

# **Estimating the Longevity of the Chemical Impact of Concrete on Near-Field Geochemical Fluids**

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# 1 ABSTRACT

Extensive use of concrete has been proposed for the construction of the proposed underground high level nuclear waste repository at Yucca Mountain, Nevada. Water that enters the emplacement drifts of the repository will react with the concrete and become highly alkaline. This high pH environment ( $\text{pH} > 10.5$ ) will impact the performance of the repository by affecting the rates and processes of waste package degradation, the release of radionuclides from the repository, and the transport of radionuclides in the unsaturated zone. The longevity of the high pH conditions needs to be determined to adequately assess the potential impacts on performance. Both the rates of leaching of the cementitious materials by infiltrating water and the rate of carbonation of the cementitious materials due to diffusion of  $\text{CO}_2$  and its reaction with  $\text{Ca}(\text{OH})_2$  in the concrete control the length of time high pH conditions will persist. Previous non-site specific estimates of the time it will take for the pH of the pore fluid to decrease below a pH of 10.5 range from 900 years to more than one million years for a variety of scenarios including the carbonation of bridges and the leaching of high pH contributing phases of various cementitious underground low-level waste repositories. Carbonation of the cementitious material at Yucca Mountain has been previously postulated to be the most rapid mechanism for alkalinity reduction.

A site specific analysis using postulated design conditions indicates that neither complete carbonation of the pre-cast concrete tunnel liner (20 cm thick) nor complete leaching of the chemical components that cause alkalinity in the concrete would occur within 10,000 years. These results indicate that high pH conditions should be assumed for performance assessments of the potential high-level nuclear waste repository.

# 2 INTRODUCTION

Construction of a permanent high level waste disposal facility is being proposed as a long term option for the storage of nuclear waste (Nuclear Waste Policy Act Amendments of 1987). The potential repository is located at Yucca Mountain in Nevada, buried inside the mountain itself. Cementitious materials will be used extensively during the construction of the site (TRW Environmental Safety Systems, Inc., 1997; hereafter referred to as TRW, 1997). The repository will consist of a series of drifts within which waste canisters will be placed. Concrete will be used to line these drifts for the purpose of providing mechanical stability (TRW Environmental Safety Systems, Inc., 1996a; hereafter referred to as TRW, 1996a). The concrete could have a number of impacts on the performance of the near field geochemical environment including creating highly alkaline conditions. Heat generated by the decay of the radioactive material further complicates the situation. For instance, this heat from the repository may cause CSH recrystallization that could affect the pH of leached fluids (Sagar, 1997). However, the persistence of highly alkaline conditions could be limited due to various chemical processes. The processes of leaching in the aqueous phase and carbonation in the vapor phase determine the persistence of the high pH. There have been a number of studies and reports that have estimated the longevity of the high pH conditions in various settings. The purpose of this report is to evaluate previous estimates and to independently calculate a site specific estimate of how long it would take to carbonate the pre-cast concrete liners in the proposed Yucca Mountain repository.

## 2.1 PROPERTIES OF CEMENT AND CONCRETE

The chemical composition of cement is fairly complicated. For simplification, a number of abbreviations are used. C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, CH = Ca(OH)<sub>2</sub>, AH = Al(OH)<sub>3</sub>, MH = Mg(OH)<sub>2</sub>, and CS = CaSO<sub>4</sub>.

Concrete is made from cement, aggregate, water, and other additives. Portland cement is the most common cement type and is what has been and will be used in the concrete at the repository (Sagar, 1997). Portland cement is composed primarily of tricalcium silicate (C<sub>3</sub>S), dicalcium silicate (C<sub>2</sub>S), tricalcium aluminate (C<sub>3</sub>A), and tetracalcium aluminoferrite (C<sub>4</sub>AF). The chemical composition limits of Portland cement by weight percent are 60-67% CaO, 17-67% SiO<sub>2</sub>, 3-8% Al<sub>2</sub>O<sub>3</sub>, 0.5-6.0% Fe<sub>2</sub>O<sub>3</sub>, .02-1.3% Na<sub>2</sub>O + K<sub>2</sub>O, 1-3% SO<sub>3</sub>, and 0.1-4% MgO (Neville, 1981).

When the components of concrete are mixed, the cement hydrates and a paste is formed. This paste dries and hardens to become concrete. Hydrates of various compounds are called gel. Calcium silicate hydrate (CSH) gels are the main constituents of hydrated cement. CSH is the principal binding phase of concrete. It is an amorphous solid and is thermodynamically metastable. It has a variable stoichiometry, with a Ca/Si ratio that generally ranges from about 0.9 to 1.7. CSH can be formulated as Ca<sub>x</sub>H<sub>6-2x</sub>Si<sub>2</sub>O<sub>7</sub>·zCa(OH)<sub>2</sub>·nH<sub>2</sub>O (Walton et al., 1990). CSH gels dissolve incongruently (Berner, 1992). In general, dissolution follows an equation of the form



This process is incongruent because the ratio of p/q does not correspond to x (Berner, 1992).

The other two main phases present in hydrated Portland cement are an aqueous phase and a crystalline solid phase of portlandite, Ca(OH)<sub>2</sub>. Portlandite crystals are embedded in a matrix of CSH gel, while the aqueous phase primarily fills pore space within the concrete.

The presence of alumina and iron oxide in concrete causes the formation of other compounds. An aluminoferrite hydrate called hydrogarnet and two sulphoaluminates, ettringite and monosulphate, are formed. The abbreviations AF<sub>t</sub> and AF<sub>m</sub> are used to refer to ettringite and monosulphate. The subscripts t and m stand for "tri" and "mono" sulphate (Atkins and Glasser, 1992).

In general, hydrated cement consists of (by weight): 40-50% CSH gel, 20-25% portlandite, 10-20% ettringite (AF<sub>t</sub>) and monosulphate (AF<sub>m</sub>), 10-20% pore solution and 0-5% minor components (NaOH, KOH, Mg(OH)<sub>2</sub>, etc.) (Berner, 1992).

The main purpose of using concrete in the potential Yucca Mountain repository is to provide mechanical stability (TRW, 1996a). Concrete can also serve as a barrier to radionuclide migration into the host rock by providing sorption sites for radionuclides.

Interactions between cement and water can affect the near field environment in a number of ways. When cementitious materials interact with water, pore fluid with pH between 10 and 13.5

is produced. This fluid moves with groundwater flow through the rock surrounding the repository. These fluids could have a number of effects on the waste and surrounding rock that could affect radionuclide release and transport.

The pH of the hyperalkaline plume is directly related to alkali content (Glasser et al., 1985). Glasser et al. (1985) evaluated conditions for a generic repository and indicated that pore fluids are expected to be dominated by potassium and sodium hydroxides for at least a thousand years after a repository is closed. These fluids are called 'early' or 'young,' whereas the succeeding fluids, expected to be dominated by calcium, are referred to as 'late' or 'evolved.' The early pore fluids are estimated to have a pH of 13.5 and the evolved pore fluids will initially have a pH of about 12.5. The pH is expected to decrease over time due to concrete leaching which results in the loss of alkalis (Savage, 1997). Processes such as carbonation can also result in a decrease in pH. For the most part, the processes that lower the pH of concrete are so slow that the chemical effects outlast the structural lifetime (Walton, et al., 1990).

## **2.2 REPOSITORY LOCATION**

The repository will be built inside Yucca Mountain, which is located in the desert of Nevada, about 120 km northwest of Las Vegas. Yucca Mountain consists of a series of welded and nonwelded tuff units. The repository will be located in the Topopah Spring tuff, a welded tuff unit in the unsaturated zone that is 500 to 750 meters thick (Wilder, 1994). The location of the repository will be at least 200 meters below the surface and at least 100 meters above the water table (TRW, 1997).

The climate at Yucca Mountain is very dry, with rainfall typically only 15 - 25 cm per year. The relative humidity (RH) conditions at Yucca Mountain are discussed in Section 7.2. The Topopah Spring member is expected to have 65% saturation (+/- 19%) and a porosity of 15% (Wilder, 1994). According to Wilder,

The Topopah Spring tuff consists of primary minerals (e.g., sanidine, plagioclase, quartz, biotite, iron-titanium oxides, allanite, and zircon) and secondary minerals (e.g., cristobalite, quartz, alkali feldspars, and smectite clays). In addition there are minerals that formed on fracture surfaces (e.g., calcite, smectite, quartz, cristobalite, alkali feldspar, and the zeolites mordenite, chabazite, clinoptilolite, and heulandite). These minerals form layers with properties distinct from those of the rock matrix and are estimated to be a maximum of 5% of the total rock mass. Some of the zeolite minerals are radionuclide sorptive so that transport would tend to be retarded or hindered if there were sufficient volume of these minerals in contact with the radionuclides.<sup>1</sup>

## **3 CHEMICAL IMPACTS ON NEAR FIELD ENVIRONMENT**

The presence of concrete will have a number of effects on the near field environment and could substantially impact the performance of the repository. For the purposes of this report:

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<sup>1</sup>Wilder, 1994, p. 1180.

The near field is defined as that portion of the repository where physical and chemical properties have been altered by the proposed repository construction operations and radioactive waste emplacement affecting performance of the proposed repository.<sup>2</sup>

Some of the potential impacts on the repository include effects on radionuclide containment, release, and transport.

### **3.1 RADIONUCLIDE CONTAINMENT AND RELEASE**

The presence of concrete in the repository could affect both the containment of radionuclides in waste containers and their release.

