reactions favoring decarbonation; (2) the initial armoring of the shotcrete by precipitation of calcite in pores could inhibit further diffusive penetration of CO₂, and (3) some of the shotcrete would be located in regions where the mean temperature excursion would be limited, and, therefore, the kinetics of carbonation would be diminished.

Hardin (1998, p. 6-38) also noted that the rate of carbonation is dependent on a number of factors, including the advective aqueous flux of CO₂ dissolved in the pore water, release of CO₂ due to pore-water boiling, aqueous phase refluxing, temperature, relative humidity, the rate of diffusion of CO₂ into the cementitious material, and the nature and composition of the cementitious material. Extrapolated carbonation rates predicted by the Papadakis (2000) model above boiling temperatures, reported in this section, would indicate, however, that a 10-cm-thick shotcrete lining the main access and exhaust drifts would be completely carbonated within 1,000 years, provided that the reaction scheme defined by the Papadakis (2000) model would be applicable between boiling and temperatures as high as 170°C, at 85% relative humidity, and that the availability of CO₂ is not mass-transport limited.

Rehydration is predicted to occur in the waste packages around the peripheries of the waste package emplacement panels. It is assumed, for the purpose of discussion, that the contiguous main access and exhaust ventilation drifts are subject to the same corresponding dryout periods between 200 and 1,200 years after closure (Section D.4.3). Table D-10 shows the carbonation depth expected during the period following rehydration, during which it is assumed that the relative humidity is close to saturation (i.e., about 95%). The relative humidity is arbitrarily set, as the Papadakis equation ignores CO₂ diffusion through the aqueous phase filling pores, and therefore, 100% relative humidity would yield zero carbonation rates. At the minimum time of 200 years, the shotcrete would have been carbonated to a depth of about 1.5 cm on the exposed face prior to repository closure (see Table D-5), and about 3 cm from either side following closure (Table D-9). These sequential carbonation depths are not additive, but it can be assumed as a first approximation that about 50% of the shotcrete thickness will have been carbonated at the time that rehydration occurs. Thus, between about 500 and 5,000 years more time would be required for complete carbonation under conditions following rehydration. The presumption would be that further carbonation occurs in situ without the generation of an alkaline plume. Current knowledge does not permit such an interpretation without further study. Thus, it must be assumed as a conservative assumption that rehydration will lead to the formation of an alkaline plume. This scenario is evaluated in Section D.4.4.4.2.

Table D-10. Shotcrete Carbonation Depth following Rehydration at 95% Relative Humidity using the Papadakis (2000) Carbonation Model

| Temperature (°C) | Carbonation Depth (cm) | | | | | |
|------------------|------------------------|-----------------|-------------------|-------------------|-------------------|--------------------|
| | After 200 years | After 500 years | After 1,000 years | After 3,000 years | After 7,000 years | After 10,000 years |
| 90 | 1.39 | 2.20 | 3.11 | 5.39 | 8.23 | 9.83 |
| 80 | 1.23 | 1.94 | 2.74 | 4.74 | 7.25 | 8.66 |
| 70 | 1.07 | 1.69 | 2.40 | 4.15 | 6.34 | 7.58 |
| 60 | 0.93 | 1.47 | 2.08 | 2.64 | 5.50 | 6.57 |
| 50 | 0.80 | 1.26 | 1.79 | 3.10 | 4.73 | 5.65 |
| 40 | 0.68 | 1.08 | 1.52 | 2.64 | 4.03 | 4.82 |
| 30 | 0.57 | 0.91 | 1.28 | 2.22 | 3.40 | 4.06 |

Source: DTN: LB0408CMATUZFT.002.

NOTE: $p\text{CO}_2 = 0.30\%$ or 3,000 ppmV.

In the event that CO_2 were to become depleted, it can be shown that CO_2 transported from the atmosphere would occur primarily through pore-water advective transport. A simple application of Fick's first law of diffusion shows that the diffusive flux of atmospheric CO_2 into the repository through the fractures of the undisturbed host rock would be so small that such a mechanism would not account for any further carbonation of cementitious materials.

Fick's first law states:

$$F = D \partial C / \partial x \quad (\text{Eq. D-12})$$

where F is the flux in moles per square meters per second, C is the concentration in moles per cubic meter, x is the diffusive distance in meters, and D is the coefficient of diffusion in square meters per second. Assuming that cementitious material carbonation is fast in relation to CO_2 diffusion, that the steady-state concentration of CO_2 at the surface of the cementitious material is zero (i.e., CO_2 diffusion is rate controlling), and that the path length from the land surface to the repository interior is x , a finite difference approximation of Fick's first law can be taken to calculate the diffusive flux into the interior of the repository from the land surface:

$$F = \tau \phi D \Delta C / \Delta x \quad (\text{Eq. D-13})$$

where τ is the fracture tortuosity coefficient and ϕ is the fracture porosity. The values and sources of the parameters used in the calculation are given in Table D-11.

Table D-11. Parameters Used to Calculate the Diffusive CO₂ Flux from the Land Surface into the Repository

| Parameter | Units | Value | Reference |
|---|-----------------------|-----------------------|----------------------------|
| Distance from the land surface to the interior of the repository, x | m | 200 | Assumed. |
| CO ₂ concentration in air | mol/m ³ | 0.01562 | Calculated, this appendix. |
| Diffusion coefficient of CO ₂ in air at 25°C | m ² /s | 1.39×10^{-5} | Lackner et al. 1999. |
| Fracture tortuosity coefficient, τ | – | 0.5 | Liu et al. 2003. |
| Fracture porosity, ϕ | – | 0.01 | Assumed. |
| Diffusive CO ₂ flux, F | mol/m ² ·s | 5.4×10^{-12} | Calculated, this appendix. |

Source: DTN: LB0408CMATUZFT.002.

