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NM5507

MOL.20000317.0262

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL COVER SHEET
Complete Only Applicable Items

1. QA: QA

2. ☒ Analysis ☒ Engineering ☐ Performance Assessment ☐ Scientific

3. ☐ Model ☐ Conceptual Model Documentation ☐ Model Documentation ☐ Model Validation Documentation

4. Title:
Seepage/Cement Interactions

5. Document Identifier (including Rev. No. and Change No., if applicable):
ANL-EBS-MD-000043 REV 00

6. Total Attachments:
None

7. Attachment Numbers - No. of Pages in Each:
N/A

	Printed Name	Signature	Date
8. Originator	D. Carpenter	D. J. Carpenter	3-15-00
9. Checker	T. Steinborn	T. Steinborn	3-15-00
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Remarks:

INFORMATION COPY
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OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL REVISION RECORD

Complete Only Applicable Items

2. Analysis or Model Title:

Seepage/Cement Interactions

3. Document Identifier (including Rev. No. and Change No., if applicable):

ANL-EBS-MD-000043 REV 00

4. Revision/Change No.	5. Description of Revision/Change
00	Initial issue

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1. PURPOSE

The Development Plan (CRWMS M&O 1999a) pertaining to this task defines the work scopes and objectives for development of various submodels for the Physical and Chemical Environment Abstraction Model for TSPA-LA

The Development Plan (CRWMS M&O 1999a) for this specific task establishes that an evaluation be performed of the chemical reactions between seepage that has entered the drift and concrete which might be used in the repository emplacement drifts. The Development Plan (CRWMS M&O 1999a) then states that the potential effects of these water/grout reactions on chemical conditions in the drift be assessed factoring in the influence of carbonation and the relatively small amount of grout. This task is also directed at: (1) developing a conceptualization of important cement/seepage interactions and potential impacts on EBS performance, (2) performing a screening analysis to assess the importance of cement/seepage interactions.

As the work progresses and evolves on other studies, specifically the Engineered Barrier System: Physical and Chemical Environment (P&CE) Model (in progress), many of the issues associated with items 1 and 2, above, will be assessed. Such issues include:

- Describing the mineralogy of the specified cementitious grout and its evolution over time.
- Describing the composition of the water before contacting the grout.
- Developing reasonable upper-bound estimates for the composition of water contacting grout, emphasizing pH and concentrations for anions such as sulfate.
- Evaluating the equilibration of cement-influenced water with backfill and gas-phase CO_2.
- Developing reasonable-bound estimates for flow rate of affected water into the drift.

The concept of estimating an "upper-bound" range for reaction between the grout and the seepage, particularly in terms of pH is based on equilibrium being established between the seepage and the grout. For example, this analysis can be based on equilibrium being established as long as any given reactant is present, for example, calcium hydroxide. Such an analysis does not account for any channelized flow within the grout, along, for example, carbonated fracture surfaces. In the event of channelized fracture flow, residual calcium hydroxide might still exist within the grout matrix but would be prevented from direct contact with the seepage due to armoring by a reaction selvage of calcite. Calcite can be included as a reactant, to accommodate limited carbonation, but this calcite is presumed to not impede dissolution of more soluble cementitious components. Another premise that can be used is that the seepage would not interact with the in drift atmosphere until after reaction with the grout, at which time a decrease in pH would be measured and precipitation of certain phases would occur.

To minimize duplication of effort a decision was made to provide the detailed results of the cement/seepage interactions and an assessment of the importance of the cement/seepage interactions in the Engineered Barrier System: Physical and Chemical Environment (P&CE)

Model (in progress). While the P&CE Model emphasizes aqueous phase reactions between the seepage and the grout, one technical item related to this topic that consequently remains to be answered is the rate of carbonation of the grout through reaction with atmospheric carbon dioxide. Addressing this sole technical item became the revised focus of this study.