Hyperalkaline pore fluid could have positive or negative effects on the waste package material depending on the pH of the fluid. Generally, an alkaline environment (pH 9 - 12) lowers the corrosion rate of carbon steel due to passive film formation that serves to protect the material from uniform corrosion. Metal solubility is also lowered. However, under moderately alkaline conditions, localized corrosion in the form of pitting or crevice corrosion can still occur. In addition, stress corrosion cracking can occur under alkaline conditions. Should the pH of fluid that contacts the container exceed a pH of 13, rapid uniform corrosion could ensue.

Changes to the waste-form itself could occur due to the presence of concrete. The dissolution and alteration of nuclear waste glass could be accelerated (Sagar, 1997). In addition, co-precipitation of some radionuclides in concrete alteration products that could form within waste packages has been observed (Savage, 1997).

### **3.2 RADIONUCLIDE TRANSPORT**

Once waste package failure has occurred, and radionuclides are released, alteration of the near field environment due to alkaline pore fluid could affect the transport of radionuclides through the geologic barrier. Radionuclide transport through the geologic system could be impacted by mineral alteration that could result in co-precipitation of radionuclides, changes in porosity and permeability due to reactions with host rock, and changes in matrix diffusion, sorption, and colloidal transport.

#### **3.2.1 Mineral Alteration**

The hyperalkaline plume could affect both the primary and secondary minerals along the radionuclide flow path within Yucca Mountain. Dissolution of sorptive secondary minerals could occur. Minerals such as clinoptilolite, mordenite, and montmorillonite, which are prevalent in the area surrounding the repository, become unstable at high pH (Sagar, 1997). In addition, the primary minerals of the tuff could be affected by the alkaline plume. According to Savage,

There will be a tendency for the de-stabilization of well-crystalline, anhydrous/poorly hydrated minerals such as silica polymorphs, feldspars, micas, carbonates, and oxides,

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<sup>2</sup>Sagar, 1997, p. 4-1.

to be replaced by poorly crystalline, more hydrous alkali/alkaline-earth zeolites, calcium silicate hydrates, and hydroxides. These transformations will change the capacity of the far-field to retard radionuclide migration.<sup>3</sup>

Precipitation of new minerals could also occur. Evidence from laboratory and analog studies such as the site in Maqarin, Jordan, suggest that the precipitation of elements such as U, Cs, Sr, Cr, Np, La, Nd, Ni, Co, Ba, Th, Se, and Pb could be precipitated with CSH and zeolites (Savage, 1997). Some of the radionuclides released from waste disposed in the repository could be incorporated into these newly formed solids, which might re-dissolve and be replaced by solids that are more stable. The new solids might not reincorporate the radionuclides that were released (Savage, 1997). Precipitation and co-precipitation take place because of the movement of sharp fronts that separate fluids of contrasting chemical composition (*i.e.*, dilute fluids of near neutral pH in the tuffs and alkaline fluids emanating from the concrete) (Savage, 1997).

### **3.2.2 Porosity & Permeability**

The presence of high pH fluids could cause an increase or decrease in host rock porosity. Precipitation of secondary phases could cause a decrease in porosity while mineral dissolution could cause porosity to increase (Sagar, 1997). Permeability is related to porosity. Therefore, an increase in porosity is likely to cause an increase in permeability.

Mineral dissolution and precipitation could cause the porosity of groundwater flowpaths to be altered. Fractures in the rock could be sealed due to precipitation of new minerals and widened due to dissolution of existing minerals. This could cause the flow of groundwater and gas to be channeled in certain directions.

Whether an increase or decrease in porosity occurs depends on the rock type and on the composition of the pore fluid. Differing results will occur depending on whether the fluids are 'early' or 'evolved.' According to Savage, it is expected that 'early' fluids moving along aluminosilicate flowpaths will cause an increase in porosity between zones of precipitates and an eventual decrease in porosity due to the sealing of flowpaths by CSH precipitation. 'Early' fluids are also expected to cause an increase in porosity in carbonate rocks due to carbonate dissolution. 'Evolved' fluids are anticipated to cause porosity decrease in aluminosilicate rocks due to flowpath sealing by CSH and minor porosity increases in carbonate rocks due to the filling of fractures by  $\text{C} \cdot \text{OH})_2$  (Savage, 1997).

### **3.2.3 Matrix Diffusion**

Matrix diffusion is a process in which dissolved species or a gas diffuses from fractures into the rock matrix. The hyperalkaline plume could affect the extent to which matrix diffusion occurs.

Changes in porosity and permeability affect matrix diffusion. Fracture sealing by calcite precipitation could cause a decrease in the ability of radionuclides to diffuse into the rock

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<sup>3</sup>Savage, 1997, p. 27.



matrix. Computer modeling studies indicate that this process takes on the order of ten to a hundred years (Savage, 1997). Matrix diffusion could also increase because of other mineral transformations. According to Savage,

A reduction in porosity of the rock matrix due to calcite precipitation is likely, but may not preclude diffusion from groundwater-filled fractures.<sup>4</sup>

Summarizing the likely effect of alkaline plume migration on matrix diffusion, Savage (1997) suggested that matrix diffusion properties are unlikely to be better than unaltered rock and could be much worse.

### **3.2.4 Sorption and Ion Exchange**

Sorption is a process in which a cation is absorbed onto or into a mineral. Transport of radionuclides can be retarded relative to the flow of the water by sorption into the geologic materials. Mineral alteration and precipitation, as well as changes in aqueous speciation due to the hyperalkaline plume, could affect the ability of minerals to sorb radionuclides.

For instance, results from U and Np sorption experiments illustrate the strong dependence of actinide sorption on pH (Sagar, 1997). Under atmospheric pCO<sub>2</sub> conditions, it has been shown that U(6+) sorption decreases by four orders of magnitude from pH ~6 to pH ~9 while Np(5+) sorption decreases by more than two orders of magnitude from pH ~8 to pH ~10 (Sagar, 1997).

Ion exchange, a process that involves the exchange of an ion in the solid for another ion in solution, is similarly affected. Ion exchange sites on minerals become saturated with cations from the concrete pore fluid, but these cations can still be exchanged for radionuclides (Savage, 1997).

In summarizing the likely effect of alkaline plume migration on sorption, including ion exchange, Savage (1997) suggested that

Sorption of radionuclides important to repository safety will be enhanced, or be no worse, in rocks altered by the migration of the alkaline plume, than in unaltered rock materials.<sup>5</sup>

### **3.2.5 Colloids**

Colloids are particles that are less than one micron (.001 mm) in size. The colloidal particles can remain in aqueous suspension indefinitely unless conditions of the fluid change causing flocculation (Strahler, 1973).

Since radionuclides can sorb to colloids or form true radiocolloids (colloids only composed of

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<sup>4</sup>Savage, 1997, p. 27.

<sup>5</sup>Savage, 1997, p. 40.

radionuclides), the formation and stability of colloids will affect radionuclide transport.

There are naturally occurring colloids present in the fluids present in the rock. The high pH pore fluid could cause changes in the quantity of colloids present. Colloid dissolution and flocculation could occur due to the hyperalkaline conditions. However, large quantities of new silica colloids could form at pH fronts due to the variation of silica solubility with pH (Savage, 1997).

In summarizing the likely effect of alkaline plume migration on colloids, Savage (1997) suggested that while colloids may be generated at the pH front, the colloidal abundance may be low in high pH fluids.

## **4 CHEMICAL PROCESSES AFFECTING THE PERSISTENCE AND EXTENT OF ALKALINE CONDITIONS**

Several processes affect the persistence and extent of alkaline conditions in the near-field environment caused by the use of cementitious materials. Leaching, carbonation, and CSH gel crystallization can cause the pH of concrete pore fluids to decrease. CSH gel crystallization and leaching are the processes that primarily determine the extent to which the pH is raised in fluids that react with the concrete.

The persistence of alkaline fluid generation is primarily affected by the carbonation and leaching processes. Carbonation of concrete will be important only if unsaturated conditions and moderate humidity conditions (RH ~ 50%) persist in the repository setting. Otherwise, the rate of leaching (*i.e.*, percolation into the emplacement drifts) of the concrete will determine the persistence of alkaline conditions.

### **4.1 LEACHING**

The process of chemical components leaching from the concrete causes the pH to decrease. The pH of concrete is initially at least 13. NaOH and KOH are leached first, causing the pH to decrease to about 12.5. This process occurs in a relatively short period of time and is followed by the leaching of  $\text{Ca}(\text{OH})_2$ , which decreases the pH to approximately 11. Once the alkalis and calcium hydroxide have been leached, the CSH gel phases dissolve incongruently, causing the pH to decrease until it eventually reaches the pH of groundwater. CSH dissolution is the part of the leaching process that takes the longest amount of time.

Leaching rates depend on the rate of water flow through the system (Walton et al., 1990). Modeling studies and literature review suggest that there is a consensus that a significant decrease in pH due to the leaching process takes tens of thousands of years. For instance, it has been estimated that, in advective environments, at least 66 m<sup>3</sup> of water is required to remove 33% of the calcium from 1 m<sup>3</sup> of typical concrete (Atkinson and Hearne, 1984).

Nevertheless, a site specific analysis of the leaching rate of concrete should be conducted for the proposed Yucca Mountain repository. Using a simple mass balance, such as that

suggested by Atkinson and Hearne (1984), between the calcium present in the concrete and the seepage rate into the emplacement drifts would give a rough estimate of how long alkaline conditions could persist at Yucca Mountain. A preliminary calculation is presented in Appendix 2.