The presumption in the above calculation is that diffusion of CO₂ occurs through the fractures of a dry impermeable rock. In fact, the vitroclastic rocks comprising the Yucca Mountain edifice are partially saturated (e.g., 61% in Table D-3) and have variable matrix porosities (e.g., 0.16 in Table D-3) (Liu et al. 2003). Thus, equilibration of CO₂ with the pore waters will take place locally at all points along the postulated 200-m diffusion path. The pore-water infiltration rate at Yucca Mountain is estimated to range between 1 and 5 mm/yr (Sonnenthal and Bodvarsson 1999). Thus, it can be shown that the aqueous phase advective flux of CO₂ to the repository horizon is between 1.8 and 9.0 mol/m²·yr, or up to 50 times faster than by gaseous diffusion through the rock fractures.

To summarize, the bounding calculations presented in this section indicate that shotcrete support liners would be extensively if not completely carbonated prior to rehydration. During the period when dryout occurs, carbonation reaction rates are so high that the rate of carbonation would be limited only by the rate of diffusion of ambient gaseous CO₂ to the shotcrete support structures. Parts of the peripheries of the waste emplacement panels could rehydrate as soon as 200 years after dryout, and contiguous access and exhaust drifts could rehydrate at about the same time. Shotcrete in the drifts, which would have been exposed to periods as short as 200 years of dryout, would be incompletely carbonated prior to rehydration. Allowing credits for partial carbonation of the shotcrete prior to repository closure and prior to rehydration, it is estimated that up to 5,000 more years would be required for complete carbonation of the cooler parts of the repository. This duration is roughly of the same order of time observed for the carbonation of Roman pozzolanic concrete (Roy and Langton 1989), and suggests an upper bound for the time required for carbonation.

D.4.4.4 Leaching of Altered Cementitious Material

Leaching of cementitious materials will occur under three conditions:

- Random wetting as a result of episodic inflows of water via fast paths
- Transient condensation of evaporated pore water from the heated rock surrounding the emplacement
- Rehydration of the repository after thermal dissipation following heating due to radioactive decay.

D.4.4.4.1 Episodic Events Inducing Flow in Fractures

During episodic events when precipitation is very high, as occurs during intense localized summer thunderstorms or during winter storms and (or) subsequent snowmelt, transient surface flooding can occur with associated rapid downward advance of a fracture-saturated wetting front (BSC 2003c, Section 6.3.4). Localized flow could be enhanced by preferential infiltration due to topographic variability and the focusing of flow through transmissive faults intersecting the surface or shallow subsurface (Pruess 1998). Rapid gravitational migration of the inflowing water could also be facilitated by sheet flow (Tokunaga and Wan 1997). Such flows can migrate very rapidly under gravity. Pruess (1998) estimates that the average seepage velocities are on the order of 1 m/s.

Should episodic flow events occur in the future, it is expected that dryout surrounding the emplacement drifts will inhibit, or at least mitigate, their impact during the postclosure repository dryout period. In contrast to steady-state percolation through the pores of the rock matrix, where lateral plume spreading would be dominated by molecular diffusion (see Section D.4.4.4.2), preferential episodic flows would be limited to lateral spreading by hydrodynamic and capillary dispersion. The former process is minor, but the latter could be substantial, particularly in desiccated or highly unsaturated rocks (Pruess 1996). However, Pruess (1998) has shown through heterogeneous fracture flow simulations under the partially saturated conditions characteristic of the welded fractured tuffs at Yucca Mountain that gravitational effects tend to dominate capillary effects. Pruess (1998) also noted that fast flow could be generated by internal focusing mechanisms due to heterogeneities in the host rock, leading to enhanced flow velocities and flow funneling. The consequence of these mechanisms is that the resulting flow would be nearly vertical with almost no lateral dispersion. The simulated behavior has been observed in the field, although it is not necessarily universal. Focused episodic flows occurring at spatially distinct localities would, therefore, be unlikely to intersect. Furthermore, the rapid flow velocities and limited duration of such fracture flows would limit their ability both to leach significant alkaline components from cementitious materials or precipitate calcite and locally degrade the permeability of the fractures. Calcite precipitation would be limited and would spread out over the full thickness of the unsaturated zone, given the modeled rapid flow velocities in relation to calcite precipitation kinetics under subsurface conditions.

D.4.4.4.2 Steady-State Percolation of Pore Water through the Rock Matrix

Given the spatial separation of a failed waste container and shotcrete support structures in the main drift turnout intersections and in the exhaust drift intersections, the question arises as to the probability that leachate plumes from both might intersect and mix at depth. The likelihood that this would occur depends on the extent of lateral spreading of the plume due to transverse dispersion with increasing depth in the unsaturated zone. There are three mechanisms that could lead to plume lateral dispersion: hydrodynamic dispersion due to heterogeneities in the host rocks, molecular diffusion through the rock matrix, and capillary dispersion. The last process could occur to a significant degree only in the event of leaching of either cementitious material or the waste package by a focused plume percolating into the dryout zone surrounding the repository prior to rehydration, such as might occur during episodic events described in Section D.4.4.4. Rehydration of the repository horizon and underlying formations would be

accompanied by equilibration of capillary pressure, and, therefore, capillary dispersion would no longer be operative.