## 4.2 CARBONATION

Under unsaturated conditions, the primary process affecting the persistence of alkaline fluid production from concrete is carbonation. This is a chemical reaction in which portlandite reacts with carbon dioxide and water to form calcite ( $\text{CaCO}_3$ ). The carbonation reaction is given by:



At high pH this equation becomes:



The effects of carbonation on concrete include shrinkage, increased strength, increased hardness, and decreased permeability. However, the decrease in pH from about 12 to about 8 is the most important aspect in terms of assessing near-field effects on performance of the repository.

Carbonation is slow beyond the surface of the concrete. The rate depends on the water to cement ratio (WCR) and on the relative humidity. The rate of carbonation is highest at intermediate humidities. If the relative humidity is too low, there will not be enough  $\text{H}_2\text{O}$  for the reaction. If relative humidity is too high, the pores in the concrete will be full of water, resulting in a slow  $\text{CO}_2$  diffusion rate. Vapor phase diffusion is roughly four orders of magnitude faster than aqueous diffusion (Walton et al., 1990). Carbonation rates are estimated to peak when relative humidity is somewhere between 50 and 65%.

Carbonation progresses through a migrating front, where there is no carbonation ahead of the front and where carbonation is complete behind the front. Carbonation can be modeled using a shrinking core model. The depth of the carbonation front is approximately proportional to the square root of time. The process of carbonation is accelerated with the addition of sulfate resisting components such as blast furnace slag and fly ash.

A site-specific calculation of the time for complete carbonation using previously postulated model equations is necessary to determine the persistence of high pH conditions in the potential Yucca Mountain repository, and is presented in Section 7.

## 4.3 CSH GEL CRYSTALLIZATION

High temperatures can cause the amorphous CSH gels to crystallize. For instance, partial transformation of CSH gel to more stable, though poorly crystallized phases such as jennite and tobermorite resulted from a modest temperature excursion to 55 °C for 6 to 12 months (Atkins and Glasser, 1992). Fluids equilibrated with the products of crystallized CSH gel are likely to have pH of less than 10 (Atkinson et al., 1989). The possibility of CSH crystallization is high at

the Yucca Mountain repository due to the high temperatures imposed by radioactive decay and the long time frame involved (Sagar, 1997). The net result of the crystallization process is a decrease in the solubility of the CSH bearing phases and a decrease in the pH of concrete-reacted fluids. The longevity of the alkaline conditions is not likely to be affected.

## **5 USE OF CONCRETE IN PROPOSED REPOSITORY**

### **5.1 GENERAL REPOSITORY DESIGN ASPECTS RELATED TO USE OF CONCRETE**

The June 1997 version of the Reference Design Description provides the most current insight into the repository design (TRW, 1997). That document provides the following general aspects. The nuclear waste at the proposed repository will be placed in underground tunnels. Either cast-in-place or pre-cast concrete will be used to line the drifts. The types of drifts will include the service main drift for access, exhaust main drifts for ventilation, and emplacement drifts. The service and exhaust main drifts will be 7.6 meters in diameter, while the emplacement drifts will have a diameter of 5.5 meters. All of the drifts in the repository will be lined with concrete. It is estimated that there will be a total of 150 km of drifts inside the repository. The exhaust main drifts will be located ten meters below the emplacement drifts and will be connected to them by ventilation raises. The emplacement drifts will be 500 to 1200 meters long. There will be 28 meters of space between the centers of each of the emplacement drifts. Concrete will also be used for inverters and possibly for waste package pedestals.

The Department of Energy's (DOE) use of concrete in the repository is constrained by several design assumptions and functional considerations. The design assumptions for the use of concrete only focus on pre-closure aspects of construction and operation of the repository, and not on post-closure performance of the repository. The functional considerations for the use of concrete addressed in DOE design documents also address potential post-closure performance aspects of concrete.

The relevant design assumptions from the Advanced Conceptual Design Document are as follows (TRW Environmental Safety Systems, Inc., 1996b; hereafter referred to as TRW, 1996b). Assumption C-3 concerns the retrievability period and states that

The repository will be designed for a retrievability period of up to 100 years after initiation of emplacement.<sup>6</sup>

The rationale given by the DOE for this assumption is that the Engineered Barrier Segment will be designed for a retrievability period of 100 years to be consistent with the repository period of retrievability. Additional design constraints are documented in assumption DCSS 027 that address rock support materials and the prohibition of organic materials. This assumption states

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<sup>6</sup> TRW, 1996b, p. 4-4.

that

Organic materials (e.g., epoxy resin, timber) are limited for use as rock support and other post-closure permanent materials in all openings. Organic admixtures used in cementitious materials should be minimized to the extent practical. Concrete and steel are allowable pre-closure construction materials in all openings.<sup>7</sup>

In DOE's discussion of functional considerations for the use of concrete, two main aspects are addressed (TRW, 1996a). Pre-closure operational considerations are that:

The invert must perform a variety of functions. The tunnel boring machine excavates a circular opening. The circular tunnel profile generally requires a roadway, such as fill or pre-cast concrete segments, placed in the invert to form a travelway for equipment. The invert must also later support the waste package and any emplacement hardware during the pre-closure phase.<sup>8</sup>

Post-closure considerations of the invert material include that it should also provide support during the post-closure phase or at least break down predictably (TRW, 1996a). The DOE also contemplates post-closure performance aspects for the concrete invert (TRW, 1996a). For instance, DOE postulates that invert material has the potential for controlling transport of radionuclides to the host rock. Radionuclides can move through the invert material by either advection or diffusion. Both can occur even in unsaturated media. The DOE asserts that to control radionuclide releases, it would be beneficial to have the invert limit diffusion of nuclides to the host rock (TRW, 1996a). Further, the DOE suggests that additional increases in performance might be achieved by the use of additives in the invert to promote sorption of radionuclides (TRW, 1996a).

Finally, the DOE indicates that the choice of an appropriate invert material will be arrived at through a functional interface between Engineered Barrier Segment development and subsurface design (TRW, 1996a).

## **5.2 DETAILS OF PROPOSED CONCRETE USAGE IN THE EMPLACEMENT DRIFTS**

The DOE has not released the exact details of the type and quantity of concrete to be used in the potential repository. For the purposes of this paper, the author has used notes on pre-decisional information provided at a Total System Performance Assessment - Viability Assessment (TSPA-VA) workshop.<sup>9</sup> Additional information on design specifications for proposed concrete usage and ventilation strategies was obtained during conversations with

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<sup>7</sup>TRW, 1996b, p. 4-34.

<sup>8</sup>TRW, 1996a., p. 7-24.

<sup>9</sup>Notes on presentation at Near Field Geochemical Workshop, on Repository Ground Support Material, presented by David Tang, Repository Geotechnical Engineer, March 5, 1997.

DOE and its contractor staff.<sup>10</sup>

The purpose of these conversations was to obtain further design details and to inform DOE of NRC's intent to use the preliminary pre-decisional information provided at the abstraction workshop to perform a preliminary evaluation of carbonation of concrete. The NRC staff assured the DOE staff that this preliminary analysis would be revised once the reference design is publicly released, should significant differences exist between the two data sources.

At the abstraction workshop, information was provided on an example concrete mix design (Table 5.1) and quantities of materials that would be used in the example concrete (Table 5.2).

Table 5.1 Example of a Concrete Mix Design

Component	Type	Amount
Cement	Type V Portland cement	660 lb/cu yd
Water	to be added	270 lb/cu yd
Coarse Aggregate	3/4" max size, Tuff aggregate	1690 lb/cu yd
Fine Aggregate	same source of coarse aggregate	1310 lb/cu yd
Silica Fume	to reduce pH	100 lb/cu yd
Water Reducing Admixture	Polyheed or similar type	10 oz/cwt
Superplasticizer	Rheobuild or similar type	25 oz/cwt
Steel Fiber	Dramix ZC or similar, 0.5% by volume	66 lb/cu yd

Information provided in the August 6, 1997 teleconference indicates that the estimates in Tables 5.1 and 5.2 are pretty close to the numbers that the DOE are currently using for their reference base case Viability Assessment (VA) design. The DOE indicated that the emplacement drifts will consist of 3.85 m<sup>3</sup> concrete per meter of tunnel, and for the reference case, Type V Portland cement will be used. Further, tuff aggregate is being used for the base design. Additional information provided indicated that the concrete walls will be 200 mm thick, there will be 5 pre-cast concrete segments that are 1-1.5 m<sup>3</sup> in length for the drifts, and the invert is the sixth segment, and will be approximately 300 mm thick at its thickest point.

The DOE has indicated that there are three options that are being considered for the material for the liner. Pre-cast concrete is one of them, and will be used in 90% of the drifts. Every 10th drift will be made from cast-in-place concrete. The purpose of the cast-in-place drift

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<sup>10</sup>A teleconference on August 6th, 1997, between DOE and contractor staff and NRC staff was conducted for the purpose of acquiring information about the current repository design. The participants were Alice Forman and Bret Leslie from the NRC, and Jack Bailey, Paul Harrington, David Sassani, Jim Blink, Dan McKenzie, and Abe van Luik from the DOE and its contractors.

Table 5.2 An Estimate of Concrete Quantities: (3.91 m<sup>3</sup> per meter length of drift)

Component	Type	Amount
Cement	Type V Portland cement	3400 lb.
Water	to be added	1400 lb.
Coarse Aggregate	3/4" max size, Tuff aggregate	8700 lb.
Fine Aggregate	same source of coarse aggregate	6700 lb.
Silica Fume	to reduce pH	500 lb.
Water-Reducing Admixture	Polyheed or similar type	24 lb.
Superplasticizer	Rheobuild or similar type	120 lb.
Steel Fiber	Dramix ZC or similar, 0.5% by volume	340 lb.

construction is to allow mapping of every 10th drift. The cast-in-place concrete will be made of the same material as the pre-cast concrete. The distinction would be that there would be no gaps between segments as there would be with pre-cast concrete. Using steel as a liner is the third option under consideration.

The ASTM standards relevant to the use of cementitious materials in the proposed repository are C150-92, C33-90, A820-90, C1116-95, C1240-95, and C109-92. Relevant information from ASTM C150-92, Standard Specification for Portland Cement, and a further discussion of the details of concrete are listed in Appendix 1.

## 6 PREVIOUS ESTIMATES OF THE PERSISTENCE OF ALKALINE CONDITIONS

There have been several estimates of the time it will take for the pH of concrete to decrease under various scenarios. These general estimates are presented individually and subsequently discussed as they relate to the potential Yucca Mountain repository.

### 6.1 CARBONATION OF CONCRETE LINER AT YUCCA MOUNTAIN BY SAGUES (1997)

During a presentation at the Workshop on Alternative Models and Interpretations Waste Package Degradation Expert Elicitation Process in May 1997, Alberto Sagues presented a paper titled "Electrochemical Modeling Issues." This paper addressed the carbonation of concrete, among other things.

Data collected from carbonation of bridges in Florida was presented. Sagues used a simple formula,  $x \approx K_c t^{1/2}$ , to describe the depth of carbonation as a function of time. Sagues stated that the rate of concrete carbonation is limited by CO<sub>2</sub> diffusion, that  $K_c$  increases slightly with

temperature, and that  $K_c$  reaches a maximum at  $RH \approx 60\%$ . Sagues estimated that the median value of  $K_c$  is approximately  $2.5 \text{ mm y}^{-1/2}$  for bridges over land. Laboratory experiments indicated that  $K_c \text{ mm y}^{-1/2}$  is about 4 to 5  $\text{mm y}^{-1/2}$  at 60% relative humidity. Sagues demonstrated that if  $K_c$  is equal to 5, it will take 900 years to carbonate 15 cm of concrete according to his formula. Finally, Sagues hypothesized that through-carbonation of the concrete liner in the emplacement drift could be possible before water flows into the emplacement space, and that even if the concrete is only partially carbonated, the water that flowed through could carbonate as it exits.

## **6.2 ESTIMATES OF CONCRETE LEACHING AT THE HANFORD SITE BY CRISCENTI ET AL. (1996)**

At the Hanford site for low-level waste, radioactive waste is mixed with cement and placed in steel barrels that will be placed underground, near the surface. Calculations by Criscenti et al. (1996) predict that a pH of above ten will be maintained for 10,000 years at the Hanford site. Ten thousand years is the period of regulatory concern for this site, and speculation into longer time frames was not provided.

Computer modeling was performed using the Contaminant Transport Model (CTM) code, developed at Pacific Northwest National Laboratory (Schramke et al., 1992). Sixteen scenarios were evaluated in which the recharge rate, influent solution, length or number of waste drums in the flow path, and mass of cement per waste drum were varied.

Based on their calculations, they concluded that portlandite dissolves completely over time. Their calculations also indicate that amorphous  $\text{SiO}_2$  may be introduced, and that cement degrades more quickly when it reacts with soil porewater as opposed to rainwater. In addition, pH values were predicted to drop below 10 when the  $\text{CaH}_2\text{SiO}_4$  component of CSH gel dissolves completely. They demonstrated that the  $\text{CaH}_2\text{SiO}_4$  component will not dissolve in 10,000 years in a waste drum filled with Type I Portland cement. In a drum one third filled with cement, the  $\text{CaH}_2\text{SiO}_4$  will not dissolve within 10,000 years with a recharge rate of 0.5 cm/yr but will dissolve with a high 5 cm/yr recharge rate over the same period of time. However, if three one-third filled drums were stacked on top of each other, the cement would not completely dissolve, and the pH would still be above 10 in 10,000 years. Criscenti et al. (1996) concluded that as long as cement hydration (weathering) products containing CSH gel are present, the pH of the surrounding water will remain above 10.

## **6.3 CEMENT LEACHING TESTS FOR THE SWEDISH REPOSITORY BY ENGVIST ET AL. (1996)**

A study was completed based on leaching tests to determine the lifetime of the high pH effect for a Swedish low-level waste repository (Engkvist et al., 1996). The three conclusions of the study are the pH in the repository will be above 12 for at least a hundred thousand years, there is no significant difference between saline and non-saline groundwater in terms of the experiment, and excessive carbonation did not occur.

In their experiments, six five-gram portions of crushed hydrated Ordinary Portland Cement (OPC) paste were equilibrated with 20 ml saline and non-saline synthetic groundwater in a



nitrogen filled glovebox. The experiments were performed at ambient temperature. Every week 60% of the water was replaced. The experiments were carried out for eighty weeks.

The authors established the time scale for the complete removal of portlandite by using a "back-of-the-envelope" calculation. They assumed the cement paste has a porosity of 15%, and a density of  $2700 \text{ kg m}^{-3}$ . They estimated that the pore volume of a 5-gram sample is approximately 0.3 ml and each leaching step would correspond to about 40 pore water exchanges. For the proposed Swedish repository, it has been calculated that under repository conditions, one pore water exchange takes about a thousand years (Lindgren et al., 1994). As a result, the 50 leaching steps the authors estimated would be needed to remove portlandite correspond roughly to 2 million years. Engkvist et al. (1996) indicated that this figure is overestimated since it assumes constant porosity and complete pore water exchanges (which was not the case in the experiments). In addition, Engkvist et al. (1996) postulated that if all the material dissolved throughout the experiment (roughly 0.6 g) is added to the porosity, this would lead to an increase of the porosity of about 12%. Thus, they concluded the conservative experimental conditions would over-predict the lifetime of the portlandite by one order of magnitude. Engkvist et al. (1996) concluded that the time scale for which a pH of 12.5 ( $\sim 0.03 \text{ M OH}^-$ ) could be expected inside or very close to the repository is more than  $10^5$  years.

#### **6.4 TIME DEPENDENCE OF PH IN A CEMENTITIOUS REPOSITORY BY ATKINSON ET AL. (1989)**

The main conclusion reached in the article was that the pH in Portland and Blast Furnace Slag cements would remain above 10.5 for on the order of several hundred thousand years as a result of leaching in a "typical" repository. The values used for typical repository conditions were a groundwater flux density of  $10^{-10} \text{ ms}^{-1}$ , a cement content of  $200 \text{ kg m}^{-3}$ , and a repository dimension in the direction of water flow of 10 meters.

Leaching experiments were performed as a part of the study. The ratio of the total volume of water that passes through the repository,  $V$ , to the total mass of anhydrous cement that was originally placed within the repository,  $M_0$ , and the aqueous solubilities of the cement constituents were considered the key parameters. The ratio  $V/M_0$  was used to make time estimates using the results from laboratory experiments.

Based on differences in results from additional experiments, it was concluded that Pulverized Fuel Ash (PFA) could reduce the pH to as low as 9 or 10. Atkinson et al. (1989) also concluded that reactions with ion-containing groundwater could reduce the time it takes for pH to drop, reactions between siliceous aggregate and calcium hydroxide can be disregarded, and crystallization of CSH gel could result in a lower pH.

#### **6.5 SERVICE LIFE OF CONCRETE BARRIERS IN LOW-LEVEL WASTE RADIOACTIVE WASTE DISPOSAL BY WALTON ET AL. (1990)**

Walton et al. (1990) discussed time estimates for the decrease in alkalinity. Based on studies by Atkinson et al. (1988) and Atkinson (1985), Walton et al. concluded that the chemical effect of concrete will last for hundreds of thousands of years, due to the fact that the processes that

lower the pH of concrete are very slow in most circumstances relevant to radioactive waste disposal. According to the article, "typical" subsurface environments approach 100% relative humidity, thus carbonation in the gaseous phase is unimportant.

## **6.6 RELEVANCE OF PREVIOUS ESTIMATES TO DESIGN CONSIDERATIONS AND PREDICTED REPOSITORY CONDITIONS AT YUCCA MOUNTAIN**

Sagues (1997) estimated that after 900 years concrete will be completely carbonated at Yucca Mountain. Criscenti et al. (1996) maintained that the pH in a site with cement-filled waste drums would remain above a value of 10 for 10,000 years. On the basis of leaching tests, Engkvist et al. (1996) concluded that the pH in a Swedish low-level waste repository would stay above a value of 12 for at least a hundred thousand years. Atkinson et al. (1989) concluded that the leaching process in a typical repository would maintain a pH value above 10.5 for several hundred thousand years. Finally, Walton et al. (1990) maintained that the high pH conditions caused by concrete would last for hundreds of thousands of years under typical repository conditions.

The assumptions and experimental approaches used in these studies are not necessarily directly applicable to the conditions at Yucca Mountain. For instance, Sagues (1997) used data from bridges in Florida, where the relative humidity is about 60%, and there is an unlimited supply of carbon dioxide. For the Yucca Mountain repository, it has been predicted that the relative humidity will be significantly less than 60% and the amount of carbon dioxide will be limited for some 100's to 1000's of years due to the thermal effects from the disposed radioactive waste (Sagar, 1997).

In the Walton et al. article (1990), the conclusions rely on data relevant to subsurface environments where relative humidities are close to 100%, and aqueous phase transport is assumed. For the potential repository at Yucca Mountain, the conditions will not be water saturated at all times and there are periods during which carbonation of concrete from gaseous diffusion may occur.