Transverse plume spreading due to intrinsic heterogeneities in the vitroclastic tuffs could be a significant factor in inducing lateral dispersion in a migrating plume. This process is essentially Fickian in nature and can be treated in the manner described by Pruess (1996). The effective transverse dispersivity, α_T , is

$$\alpha_T = \frac{1}{2} \frac{d}{dz} (\sigma_T^2) \quad (\text{Eq. D-14})$$

where σ_T^2 is the variance of the transverse distribution of solute concentration in the plume, and z is the vertical distance of migration. Consider a hydrologically unsaturated rock consisting of separate idealized cubic matrix blocks of length d , bounded by continuous fractures, such that each block is in contact with its neighbors. The contacts (asperities) represent only a fraction of the total surface area of the bounding fracture surfaces. It is assumed that the fracture surfaces represent impermeable capillary barriers, that the pore waters percolate under gravity, and that they only flow across blocks through the fracture asperities. Consider a point source contaminant originating in one block as the source of the contaminant plume and that this plume migrates vertically downward within the block. When the flow encounters the impermeable barrier at the bottom of the block, it is assumed to split into two separate equal flows at $x = +d_x/2$ and $x = -d_x/2$ in underlying contiguous blocks, where d_x is the horizontal dimension of the block. The increase in the variance due to this process, $\Delta\sigma_T^2$, is:

$$\Delta\sigma_T^2 = 1/2 \{ (+d_x/2)^2 + (-d_x/2)^2 \} = d_x^2/4 \quad (\text{Eq. D-15})$$

Given that the matrix blocks are assumed to be of uniform size, the impermeable barriers occur in the vertical direction with a separation, d_z , the vertical dimension of the block, then the transverse dispersivity can be expressed as:

$$\alpha_T = 1/2(\Omega/d_z)(d_x^2/4) \quad (\text{Eq. D-16})$$

where Ω is the probability of encountering a capillary barrier at the block intersection. If it is assumed that the asperities represent one-third of the block in contact, then $\Omega = 1-1/3 = 2/3$. Assuming that $d_z = d_x = 0.377$ m (Liu et al. 2003, Table 1), then $\alpha_T = 0.0314$ m.

The plume width, x , can be approximated by $(D_d t)^{1/2}$, where D_d is the dispersion coefficient and equals $\alpha_T v$, t is time, and v is the percolation velocity. Given that $z = vt$, x can be expressed as:

$$x = (\alpha_T z)^{1/2} \quad (\text{Eq. D-17})$$

The value of x , calculated at the 300-m depth of the water table below the repository horizon (BSC 2004k), is approximately 3.1 m.

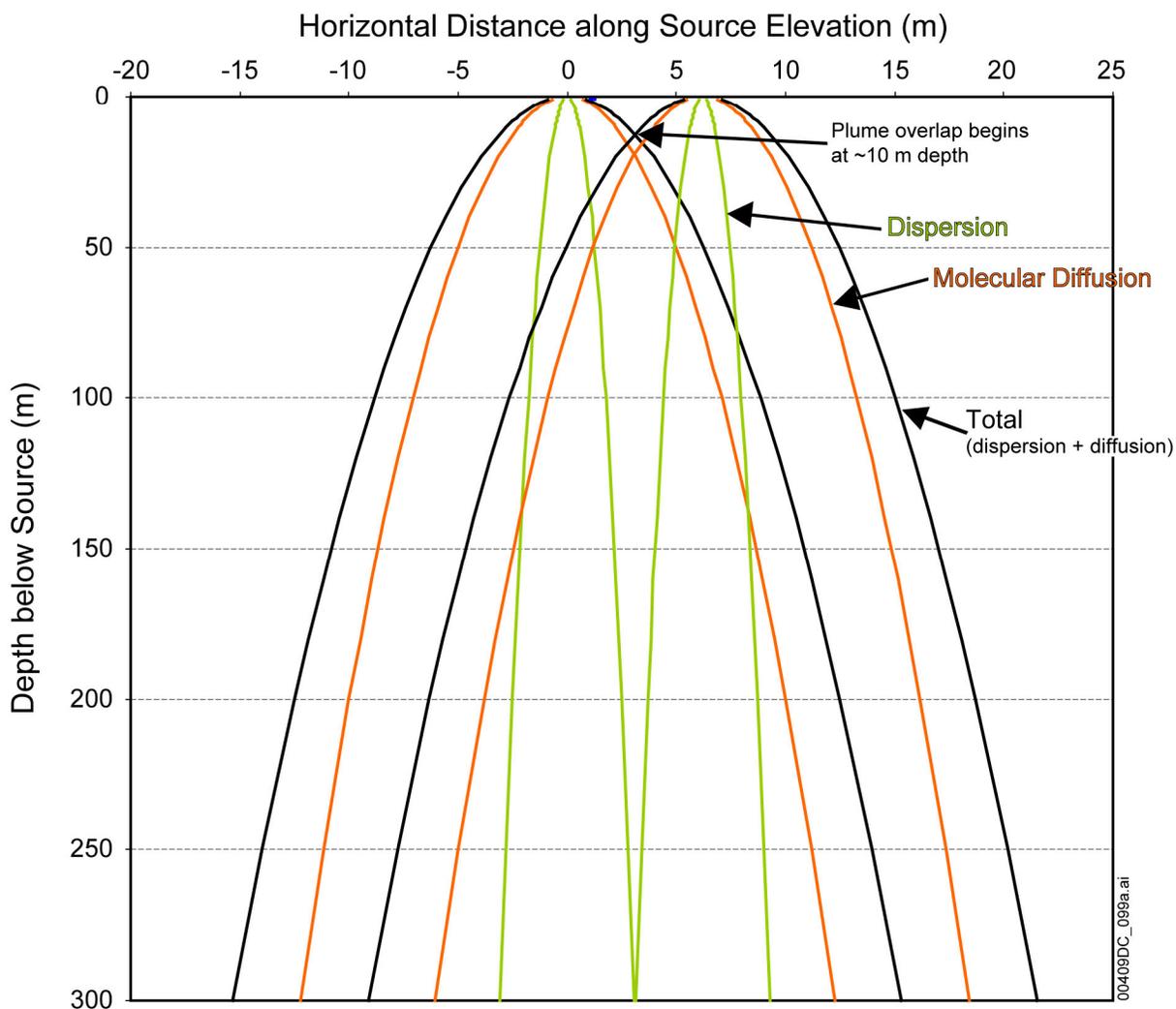
Dispersivity arising from molecular diffusion, α_{md} , can be calculated from the effective molecular diffusion coefficient D_e and v :

$$\alpha_{md} = D_e/v \quad (\text{Eq. D-18})$$

Assuming an average molecular diffusion coefficient of 10^{-9} m²/s (Sonnenthal and Bodvarsson 1999), a tortuosity factor of about 0.5 (Liu et al. 2003), and a porosity of 0.16 (Liu et al. 2003), D_e is 8×10^{-11} m²/s. Assuming an infiltration rate of 5 mm/yr or 1.6×10^{-10} m/s gives a α_{md} value approximately equal to 0.50 m. Dispersion due to molecular diffusion will, therefore, contribute overwhelmingly to plume lateral dispersion, and this effect will lead to a mean plume width of 24 m at the water table. The total estimated plume width at the water table 300 m below the repository horizon is the sum of the mean plume width due to molecular diffusion (24.5 m) and heterogeneity (3.1 m), or 27.6 m (see Figure D-5). These results are comparable with chloride lateral diffusion illustrated by Sonnenthal and Bodvarsson (1999).

An alkaline leachate plume could mix with a water-borne radionuclide plume from a failed waste package if the distance between the cementitious material and a failed waste package at the repository horizon is less than the plume width. The failure scenario of greatest concern is that which involves the failure of either of the outside waste packages in the emplacement drift. The end of the last waste package will be separated from the end of the turnout by a minimum horizontal distance of 1.5 m (BSC 2003d, Section 6.3). However, current plans involve the removal of all nonsupport concrete, including inverts, from the repository prior to closure (BSC 2003d; BSC 2004g). The 0.45 ton of grout associated with rock bolt supports will remain, but calculations elsewhere in this appendix (see Section D.4.4.3) indicate that this grout would be effectively carbonated prior to rehydration and would have negligible effect on repository performance. Therefore, the separation of the last emplaced waste package and the remaining committed cementitious support material (i.e., shotcrete) in the main access drift turnout intersection would be approximately 60 m (BSC 2004n) (Figure D-1). This separation would be sufficient to prevent the intersection of cementitious leachate plume with that of a plume transporting radionuclides from the last emplaced waste package if it were to fail.

The situation is somewhat different with respect to the first-emplaced waste package on the exhaust drift side, where a minimum standoff of 15 m would be maintained between the end of the first emplaced waste package and the centerline of the exhaust main (BSC 2003d, Section 6.3). Approximately 8.8 m of this distance would be shotcreted (BSC 2004i). Therefore, the separation between the start of an emplacement drift and the shotcreted intersection would be a little over 6 m. Thus, a potential exists for the intersection of cementitious leachate plume with a radionuclide-containing plume from the first-emplaced waste package. The nature and extent of predicted plume overlap from a hypothetical initiation of concurrent alkaline and radionuclide-bearing plumes is illustrated in Figure D-6. Note that the horizontal scale is exaggerated in relation to the vertical scale, creating a misleading impression that plume spreading is greater than is actually the case. The potential effects of this interaction are discussed below.



Source: DTN: LB0408CMATUZFT.003.

NOTE: Horizontal scale is exaggerated by a factor of approximately 7.5.

Figure D-6. Plume Spreading with Depth Due to Lateral Dispersion and Molecular Diffusion

D.4.4.4.3 Transient Condensation

Condensation of water vapor in the main drifts as a result of pore-water evaporation from host rocks surrounding the emplacement drifts will occur during the initial phase of heating after waste emplacement. This phenomenon arises because of transient temperature differences between the emplacement and main access and ventilation drifts when the latter will be cooler. The leaching of cementitious material by this condensate will take place under conditions when the cementitious material is still young and will be similar to those due to dewatering. The consequences will, therefore, be analogous to those described in Section D.4.4.1.

D.4.4.4 Rehydration

The composition and pH of the cementitious material leachate plume following rehydration of the repository would depend on the nature and extent of preceding recrystallization and carbonation under high pH (Hardin 1998). With total carbonation, the leachate plume composition would differ little from that of the ambient pore water (Hardin 1998, p. 6-28). The possible excess of sodium and potassium in the altered cementitious material (DTN: LL020805523125.002) might result in the transient release of NaHCO_3 (most potassium would be fixed in secondary illitic clay), and the pH could rise initially to more than 9, but this excursion is expected to be minimal in duration and, overall, influence only trace amounts of calcite likely to precipitate through interactions of the NaHCO_3 leachate with Ca^{2+} in the pore water. Therefore, if total carbonation of the cementitious material were to occur together with subsequent leaching, there would be no impact on repository performance or radionuclide migration. This condition could be achieved with respect to shotcrete support structures in the inner part of the repository, where the dryout period is about 1,000 years in duration (Section D.4.4.3).