For the Swedish repository (Engkvist et al., 1996) and the Hanford site (Criscenti et al., 1996) studies, as well as the Atkinson et al. (1989) studies, leaching is the prime consideration. The experiments for the Swedish repository were performed in a nitrogen-filled glovebox, where no carbon dioxide was present. Therefore carbonation could not occur, and the results only prove that the leaching process will occur in the specified time period. Carbonation was not referred to in the Hanford site study (Criscenti et al., 1996) or by Atkinson et al. (1989). Therefore, no conclusions can be drawn from these articles about the time for pH decrease due to carbonation.

One conclusion that can be drawn from the studies is that the process of leaching takes a long time, on the order of several hundred thousand years. Therefore, we will focus on the carbonation process to determine if reduction of pH will occur due to carbonation in a shorter period of time. However, if possible, site specific calculations should be performed for both leaching and carbonation. More information about CSH gel crystallization is needed to

determine its effect on concrete alkalinity.

## 7 CALCULATIONS

Information presented in previous studies is not directly applicable to the high-level waste repository at Yucca Mountain. Thus, performing calculations on the persistence of the high pH effect of concrete is necessary. The composition of the concrete, the groundwater, and the gas phase are fundamental to the determination of the potential longevity of the alkaline conditions. Since carbonation was considered to be the process that could effectively shorten the leaching time, an evaluation of the carbonation of concrete at the proposed repository was completed. A brief calculation regarding the leaching process was also performed for the purpose of confirming the expected result that leaching would not effectively reduce the pH in the concrete at the proposed repository in the given time frame.

### 7.1 MODELING CARBONATION OF CONCRETE

Papadakis et al. (1989) presented a complex mathematical model for concrete carbonation. However, after a series of simplifying assumptions, the model was reduced to a simple equation. This equation was demonstrated to be in good agreement with existing experimental data.

According to Papadakis et al. (1989), concrete alkalinity is due to portlandite. Carbonation products have higher molar volumes than CH and CSH, so there is a decrease in porosity during carbonation, and a decrease in the average pore radius (Papadakis et al., 1989).

One of the simplifying assumptions that Papadakis et al. (1989) made is that a "carbonation front" is formed. The front separates fully-carbonated areas from ones where no carbonation has occurred. All quantities in the Papadakis et al. (1989) model refer to the total mass of concrete. CSH, although in actuality it has variable stoichiometry, was simplified by the authors as  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  in their model. Additionally, partially saturated conditions and vapor phase diffusion were assumed.

Other assumptions used by Papadakis et al. (1989) include an initially macroscopically uniform medium, and uniform and steady local humidity. Based on a list of typical model parameter values, a series of simplifying assumptions to the model were made in which certain terms were neglected or replaced. Additionally, the cement was considered to be completely hydrated.

The simplified equation is:

$$x_c = [(2[\text{CO}_2]^0 D_{e,\text{CO}_2} t) / ([\text{Ca}(\text{OH})_{2(s)}]^0 + 3[\text{CSH}]^0)]^{1/2} \quad (4)$$

where  $x_c$  is the carbonation depth in meters,  $t$  is the time since the beginning of carbonation in seconds,  $[\text{CO}_2]^0$  is the initial molar concentration of  $\text{CO}_2$  in the gas phase in  $\text{mol}/\text{m}_g^3$ ,  $[\text{Ca}(\text{OH})_{2(s)}]^0$  is the initial molar concentration of  $\text{Ca}(\text{OH})_{2(s)}$  in  $\text{mol}/\text{m}_i^3$ ,  $[\text{CSH}]^0$  is the initial molar concentration of CSH in  $\text{mol}/\text{m}_i^3$  and  $D_{e,\text{CO}_2}$  is the effective diffusivity of  $\text{CO}_2$  in  $\text{m}_g^3/\text{m}_i \cdot \text{s}$ . The superscript 0 represents quantities referring to initial conditions ( $t = 0$ ). The subscript g

represents quantities referring to the gas phase in the pores, the subscript s refers to quantities in the solid phase, and the subscript t represents quantities referring to total volume of concrete.

This equation provides a theoretical basis for predicting the proportionality constant A in the empirical expression  $x_c = At^{1/2}$  that has been described in various sources, including Sagues (1997).

The velocity of the carbonation front depends crucially on the effective diffusivity of  $\text{CO}_2$  in the pores of carbonated concrete.  $D_{e,\text{CO}_2}$  can be estimated using models or measured experimentally. The effective diffusivity is typically on the order of  $10^{-8} \text{ m}^2/\text{s}$ , depends on the water to cement ratio (WCR), and decreases with ambient RH.

Agreement between experimental data and the model prediction is excellent for relative humidities above 50%. However, the equation predicts that the velocity of the carbonation front will continue to increase as the relative humidity decreases below 50%. This disagrees with experimental results, and the general observation that carbonation hits a maximum between 50 and 65% relative humidity. According to Papadakis et al. (1989), the reason for the disagreement is that the model simplifications leading to the equation are not valid in the region of relative humidity below 50%. This is due to the fact that

In this region, diffusion of  $\text{CO}_2$  ceases to be the rate-limiting step of the carbonation process and the chemical kinetics of the carbonation reaction become important.<sup>11</sup>

## 7.2 RELATIVE HUMIDITY

Some insights on the relative humidity of air to be used for ventilation are provided in DOE design documents. For instance, in the Advanced Conceptual Design Document, assumption TDSS 021 regarding surface air temperature and humidity, states that surface air temperature ranges from 42.2 °C to -25.6 °C with an annual average of 12.7 °C, and that surface air humidity ranges from 13% to 71% with an annual average of 54% (TRW, 1996b). Plots of RH versus time provided by Nye County corroborate this assumption (Nye County Nuclear Waste Project Office, 1996, Figures 4-15a-m). After emplacement of the waste, radioactive decay will cause the temperature of the repository to rise. This will cause drying of the host rock and will decrease the relative humidity at the repository horizon (Sagar, 1997). Over time, the temperature in the repository will decrease, and the relative humidity will gradually rise to its previous level. The relative humidity conditions on the surface of the waste package inside the emplacement drift, assuming no drift liner, are estimated in the Engineered Barrier System Performance Assessment Code (EBSPAC) manual (Mohanty et al., 1996). With no drift liner and no backfill, the relative humidity at the surface of the waste package will approximate that of the rock surrounding the emplacement drift. The conditions of the rock do not necessarily exactly match the conditions inside the emplacement drift due to the lower permeability of concrete relative to the host rock. The concrete liner will mechanically degrade with time and consequently so will its ability to act as low permeability material that could effectively shield the

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<sup>11</sup>Papadakis et al., 1989, p. 1648-1649.

emplacement drift from moisture emanating from the surrounding rock. Although when the drift liner would mechanically fail is unclear, the DOE is unlikely to claim credit for its mechanical integrity for a period of more than 150 years.<sup>12</sup>

When mechanical failure of the tunnel liner occurs, the drift liner will no longer serve as an effective permeability barrier and the conditions in the emplacement drifts should match the conditions of the surrounding rock. According to the EBSPAC manual, the RH increases to 50% at about 1800 years. RH gets close to 100 (>95%) at 3500 years or so (Mohanty et al., 1996).

Other relative humidity figures are provided by Tom Buscheck in the Near-Field and Altered-Zone Environment Report (Wilder, 1996). According to the July 1997 DOE-NRC Technical Exchange presentation by Francis (Francis, 1997), RH starts at 50%, decreases below 20% before 10 years (post-emplacement of waste), hits a low at 11 years or so, increases gradually, hits 50% at 300 years or so and is at about 90% by 1000 years for the 21 pressurized water reactor (PWR) (Hot) commercial spent nuclear fuel (CSNF). For the 21 PWR (Medium) CSNF, RH starts higher and hits 50% closer to 100 years.

The post-closure relative humidity predictions from the various sources differ in specific details, but agree in terms of the general behavior. The relative humidity data from the EBSPAC manual is what will be used in the calculations.

### 7.3 GAS PHASE COMPOSITION AND VENTILATION CONSTRAINTS

While the concentration of CO<sub>2</sub> in the unsaturated zone gas is greater than the atmospheric concentration, the saturation and relative humidity of the rock are high (Nye County Nuclear Waste Repository Project Office, 1996). This would tend to limit the diffusivity of CO<sub>2</sub> in the gas phase and lower the potential for carbonation of the exterior of the concrete liner. During the pre-closure period, the concrete-lined emplacement drifts will be ventilated with surface air that will have a CO<sub>2</sub> composition of the atmosphere and a relative humidity reflective of the external environment. Thus, carbonation of the liner should precede from the internal surface of the liner outward. Once waste is emplaced in the drift, the flow of the gas phase in the rock should be radially away from the drift (Wilder, 1996). This thermal process should push the higher CO<sub>2</sub> concentration gas found in the rock away from the repository. The exact composition of CO<sub>2</sub> in the air fraction within the drifts during the post-closure phase is unknown. For our calculations, once the concrete fails, the percentage of air that is carbon dioxide will be conservatively assumed to be atmospheric in composition. According to Felder and Rousseau, the mole fraction of carbon dioxide in air is 0.03%. The percentage of the gas phase that is air will vary over time.

As the temperature of the repository rises, there will be large volumes of water vapor expelled from the pore fluids in the air due to evaporation. This will have the effect of decreasing the air mass fraction by displacing the air with water vapor. As the radioactive waste decays, the

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<sup>12</sup>Notes on presentation at Near Field Geochemical Workshop, on Repository Ground Support Material, presented by David Tang, Repository Geotechnical Engineer, March 5, 1997.

temperature will go down and the air mass fraction is expected to rise as the amount of water vapor decreases due to condensation.