Conditions would be somewhat different if only partial carbonation were to occur before rehydration, as would be expected in the peripheral parts of the repository (Section D.4.4.3). In this case, residual calcium silicates, such as gyrolite, xonotlite, tobermorite, and hillebrandite, could still be present (Hardin 1998, p. 6-37) (Figure D-3), depending on the amount of silica fume added to the shotcrete and the extent of reaction with the fine aggregate. In the presence of percolating pore water, the leachate composition could be elevated in calcium, and the pH could range between 10 and 12, depending on the chemical composition of the original Portland cement and the extent of subsequent interaction of the cement with the associated fine aggregate (Section D.4.4.2). The interaction of cementitious C-S-H phases with alkali feldspar in the fine aggregate of the shotcrete could also lead to modification of the resulting shotcrete phase assemblage, with Na_2O substituting in gyrolite, and Al_2O_3 substituting in tobermorite (Section D.4.4.2). These reactions could also modify the composition of the initial leachate. Studies to evaluate this phenomenon have yet to be undertaken.

In Table D-12, the chemical composition of the aqueous phase in equilibrium with binary two-phase assemblages in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ have been calculated at 25°C using EQ3 V 7.2b (Wolery 1992) and the associated Data0.dat database. The results are for illustrative purposes only, as the cementitious materials contain chemical components other than those employed to illustrate this simple system. Despite these limitations, the calculations clearly show the importance of the ultimate $\text{C}/(\text{C}+\text{S})$ ratio of the cementitious reaction product in minimizing the release of Ca^{2+} to the environment through leaching following rehydration.

Table D-12. Chemical Composition of Cementitious Materials Leachate as a Function of the Mineralogy after Hydrothermal Alteration

| Phase Assemblage | Total SiO ₂ (aq) (mg/kg H ₂ O) | Total Ca ²⁺ (mg/kg H ₂ O) | pH |
|-------------------------------|---|--|-------|
| Portlandite-hillebrandite | 0.14 | 625 | 12.37 |
| Hillebrandite-tobermorite-14A | 0.20 | 559 | 12.33 |
| Tobermorite-14A-gyrolite | 18.4 | 16.9 | 10.74 |
| Gyrolite-cristobalite(alpha) | 51.9 | 12.8 | 10.09 |
| Calcite ^a | - | 43.9 | 7.62 |

Source: DTN: LB0408CMATUZFT.004; EQ3 Version 7.2b (Wolery 1992).

NOTE: ^aAssumed $\log(p\text{CO}_2) = 2.52$ (3,000 ppmV).

Table D-12 shows that the reaction of the cement components of the shotcrete with silica fume and the fine aggregate could produce mineral assemblages such as tobermorite-14A-gyrolite or gyrolite-cristobalite(alpha). The coexisting aqueous phase at equilibrium with these mineral pairs differ in Ca²⁺ and SiO₂(aq) concentrations only incrementally from those of existing pore waters, and, therefore, a leachate from such mineral assemblages would not generate a deleterious alkaline plume.

Any alkaline leachate would be subject to reaction and neutralization by the ambient CO₂ in the gaseous phase filling the fractures in the host rock. The approximate rate of neutralization in the presence of elevated $p\text{CO}_2$ in the time period following rehydration can be estimated from experimental work and associated model simulations (DTNs: LL030211423125.005, LL030211523125.006). This work demonstrates that CO₂ uptake and neutralization at 25°C could take place in the field within a matter of weeks, a time period that is essentially instantaneous when considered within the context of repository timescales of interest. Such rapid rates of neutralization would suggest that plume neutralization would occur locally (i.e., within a few centimeters of the shotcrete interface). Field observations involving groundwater interactions with subsurface concrete structures corroborate these rapid reaction rates (Liu and He 1998). Ambient gaseous CO₂ uptake and aqueous phase carbonate diffusion rates would also suggest that much of the neutralization of the alkalinity and precipitation of calcite could occur within the pores of the shotcrete. However, additional modeling would be required to confirm this possibility. Therefore, it can be concluded that the generation of an alkaline plume following rehydration, which could affect radionuclide transport, would be extremely unlikely. If the cementitious material were to be incompletely carbonated, the leachate itself would be carbonated and the pH lowered to ambient pore-water values. The leaching of a partially carbonated cementitious material would, therefore, produce an outcome similar to that for a fully carbonated cementitious material, and the impact on radionuclide migration would be minor.

Even if an alkaline plume were to form, it would encounter elevated concentrations of CO₂ below the repository horizon. Dryout of the repository horizon would induce diffusive migration of CO₂ in the gaseous phase, which would be absorbed by groundwater and collect as a blanket beneath the repository horizon (CRWMS M&O 2000, pp. 79 to 81; DTN: LL030211423125.005), thereby providing added capacity for alkaline plume neutralization in the underlying unsaturated zone and inhibiting further plume migration. This blanket would,

however, be relevant primarily in neutralizing episodic fast flows, as discussed in Section D.4.4.4.1.

D.4.4.5 Precipitation of Secondary Calcite in Devitrified Tuff Host Rocks

One of the technical requirements of the response to ENFE 1.04 is an assessment of the potential effect of leaching of the emplaced cementitious materials and how the consequent precipitation of minerals within the host rock would impact the hydrologic properties of the unsaturated zone. Modification of the hydrologic regime could result in percolating pore water being diverted toward the waste packages in the emplacement drifts with undesired consequences in the event of a waste package failure. If alkaline plumes were to form due to incomplete carbonation, their neutralization would decrease the concentration of gas-phase CO₂ in the host-rock fractures and cause the precipitation of calcite in the rock pores and fractures below the repository horizon, with concomitant reduction of dissolved calcium. The plumes could also react with the vitroclastic tuffs of the host rock and precipitate secondary calcium aluminosilicates in the matrix pores and on fracture surfaces, causing further reduction in rock permeability, although this phenomenon is expected to be minor. As is discussed elsewhere in this appendix, the hydrologic impact would depend substantially on the extent to which the cementitious constituents are converted in situ into calcite during the period when the repository environment would have undergone dryout. Work done to date does not provide any quantitative predictions of the extent of carbonation during this period.

Given the uncertainties associated with estimates of the extent of cement carbonation during the dryout period prior to rehydration, it is instructive to consider a worst-case scenario in which all of the most highly reactive constituent (portlandite) that would be present initially in the shotcrete is leached at a specified location, such as a turnout intersection from the main access drift into one of the emplacement drifts or the exhaust side intersection from the emplacement drift, as illustrated in Figure D-1. At representative intersections, 665 m² and 220 m² of shotcrete, 0.1 m thick, or 66.5 m³ and 22 m³, will be applied, respectively, at these two intersections. It is assumed that the gross footprint of each turnout intersection is 36 × 10 m and 15 × 13 m, respectively, and that all of the initial portlandite, approximately 1,821 mol/m³, contained in the cementitious materials would be dissolved, transported, and precipitated as calcite in the fractures immediately beneath these footprints, as would be predicted from laboratory experiments (DTN: LL030211423125.005).

If the calcite precipitates in the matrix (16.4 vol %; Liu et al. 2003) and in the fractures (1 vol %; estimated, this appendix) for a total of 17.4 vol %, then the total filled thickness in the rock below the turnout intersection would be 7.14 cm (Table D-13). Under these conditions, the rock would be rendered impermeable and all percolation would be diverted around this impermeable barrier. However, this calculation ignores completely the nature of the precipitation process in fractures in the unsaturated zone. Fractures are not of uniform width and contain numerous asperities. Localized precipitation at these asperities and irregular rimstone or calc-sinter deposition elsewhere within the fracture voids could result in the formation of a spongy tufa with a high porosity and low permeability. Very little of such material could reduce the transmissivity or totally seal the affected fractures after only minimal precipitation and divert the flow laterally, only to cause the process to be repeated in adjacent fractures. Thus, the hydrologic diversion of unsaturated zone groundwater flow around sealed regions below the shotcreted drifts could

become significant. It could be arbitrarily assumed that the calcite filled only the first centimeter of rock before lateral diversion took place, after which all further calcite precipitation took place to the same depth around the margins of the footprint. In this case, the affected area would be 2,571 m², and the margin would extend 13.4 m from the end of the shotcreted portion of the main access drift. This would place the margin about 49 m away from the first waste package. This would suggest that the hydrologic impact of calcite precipitation on the emplacement drift environment would be minimal.

Table D-13. Estimated Depth of Rock Voids Filled with Calcite Due to the Leaching of Portlandite from Shotcrete in a Main Access Drift Turnout Intersection

| Parameter | Units | Value | Reference |
|---|-------------------------|-----------------|--|
| Volume of shotcrete, main access drift intersection | m ³ | 66.5 | BSC 2004h. |
| Assumed shotcrete footprint, main access drift intersection | m ² | 360 | This appendix. |
| Assumed shotcrete footprint, exhaust drift intersection | m ² | 195 | This appendix. |
| Volume of shotcrete, exhaust drift intersection | m ³ | 22.0 | BSC 2004b. |
| Mass of portlandite in shotcrete | mol/m ³ | 1.821 | This appendix. |
| Solubility of portlandite at 25°C | mol/kg H ₂ O | 0.0156 | EQ3/6 V.7.2b Data0.dat (Wolery 1992). |
| Equivalent volume of calcite | m ³ | 4.47 | This appendix. |
| Density of calcite | g/cm ³ | 2.710 | Calculation from Table D-2. |
| Molecular weight of calcite | g/mol | 100.09 | Lide 2000, p. 4-50. |
| Total void-space fraction in rock | – | 0.174 | Matrix volume from Liu et al. 2003. Fracture volume assumed. |
| Infiltration rate | mm/yr | 1 to 5 | Sonnenthal and Bodvarsson 1999. |
| Depth filled with calcite, main access drift intersection | cm | 7.14 | This appendix. |
| Depth filled with calcite, exhaust drift intersection | cm | 4.36 | This appendix. |
| Time to precipitate calcite | years | 4,313 to 21,565 | This appendix. |

Source: DTNs: LB0408CMATUZFT.002, LB0408CMATUZFT.004.

Another aspect regarding alkaline plume neutralization is the time it would take to precipitate calcite in the rock pores and fractures. The infiltration rate at Yucca Mountain is estimated to range from 1 to 5 mm/yr (Sonnenthal and Bodvarsson 1999). Therefore, if the percolating pore water were to be saturated with respect to portlandite on contact with the cementitious materials at 25°C, it would contain approximately 0.0156 mol/kg H₂O·Ca(OH)₂(aq) (EQ3/6 V7.2b, Data0.dat; Wolery 1992). Mass-balance considerations show that this would lead to the deposition of between 5.62 and 28.1 mol/yr of calcite. Thus, the time required to leach all of the initial portlandite from the cementitious materials with essentially concurrent deposition in underlying pores of the host rock would be between 4,313 and 21,565 years. Because portlandite has retrograde solubility with temperature, leaching at higher temperatures would slow down the rate. The percolation rate following rehydration would be expected to be higher, thereby decreasing the overall time for precipitation of calcite due to plume neutralization. As noted elsewhere, the precipitation rate would likely be fast in relation to the leaching rate. The availability of CO₂ through diffusion would be expected to become rate controlling, because the

leaching rate of $\text{Ca}(\text{OH})_2$ would be slow in relation to CO_2 gaseous diffusion rates (Section D.4.3.4).