Two sources of information are available that provide estimates of the predicted behavior of the air mass fraction as a function of time. According to the Technical Exchange presentation by Francis, the air mass fraction decreases rapidly and stays close to zero until about 3000 years (Francis, 1997). According to notes on the Near Field Geochemical Environment (NFGE) TSPA-VA workshop presentation by Buscheck<sup>13</sup>, the air mass fraction starts to rise from less than 5% at about 2000 years and rises to about 80% at about 6000 years. Further details on the possible air mass fraction behavior are presented in Table 8.1.

Table 8.1. Air mass fraction as a function of time and position within the repository<sup>14</sup>

Outer 10% of repository	$\chi_{\text{air, gas}}$	time (yr)
	$< 10^{-5}$	40-700
	$< 10^{-2}$	50-1000
	$< 10^{-1}$	60-1200
	$< 0.5$	1000-2000
	$< 0.9$	10,000-15,000
Inner 50% of repository	$\chi_{\text{air, gas}}$	time (yr)
	$< 10^{-5}$	950-1000
	$< 10^{-2}$	1250-1400
	$< 10^{-1}$	1700-2200
	$< 0.5$	3500-7000
	$< 0.9$	20,000-25,000

Buscheck has argued that the air mass fraction in the gas phase ( $\chi_{\text{air, gas}}$ ) depends on the vapor generation rate relative to diffusive/convective mixing in the gas phase. He asserted that the air mass fraction does not depend on magnitude of rock dry-out (or percolation flux). Further, he indicated that  $\chi_{\text{air, gas}}$  decreases with increasing heating rate (MTU/acre), decreasing proximity to repository edge, and decreasing diffusive/convective gas-phase mixing. Finally, he suggested that the greatest variability in  $\chi_{\text{air, gas}}$  occurs in the outer 10% of the repository, while the least variability occurs over the inner 50% of the repository. The air mass fraction data derived from

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<sup>13</sup>Notes on Thomas Buscheck presentation "Gas Evolution Under Repository Conditions" at NFGE TSPA-VA Abstraction workshop, 1997.

<sup>14</sup>Notes on Thomas Buscheck presentation "Gas Evolution Under Repository Conditions" at NFGE TSPA-VA Abstraction workshop, 1997.

the notes of Buscheck's presentation are what will be used in the calculations.<sup>15</sup>

Some information on the ventilation strategy for the proposed repository has been provided in a teleconference with DOE.<sup>16</sup> This information provides some constraints for the carbonation calculation. The table below (Table 8.2) provides information on pre-closure aspects of ventilation. For the post-closure period there will be no ventilation.

Table 8.2 Ventilation data provided by the DOE

Development System	Linear Velocity	Duration
Evacuation	100 ft/min (0.5 m/s)	2 - 3 months
Any time workers are present	100 ft/min (0.5 m/s)	6 months
Drift in idle condition, no activity	50 ft/min (0.25 m/s)	1 - 10 years
Emplacement System		
Idle, awaiting emplacement	50 ft/min (0.25 m/s)	1 - 10 years
Active emplacement operations	100 ft/min (0.5 m/s)	3 - 5 months
Caretaker (drift full of packages)	1.0 ft/min (.005 m/s)	76 - 99 years*

\*assumes 100 year retrievability period. For a 50 yr retrieval period, the values are 26 - 49 years.

## 7.4 CALCULATIONS

Before waste is emplaced in the repository, there will be ventilation and the average relative humidity is assumed to be 54% (TRW, 1996b). While there is information from various sources that indicate both the post-closure behavior of the air mass fraction and RH behavior with time, the results differ in the details but agree in general. After emplacement, the temperature will rise, and this will cause drying of the rock mass which should decrease the relative humidity. Once the temperature decreases, the relative humidity should increase. The air mass fraction will decrease after ventilation ceases. The large volumes of water vapor in the air due to evaporation during the heating phase of the rock will cause the air mass fraction to decrease further. As the temperature decreases in the rock, the air mass fraction should increase to ambient conditions.

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<sup>15</sup>Notes on Thomas Buscheck presentation "Gas Evolution Under Repository Conditions" at NFGE TSPA-VA Abstraction workshop, 1997.

<sup>16</sup>A teleconference on August 6th, 1997, between DOE and contractor staff and NRC staff was conducted for the purpose of acquiring information about the current repository design. The participants were Alice Forman and Bret Leslie from the NRC, and Jack Bailey, Paul Harrington, David Sassani, Jim Blink, Dan McKenzie, and Abe van Luik from the DOE and its contractors.

Based on the ventilation data provided by the DOE, the time between concrete emplacement and waste emplacement is 3 to 20 years for any given drift. Assuming that, in all but the last drifts built, waste is not immediately emplaced, 15 years is a good approximation for the time after concrete emplacement and before waste emplacement. During this period a relative humidity of 54% and 100% air mass fraction with 0.03 mol % CO<sub>2</sub> content will be assumed. Further, we assume that it will take another ten years for the temperature to rise to levels where the RH will be lowered significantly and the air mass fraction will decrease to very low levels. Thus we will assume that there is a period of 25 years under which carbonation of the drift liner could occur under ambient atmospheric conditions.

For the post-waste emplacement period when the relative humidity is less than 50%, carbonation is likely to be limited by kinetics and should be low (Papadakis et al., 1989). Once the relative humidity reaches 50%, as given by the EBSPAC manual, the air mass fraction data of Buscheck will be used to calculate the CO<sub>2</sub> concentration.

The following equation is used to calculate the time to carbonate the liner:

$$t = \frac{x_c^2 * ([Ca(OH)_{2(s)}]^0 + 3 [CSH]^0)}{(2 [CO_2]^0 * D_{e,CO_2})} \quad (5)$$

where  $x_c$  is the carbonation depth in meters,  $t$  is the time since the beginning of carbonation in seconds,  $[CO_2]^0$  is the initial molar concentration of CO<sub>2</sub> in the gas phase in mol/m<sup>3</sup>,  $[Ca(OH)_{2(s)}]^0$  is the initial molar concentration of Ca(OH)<sub>2(s)</sub> in mol/m<sup>3</sup>,  $[CSH]^0$  is the initial molar concentration of CSH in mol/m<sup>3</sup> and  $D_{e,CO_2}$  is the effective diffusivity of CO<sub>2</sub> in m<sup>2</sup>/s. The superscript 0 represents quantities referring to initial conditions ( $t = 0$ ). The subscript g represents quantities referring to the gas phase in the pores, the subscript s represents quantities in the solid phase, and the subscript t represents quantities referring to total volume of concrete.

Using this equation and the assumptions outlined above, calculations are completed for two scenarios with different additional assumptions. Details of the calculations are presented in Appendix 2. Both scenarios envision a 25-year period for carbonation to occur prior to RH and air mass fraction conditions changing in the emplacement drifts, inhibiting carbonation. Once the relative humidity increases to 50%, after 1800 years, carbonation is calculated two ways. Under one assumption, carbonation is calculated assuming a constant RH of 50% and a constant air mass fraction of 10%. Alternatively, the air mass fraction is assumed to be 100%, the RH is 50%, and both remain constant. Since the carbonation rate is at a maximum when the relative humidity is 50-65%, and the relative humidity will continue to increase with time, these estimates could underestimate the time for complete carbonation of the drift liners.

Assuming 25 years of carbonation before closure, the time to completely carbonate the liner using 10% air mass fraction is 84,000 years. Using 100% air mass fraction,  $t = 10,000$  years.

Carbonation depth in the first 25 years, and from 1800 - 3500 years, when RH and air mass fraction conditions are optimal for carbonation is 0.04 m with 10% air mass fraction (20% carbonation) and 0.10 m with 100% air mass fraction (50% carbonation).



A brief calculation was also done for leaching using the Atkinson & Hearne (1984) estimate of at least 66 m<sup>3</sup> of water required to remove 33% of the calcium from 1 m<sup>3</sup> of concrete. The result of the calculation was that approximately 60% of Ca is leached in 10,000 years.

## 8 CONCLUSIONS

The presence of concrete can have both positive and negative effects on the near field environment. Effects on radionuclide release include either reducing or increasing uniform corrosion of steel waste packages depending the pH of fluids that have reacted with cementitious materials, causing stress corrosion cracking of steel, dissolution and alteration of nuclear waste glass, and co-precipitation of some radionuclides in concrete alteration products.

Effects on radionuclide transport are likely to include dissolution of sorptive secondary minerals, precipitation of new minerals, and either an increase or a decrease in rock porosity. Matrix diffusion properties are unlikely to be improved, and could be greatly worsened. Sorption of radionuclides is not likely to be worsened, and could be enhanced. Colloid abundance may be low, but colloids could be generated at the pH front.

The processes of leaching and CSH gel crystallization affect the severity of the alkaline conditions caused by the presence of cementitious materials. Carbonation and leaching affect the persistence of high pH conditions. Carbonation and leaching permanently alter the pH of the concrete. The rate of leaching is proportional to the flux of water through the concrete.

Carbonation primarily occurs under moderately saturated conditions. Conditions for carbonation are optimal where the relative humidity is 50 to 65%. The presence of carbon dioxide is needed for the reaction to occur. There is a limited time period in the repository for which carbonation could occur at rates that are not prohibitively low. Carbonation can occur at two times during the repository's history. First, carbonation can occur before and shortly after radioactive waste emplacement, prior to the point where the relative humidity will be driven down dramatically by rising temperatures, and when there is ventilation providing the needed carbon dioxide. The second time when conditions are optimal for carbonation is when the temperature has decreased such that the relative humidity is between 50 and 65%.