Other aspects of the above process should also be considered, which would modify the distribution of precipitated calcite. Before advective transport, the alkaline leachate must diffuse out of the concrete, which would be shielded by a rind of precipitated calcite within the shotcrete pores. The leachate would be exposed to CO_2 during this process and would have a tendency to precipitate at or near the concrete air–water interface. Subsequently, unneutralized leachate would initially percolate mainly through the rock matrix under a presumed normal percolation flux. The rate of neutralization by CO_2 would depend largely on the liquid–gas interfacial area, but this interfacial area would be expected to be limited by fracture interfaces in the relatively small volume of affected rock beneath the turnout intersection. This could retard calcite precipitation and cause it to be distributed over a larger volume of rock underlying the footprint. However, quantitative calculations have not been performed to evaluate this possibility. As noted in Section D.4.3.5.1, episodic flows could rapidly leach and transport alkaline solutions from the shotcrete and distribute the precipitated calcite over a large volume of rock in a subvertical region beneath the footprint.

Given the possibility that complete carbonation of shotcrete and grout could occur in most of the repository, some consideration should also be given to the impact that the resulting mineralogy would have on the hydrology and radionuclide transport in this limiting case. The mineralogic composition of a completely carbonated cementitious material will depend, to a certain extent, on the original formulation of the cementitious material (i.e., the $\text{C}/(\text{S}+\text{C})$ ratio), as determined by the addition of silica fume and on the concentration of alumina and additives, such as gypsum (Nelson 1990). As noted in Section D.4.4.2, C-S-H gel could either alter directly to calcite after the substantial alteration of CH, or it could transform to calcite through intermediate secondary calcium silicates. Whichever path is taken, the resulting product would consist of calcite plus opaline silica. The remaining residual phases would consist dominantly of secondary and potassic or calcic clays, depending on the quantities of alumina and magnesia in the original cementitious material. A leachate from this mineral assemblage would not possess significant alkalinity, as shown in reaction progress simulations after 10,000 years (CRWMS M&O 1998, Figure 4-41) and would neither precipitate significant secondary calcite outside the cementitious material nor adversely affect radionuclide retardation (Section D.4.4.6).

D.4.4.6 Generation and Transport of Colloids from Grout

Another issue of concern regarding the emplacement of cementitious materials in the repository is the potential for colloidal particles to be generated and for these colloids to be advectively transported by groundwater and act as a substrate for radionuclide sorption or precipitation. This issue was raised in earlier publications (e.g., Hardin 1998, pp. 6-36, 6-59), citing supporting evidence by Ramsay et al. (1988). Such a scenario, while theoretically possible, is highly implausible for the following reasons:

- Significant release of colloids is plausible only from freshly prepared cementitious material before it has significantly recrystallized through exposure to elevated temperatures at high relative humidity. The colloidal C-S-H phase formed in the

cementitious material immediately after cement is mixed with water is a potential source of migrating colloids.

- During the time when mobile colloids could form and be transported, the ionic strength of the leachate is expected to be sufficiently high to destabilize the colloidal particles, causing them to aggregate or adhere to siliceous rock surfaces, thereby decreasing their concentration in solution to background levels.
- The effective diffusivity of colloidal particles into the rock matrix is many orders of magnitude lower than for molecular or ionic species. The advective transport of colloidal particles is restricted to episodic flow along transmissive faults under fast flow path conditions. Fast transport of colloidal particles is, therefore, severely restricted in volume and location within the repository. Therefore, lateral diffusion of colloids in a plume would be negligible, and the lateral spreading of colloids would be due to physical dispersion of the plume (Section D.4.4.4.2).
- During the period when colloids could be leached and transported from the grout, waste package failure is improbable. Therefore, the intersection of a leachate plume containing cementitious colloidal particles with a radionuclide-bearing leachate plume from a failed waste package is temporally improbable.
- The colloidal C-S-H phase formed in the grout during setting (the potential source of migrating colloids) is highly reactive and, thus, would be transformed to calcite or secondary C-S-H phases at the elevated temperatures, relative humidity, and $p\text{CO}_2$ following repository closure (provided CO_2 availability is not restricted).
- Any colloidal particles that survive aggregation or adhesion, as noted above, would be thermodynamically unstable in the ambient pore-water environment of the unsaturated zone, preferentially releasing calcium that precipitates as calcite under the calcite-saturated conditions present in the unsaturated zone at Yucca Mountain.

In order to substantiate the statements listed above, it is necessary to explain the characteristics of Portland cement, the principal reactive ingredient of shotcrete, and its behavior after contact with water. If recently set Portland cement is leached with distilled water, the CH readily dissolves to produce a highly alkaline solution with a pH in excess of 12, consisting primarily of dissolved $\text{Ca}(\text{OH})_2$, with minor concentrations of NaOH and KOH (DTN: LL020805523125.002; Wieland et al. 2004, p. 120). The leaching process can also mobilize colloidal C-S-H gel particles (Ramsay et al. 1988; Wieland and Spieler 2001). Wieland and Spieler (2001) measured particle sizes between 50 and 1,000 nm, but they assumed that the total population ranged in size to as low as 1 nm. Ramsay et al. (1988), however, observed particles between 2,000 to 5,000 nm in diameter, which aggregated (Ramsay et al. 1988, pp. 121, 123). Furthermore, they found evidence of particle growth (Ramsay et al. 1988, Figure 7b, pp. 122 and 123), reflecting Ostwald ripening (Steeffel and Van Cappellen 1990). Wieland and Spieler (2001, p. 521) also determined that colloidal particle concentrations in solution were strongly dependent on ionic strength and that a leachate saturated with calcium hydroxide induces substantial colloidal aggregation, leading to a very low residual colloid concentration of about 0.01 mg/L. They showed that this concentration is equivalent to or less than the colloidal concentrations

found in natural groundwater (see also *Waste Form and In-Drift Colloids-Associated Radionuclide Concentrations: Abstraction and Summary* (BSC 2003a, p. 30)).

Because the concentration of produced cementitious colloidal particles would be at concentrations similar to those found to occur naturally in groundwater, their presence would be inconsequential except for the very high experimentally determined partition coefficients for uranium and neptunium on such particles (Hardin 1998, pp. 6-39 to 6-45). However, the capacity for these colloidal particles to be transported is limited to high permeability zones or open faults within Yucca Mountain and the coincidence of the positioning of emplaced grout within or immediately above such high permeability zones. Additionally, the capacity of these particles to transport uranium and neptunium depends on collocation of the colloids and radionuclides, which is unlikely. The findings of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003e, pp. 177 to 188, Attachments VI and VII) support this conclusion.

Leaching of the colloids from the grout would have to take place before the C-S-H colloid recrystallizes through thermal heating during the period of high relative humidity. This could only occur before dryout of the repository horizon, during or prior to emplacement of the waste packages. Thus, the release of colloids is temporally distinct from potential waste package failure.

The bases presented above, together with supporting documentation, lead to the conclusion that the release of colloidal particles from cementitious materials would be unlikely to affect repository performance or radionuclide migration.

D.4.5 Summary

Cementitious material (shotcrete and grout for rock bolt emplacement) is planned for use in the Yucca Mountain repository for ground support at the emplacement drift intersections with the main access drifts and the exhaust drifts. The retention of this material in the repository poses two concerns. The first is that the leaching of these cementitious materials will affect repository performance by modifying the hydrologic properties of the surrounding rock and diverting the flow of water entering the drifts. The second concern is that an alkaline plume resulting from leaching of this material could enhance radionuclide transport to the accessible environment, either through the complexation of radionuclides or through transport by pseudocolloids. Both concerns become relevant only after the repository environment rehydrates following a period of dryout due to heating caused by radioactive decay of the emplaced waste.

The first step in evaluating the concerns was to investigate the extent of chemical alteration of the shotcrete, formulated with Type II cement, prior to repository closure and during the postclosure dryout period. Chemical alteration of the cement component of the shotcrete would occur through recrystallization, reaction with silica fume and aggregate, and carbonation. The second step was to determine the consequences of this alteration on the formation of alkaline plumes caused by leaching the shotcrete following rehydration. The third and final step was to evaluate the potential impact of plume neutralization by CO₂ on the hydrology of the unsaturated zone, whether and where a shotcrete leachate plume would interact with a leachate waste plume from a failed waste package, and whether radionuclide migration would be affected.

Several important findings were obtained from the evaluation. The first was that recrystallization of the cement and its further reaction with silica fume additive and with the fine aggregate included in the shotcrete formulation would lead to the formation of a silica-rich calcium silicate hydrate assemblage. Carbonation of the cement component of the shotcrete would take place both before and after repository closure and simultaneously with recrystallization. Calculations indicate that carbonation would be substantial to complete, where the repository environment is hot enough that rehydration occurs after more than 1,000 years. Elsewhere, where rehydration occurs in less than 1,000 years, carbonation could be incomplete. During the dryout period, carbonation rates are limited by gaseous phase CO₂ diffusion through the host rocks, rather than by the carbonation reaction itself, which would be fast. Following rehydration, carbonation would continue at a reduced pace, the rate being limited by aqueous phase CO₂ diffusion into the pores of the shotcrete. Upon rehydration, the pore waters would leach the silica-rich calcium silicate hydrates, but their solubilities would be so low that calcium and silica concentrations would be comparable to those of ambient pore water, and the alkalinity would be low. Neutralization of this alkalinity would be very rapid, and, if any calcite were to precipitate, it would occur in the immediate vicinity or even within the pores of the shotcrete. The resulting plume would have a composition similar to that of the ambient pore water.

The proximity of shotcrete in the exhaust drift intersection to the nearest waste package in the emplacement drift indicates that a shotcrete leachate plume could intersect a radionuclide-bearing plume from the waste package below the repository horizon, but that this plume would have little or no impact on radionuclide migration. Because of the extensive recrystallization and modification of the mineralogy of the shotcrete and partial to complete carbonation, extensive precipitation of calcite in the pores of the host rock is unlikely, and, therefore, hydrologic modification of the unsaturated zone by the retention of ground support cementitious material is likewise considered unlikely.

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D.5.2 Data, Listed by Data Tracking Number

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LB0408CMATUZFT.001. Hydrothermal Recrystallization—Supporting Calculations. Submittal date: In progress.

LB0408CMATUZFT.002. Carbonation—Papadakis Model Calculations for Carbonation Distances. Submittal date: In progress.

LB0408CMATUZFT.003. Leaching of Altered Cementitious Materials—Estimates of Molecular Diffusion/Dispersion in Cementitious Material Transport. Submittal date: In progress.

LB0408CMATUZFT.004. Leaching of Altered Cementitious Materials—EQ3/6 Simulations for Cementitious Material Transport. Submittal date: In progress.

LL020711323125.001. Pre-Test Calculations for Grout Carbonation Experiments. Submittal date: 08/13/2002.

LL020805523125.002. Experimental Studies of Cement Grout-Water Chemical Interaction. Submittal date: 08/28/2002.

LL030211423125.005. Cementitious Grout-Seepage Water Interaction. Submittal date: 02/02/2004.

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