The smallest time estimate for complete carbonation of the concrete drift liner was 10,000 years. This estimate is unrealistic and overly conservative because the relative humidity of the drift liner will have risen to close to 100% before this time period has elapsed. In fact, it is estimated that the relative humidity will have risen to 95% in 3500 years. During the time period for which carbonation conditions are optimal, 20 - 50% carbonation will occur, depending on the air mass fraction. It can be concluded that aqueous phase diminution (leaching) will be the predominant process after the rock has become rehydrated to ambient conditions. The leaching calculation demonstrates that complete leaching of the concrete components that cause high pH will not occur in 10,000 years. Given this information, it can be concluded that high pH conditions for fluids released from emplacement drifts should be assumed as the base case for the entire 10,000 year period of regulatory concern.

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## APPENDIX 1 ASTM STANDARDS

In this appendix, information is provided about the past usage of concrete in the exploratory studies facility (ESF), and projected use of concrete in the repository. Type II Portland cement with a water/cement ratio of 0.38 has been used in the concrete for the ESF (Sagar, 1997) and has been used in Center for Nuclear Waste Regulatory Analyses (CNWRA) modeling analyses. The aggregate used in the concrete has not been tuff, but is obtained from a southern Nevada aggregate supplier. The aggregate, cement, and concrete has been used in accordance to the American Society of Testing and Materials (ASTM) standards listed in Table A.1.

Table A.1 ASTM Standards

Standard Number	Title
C 150 - 92	Standard Specification for Portland Cement
C 33 - 90	Standard Specification for Concrete Aggregates
A 820 - 90	Standard Specification for Steel Fibers for Reinforced Concrete
C 1240 - 95	Standard Specification for Silica Fume for Use as a Mineral Admixture in Hydraulic-Cement Concrete, Mortar and Grout
C 109 - 92	Test Specification for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or (50-mm) Cube Specimens)
C1116 - 95	Specification for Fiber-Reinforced Concrete and Shotcrete

Based on information obtained in a teleconference with DOE and its contractors, Type V Portland cement will be used as the base case design<sup>1</sup>. It is anticipated that tuff derived from the excavation of the repository will be used as the aggregate. Type II Portland cement is for general use, more especially when moderate sulfate resistance or moderate heat of hydration is desired. Type V Portland cement is for use when high sulfate resistance is desired. Characteristics of each type of cement are listed in Table A.2

### Optional Chemical Requirements

For low alkali cement or any type, a maximum of 0.60% Alkalis ( $\text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$ ) is set. This limit may be specified when the cement is to be used in concrete with aggregates that may be deleteriously reactive. Reference should be made to Specification C 33 for suitable criteria of deleterious reactivity.

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<sup>1</sup>A teleconference on August 6th, 1997, between DOE and contractor staff and NRC staff was conducted for the purpose of acquiring information about the current repository design. The participants were Alice Forman and Bret Leslie from the NRC, and Jack Bailey, Paul Harrington, David Sassani, Jim Blink, Dan McKenzie, and Abe van Luik from the DOE and its contractors.

Table A.2 ASTM C 150 - 89 Standard Specification for Portland Cement

Standard Chemical Requirements	Type II	Type V
Silicon dioxide, $\text{SiO}_2$ , min, %	20.0	...
Aluminum oxide, $\text{Al}_2\text{O}_3$ , max, %	6.0	...
Ferric Oxide, $\text{Fe}_2\text{O}_3$ , max, %	6.0	...
Magnesium Oxide, $\text{MgO}$ , max, %	6.0	6.0
*Sulfur trioxide, $\text{SO}_3$ , max, %		
When $\text{C}_3\text{A}$ is 8% or less	3.0	2.3
Loss on ignition, max, %	3.0	3.0
Insoluble residue, max, %	0.75	0.75
Tricalcium silicate ( $\text{C}_3\text{S}$ ) max, %	...	...
Dicalcium silicate ( $\text{C}_2\text{S}$ ) min, %	...	...
Tricalcium aluminate ( $\text{C}_3\text{A}$ ) max, %	8	5**
$\text{C}_4\text{AF} + 2(\text{C}_3\text{A})$ or $\text{C}_4\text{AF} + \text{C}_2\text{F}$ , max, %	...	25**

\* in some cases, more  $\text{SO}_3$  is allowed if it's beneficial

\*\* does not apply when the sulfate expansion limit in Table 4 is specified

## APPENDIX 2 DETAILS OF CALCULATIONS

### Data Used in Calculations:

#### DOE Info:

The emplacement drifts will consist of 3.85 m<sup>3</sup> concrete per meter of tunnel. For the reference case, Type V Portland cement will be used. Tuff aggregate is being used for the base design. The concrete walls will be 200 mm thick. For the drifts, there will be 5 precast concrete segments that are 1-1.5 m<sup>3</sup> in length. The invert is the sixth segment and will be approximately 300 mm thick at its thickest point.

**Table A.1 Air mass fraction for center portion of repository<sup>1</sup>**

Inner 50% of repository	$\chi_{\text{air,gas}}$	time (yr)
	$< 10^{-5}$	950-1000
	$< 10^{-2}$	1250-1400
	$< 10^{-1}$	1700-2200
	$< 0.5$	3500-7000
	$< 0.9$	20,000-25,000

RH hits 50% at 1800 years according to EBSPAC. Air mass fraction will be  $10^{-1}$  at this point.

**Table A.2 Example of a Concrete Mix Design<sup>2</sup>**

Component	Type	Amount
Cement	Type V Portland cement	660 lb/cu yd
Water	to be added	270 lb/cu yd
Coarse Aggregate	3/4" max size, Tuff aggregate	1690 lb/cu yd
Fine Aggregate	same source of coarse aggregate	1310 lb/cu yd
Silica Fume	to reduce pH	100 lb/cu yd
Water Reducing Admixture	Polyheed or similar type	10 oz/cwt
Superplasticizer	Rheobuild or similar type	25 oz/cwt
Steel Fiber	Dramix ZC or similar, 0.5% by volume	66 lb/cu yd

<sup>1</sup>Notes on Thomas Buscheck presentation "Gas Evolution Under Repository Conditions" at NFGT TSPA-VA Abstraction workshop, 1997.

<sup>2</sup>Notes on presentation at Near Field Geochemical Workshop, on Repository Ground Support Material, presented by David Tang, Repository Geotechnical Engineer, March 5, 1997.

Density:

Total of first 4 components: 3930 lb/yd<sup>3</sup>

Converted to 2331 kg/m<sup>3</sup>

**Table A.3 An Estimate of Concrete Quantities: (3.91 m<sup>3</sup>/m)<sup>3</sup>**

Component	Type	Amount
Cement	Type V Portland cement	3400 lb.
Water	To be added	1400 lb.
Coarse Aggregate	3/4" max size, Tuff aggregate	8700 lb.
Fine Aggregate	same source of coarse aggregate	6700 lb.
Silica Fume	to reduce pH	500 lb.
Water-Reducing Admixture	Polyheed or similar type	24 lb.
Superplasticizer	Rheobuild or similar type	120 lb.
Steel Fiber	Dramix ZC or similar, 0.5% by volume	340 lb.

Total of first four components: 20200

Total of all components: 21184

Percent of water+cement in concrete = 23 - 24%

Water to cement ratio (WCR) = 0.41

Aggregate to cement ratio (ACR) = 4.5

The amount of concrete in the entire repository is estimated as 3.85 m<sup>3</sup> concrete per m tunnel X 150 X 10<sup>3</sup> m tunnel = 577,500 m<sup>3</sup> total volume concrete.

**Papadakis Equation:**

$$x_c = [(2[CO_2]^0 D_{e,CO_2} t) / ([Ca(OH)_2(s)]^0 + 3[CSH]^0)]^{1/2} \quad (4)$$

This equation is valid only at >50% RH (Papadakis et al., 1989).

$x_c$  = carbonation depth, m

$[CO_2]^0$  = initial molar concentration of CO<sub>2</sub> in the gas phase, mol/m<sub>g</sub><sup>3</sup>

$[Ca(OH)_2(s)]^0$  = initial molar concentration of Ca(OH)<sub>2</sub>(s), mol/m<sub>t</sub><sup>3</sup>

$[CSH]^0$  = initial molar concentration of CSH, mol/m<sub>t</sub><sup>3</sup>

$D_{e,CO_2}$  = effective diffusivity of CO<sub>2</sub>, m<sub>g</sub><sup>3</sup>/m<sub>t</sub> · s

$t$  = time since the beginning of carbonation, s

Superscript 0 = quantities referring to initial conditions ( $t = 0$ )

Subscript g = quantities referring to the gas phase in the pores

Subscript t = quantities referring to total volume of concrete

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<sup>3</sup>Notes on presentation at Near Field Geochemical Workshop, on Repository Ground Support Material, presented by David Tang, Repository Geotechnical Engineer, March 5, 1997.

Subscript s = quantities referring to the solid phase  
 CSH =  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  in this model

From Figure 6 in Papadakis et al. (1989),  $D_{e,\text{CO}_2}$  for relative humidity of 55% and WCR of 0.5 = about  $2.2 \cdot 10^{-8}$ . Extrapolating to 50% would give effective diffusivity of about  $3 \cdot 10^{-8}$ . This will be smaller at the WCR of 0.41. A reasonable estimate based on the graph would be  $2 \cdot 10^{-8} \text{ m}^2/\text{s}$  for the effective diffusivity for  $\text{CO}_2$ .

$$t = \frac{x_c^2 \cdot ([\text{Ca}(\text{OH})_{2(s)}]^0 + 3 [\text{CSH}]^0)}{(2 [\text{CO}_2]^0 \cdot D_{e,\text{CO}_2})} \quad (5)$$

$x_c = 200 \text{ mm} = .2 \text{ m}$   
 $D_{e,\text{CO}_2} = \text{approximately } 2 \cdot 10^{-8} \text{ m}^2/\text{s}$

Molecular weights used:

(Ca = 40.078; O = 15.999; H = 1.0079; Si = 28.086, C = 12.011, N = 14.007)

$[\text{CO}_2]^0$

According to Felder & Rousseau, air has 0.03 mol %  $\text{CO}_2$   
 $0.0003 \text{ mol CO}_2/\text{mol air} \times 0.1 \text{ mol air/mol gas} = 0.00003 \text{ mol CO}_2/\text{mol gas}$   
 22.41 L per mol ideal gas at STP  
 $0.00003 \text{ mol CO}_2/\text{mol gas} \times (1 \text{ mol}/22.41 \text{ L}) \times 1000 \text{ L}/\text{m}^3 =$   
 $[\text{CO}_2]^0 = 0.0013 \text{ mol CO}_2 \text{ per m}^3 \text{ gas}$

$[\text{Ca}(\text{OH})_{2(s)}]^0$

hydrated cement is 20-25% portlandite (wt %)  
 Percent of water+cement in concrete = 23-24% (wt %)  
 Percent portlandite in concrete =  $20 \cdot 23\% - 25 \cdot 24\% = 4.6 - 6.0 \text{ wt } \%$   
 $\text{MW Ca}(\text{OH})_2 = 74.0918$   
 $.046 \text{ g portlandite per g concrete} / 74.0918 \text{ g/mol} = .00062 \text{ mol Ca}(\text{OH})_2 \text{ per g concrete}$   
 $.060 \text{ g portlandite per g concrete} / 74.0918 \text{ g/mol} = .00081 \text{ mol Ca}(\text{OH})_2 \text{ per g concrete}$   
 Concrete density  $2330 \text{ kg}/\text{m}^3$   
 $.00062 \text{ mol Ca}(\text{OH})_2 \text{ per g concrete} \times 2330 \text{ kg}/\text{m}^3 \times 1000 \text{ g}/\text{kg} =$   
 $1400 \text{ mol Ca}(\text{OH})_2 \text{ per m}^3 \text{ concrete} - \text{lower bound}$   
 $.00081 \text{ mol Ca}(\text{OH})_2 \text{ per g concrete} \times 2330 \text{ kg}/\text{m}^3 \times 1000 \text{ g}/\text{kg} =$   
 $1900 \text{ mol Ca}(\text{OH})_2 \text{ per m}^3 \text{ concrete} - \text{upper bound}$   
 $[\text{Ca}(\text{OH})_{2(s)}]^0 = 1400 - 1900 \text{ mol Ca}(\text{OH})_2 \text{ per m}^3 \text{ concrete}$

$[\text{CSH}]^0$

hydrated cement is 40-50% CSH  
 Percent of water+cement in concrete = 23-24%  
 Percent CSH in concrete =  $40 \cdot 23\% - 50 \cdot 24\% = 9.2 - 12.0 \text{ wt } \%$   
 $\text{MW CSH (assuming CSH} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}) = 342.47 \text{ g/mol}$   
 $.092 \text{ g CSH per g concrete} / 342.47 \text{ g/mol} = .00027 \text{ mol CSH per g concrete}$   
 $.120 \text{ g CSH per g concrete} / 342.47 \text{ g/mol} = .00035 \text{ mol CSH per g concrete}$   
 Concrete density  $2330 \text{ kg}/\text{m}^3$



.00027 mol CSH per g concrete X 2330 kg/m<sup>3</sup> X 1000 g/kg =  
 630 mol CSH per m<sup>3</sup> total volume concrete  
 .00035 mol CSH per g concrete X 2330 kg/m<sup>3</sup> X 1000 g/kg =  
 820 mol CSH per m<sup>3</sup> total volume concrete  
**[CSH]<sup>0</sup> = 630 - 820 mol CSH per m<sup>3</sup> total volume concrete**

To maintain WCR, max Ca(OH)<sub>2</sub> will correspond to min CSH and vice versa.  
 1400 + 3\*820 = 3860  
 1900 + 3\*630 = 3790  
**[Ca(OH)<sub>2(s)</sub>]<sup>0</sup> + 3 [CSH]<sup>0</sup> = 3800**

#### Initial Calculation:

Based on the ventilation data provided by the DOE, the time between concrete emplacement and waste emplacement is 3 to 20 years for any given drift. Assuming that, in all but the very last drifts that are built, waste is not immediately emplaced, 15 years is a good approximation for the time after concrete emplacement and before waste emplacement. At this time, 54% RH and 100% air mass fraction with 0.03 mol % CO<sub>2</sub> content will be assumed. Add another ten years for the temperature to rise to levels where the RH will be lowered significantly and the air mass fraction to decrease to approx. zero.

[CO<sub>2</sub>] = 0.013  
 [Ca(OH)<sub>2(s)</sub>]<sup>0</sup> + 3 [CSH]<sup>0</sup> = 3800  
 D<sub>e,CO2</sub> = 2\*10<sup>-8</sup>  
 t = t<sub>1</sub> + t<sub>2</sub> + t<sub>3</sub>  
 t<sub>1</sub> = 25 years = 7.89\*10<sup>8</sup> s  
 t<sub>2</sub> = 1800 years  
 x<sub>1</sub> = .2 m  
 x<sub>3</sub> = x<sub>1</sub> - x<sub>2</sub>

solve for x<sub>2</sub>  

$$x_2 = [(2[CO_2]^0 D_{e,CO_2} t) / ([Ca(OH)_{2(s)}]^0 + 3[CSH]^0)]^{1/2} \quad (4)$$

$$[(2 \times 0.013 \times 2 \times 10^{-8} \times 7.89 \times 10^8) / 3800]^{1/2}$$
 x<sub>2</sub> = 0.01 m

Then, there will be no carbonation for 1800 years.

x<sub>3</sub> = .2 - 0.01 m = 0.190 m  
 [CO<sub>2</sub>] = 0.013  
 D<sub>e,CO2</sub> = 2\*10<sup>-8</sup>  
 [Ca(OH)<sub>2(s)</sub>]<sup>0</sup> + 3 [CSH]<sup>0</sup> = 3800

t<sub>3</sub> = (0.19 m)<sup>2</sup> X (3800)/(2(.013)\*2\*10<sup>-8</sup>) = 2.6 X 10<sup>11</sup> s = 8200 years  
 or 82,000 years with 10% air mass fraction

**t = 25 + 1800 + 82,000 = 84,000 years with 10% air mass fraction**  
**t = 25 + 1800 + 8200 = 10,000 years with 100% air mass fraction**

### Second Calculation:

$$x = x_1 + x_2$$

$$x_1 = 0.01 \text{ m}$$

According to EBSPAC, the RH hits 50% at about 1800 years. RH gets close to 100 (>95%) at 3500 years or so. Carbonation will occur between these two times.

$$t = 3500 - 1800 \text{ years} = 1700 \text{ years} = 5.36 \times 10^{10} \text{ s}$$

$$x_2 = [(2[\text{CO}_2]^0 D_{\text{e,CO}_2,t}) / ([\text{Ca}(\text{OH})_2]_0 + 3[\text{CSH}]_0)]^{1/2} \quad (4)$$

$$[(2 \times 0.0013 \times 2 \times 10^{-8} \times 5.36 \times 10^{10}) / 3800]^{1/2}$$

$$x_2 = 0.03 \text{ m with 10\% air mass fraction}$$

$$[(2 \times 0.013 \times 2 \times 10^{-8} \times 5.36 \times 10^{10}) / 3800]^{1/2}$$

$$x_2 = 0.09 \text{ m with 100\% air mass fraction}$$

**$x = 0.04 \text{ m}$  with 10% air mass fraction = 20% carbonation**

**$x = 0.10 \text{ m}$  with 100% air mass fraction = 50% carbonation**

### Third Calculation:

The above calculations demonstrate that complete carbonation will not occur in 10,000 years. Will leaching cause the pH to decrease below 10.5 in 10,000 years?

It has been estimated that, in advective environments, at least  $66 \text{ m}^3$  of water is required to remove 33% of the calcium from  $1 \text{ m}^3$  of typical concrete (Atkinson and Hearne, 1984). Thus  $2 \text{ m}^3$  of water will remove 1% of Ca from  $1 \text{ m}^3$  of concrete.

Assume 100 m thickness is volatilized due to thermal effects. Assume that the porosity of the rock is 15% and that the saturation of the rock is 80%. Assume that the diameter of the drift is 5 meters and that  $3.85 \text{ m}^3$  per m length of drift liner is used. Thus, there is about  $0.8 \text{ m}^3$  of concrete per  $\text{m}^2$  of drift.

Therefore,  $12 \text{ m}^3$  of  $\text{H}_2\text{O}$  per  $\text{m}^2$  of drift would be mobilized via thermal heating.

Thus, the volatilized water, should it all leach the concrete, could only remove ~ 7.5% of Ca from the concrete.

Assume percolation is equivalent to infiltration and is  $10 \text{ mm/year} = 10 \times 10^{-3} \text{ m}$

For  $1000 \text{ yr} = 10 \text{ m}^3/\text{m}^2$  of drift

Over 10,000 yr ~  $100 \text{ m}^3 \text{ H}_2\text{O}/\text{m}^2$  of drift. Thus percolation, assuming a rate of  $10 \text{ mm/yr}$ , would remove about 60% of the calcium over 10,000 years.

Complete leaching of the concrete components that cause high pH will not occur in 10,000 years. Since complete carbonation will not occur either, it can be concluded that the pH will remain above 10.5 for the entire 10,000 year period.