The specific purpose of this analysis is to predict the time required for carbonation of the calcium hydroxide present within the grout used to anchor rockbolts. This analysis estimates the time required for carbonation to take place at three different partial pressures of carbon dioxide: 1 ppmv, 100 ppmv, and 1,000 ppmv, expressed as parts per million on a volume basis (the CO_2 partial pressure in an ideal gas mixture is equal to the total pressure multiplied by the volume fraction of CO_2). The basis for the range of values used in this analysis stems from the ambient carbon dioxide concentration of 1,000 ppmv in the unsaturated zone being used in another study (Engineered Barrier System: Physical and Chemical Environment (P&CE) Model (in progress) (CRWMS M&O 2000d, p. 1 of 1). This value was used to establish an upper bound. It is recognized that boiling would cause a decrease in the air-mass fraction and thereby a decrease in the concentration of carbon dioxide. Essentially this analysis assesses the rates of carbonation predicted at air-mass fractions of 0.001, 0.1, and 1.0.

Whereas the seepage entering the drift quickly can equilibrate with the atmospheric gasses, equilibration between the reactive components of the grout and the drift atmosphere requires a longer period of time. As noted, it is the purpose of this analysis to predict the period of time that is required for equilibration to occur. This analysis also includes estimates regarding the relationship between the depletion of atmospheric carbon dioxide and the distance from a grouted rockbolt, and the amount of aqueous phase carbon dioxide available for reaction. The results of this analysis complete Task 8 of the development plan entitled *Provide Sub-models for the Physical and Chemical Environmental Abstraction Model for TSPA-LA* (CRWMS M&O 1999a).

The significance of carbonation of calcium-bearing cementitious minerals is that highly alkaline components, such as calcium hydroxide, are transformed into a less alkaline component, calcite. This transformation has importance in terms of the subsequent reactions between the grout and seepage. The estimated equilibrium pH is fixed until all of the calcium hydroxide is leached from the grout or is carbonated (and prior to contact with In-Drift atmospheric carbon dioxide and backfill). As will be shown in Section 6.4 below, the time required for complete carbonation stemming solely from reaction with aqueous phase carbon dioxide is exceedingly long. However, given the gaseous atmospheric carbon dioxide inventory available for a carbonation reaction with the calcium-bearing components of the grout, as will be shown in Section 6.3 below, the time required for complete carbonation of the grout is estimated to be significantly reduced under elevated carbon dioxide concentrations. The importance of this more rapid transformation of the grout from a calcium hydroxide-dominated system to a calcite-dominated system is the timing when the seepage pH equilibrates only with calcite versus a more alkaline cementitious mineral (such as calcium hydroxide) and maintains a less alkaline pH.

The proposed rockbolt grout formulation to be used is reported in *Longevity of Emplacement Drift Ground Support Materials* (CRWMS M&O, 2000a, Section 6.4).

This analysis does not address (1) the geotechnical aspects of carbonation on the physical characteristics of the grout, (2) the efficacy of the use of grouted rockbolts, or (3) the geotechnical basis for selection and design of the rockbolting scheme.

2. QUALITY ASSURANCE

The Quality Assurance (QA) program applies to the development of this model. The responsible manager for the Performance Assessment Department has evaluated the technical document development activity in accordance with QAP-2-0, *Conduct of Activities*. The QAP-2-0 activity evaluation, *Conduct of Performance Assessment* (CRWMS M&O, 1999b), has determined that the preparation and review of this technical document is subject to the requirements of *Quality Assurance Requirements and Description* (DOE, 2000). Preparation of this analysis did not require the classification of items in accordance with QAP-2-3, *Classification of Permanent Items*. This activity is not a field activity. Therefore, an evaluation in accordance with NLP-2-0, *Determination of Importance Evaluations*, was not required.

3. COMPUTER SOFTWARE AND MODEL USAGE

No engineering or scientific design computer software programs were used in the preparation of this analysis.

4. INPUTS

4.1 DATA AND PARAMETERS

4.1.1 Carbonation Reactions

Carbonation reactions typically only consider $Ca(OH)_2$ as a carbon dioxide reactive phase in cementitious products (Neville, 1996, p. 498). Typically neat hydrated cement pastes may contain from 20 to 25 percent, by volume, calcium hydroxide [$Ca(OH)_2$] (or Portlandite) (Mindess and Young, 1981, p. 97). However, calcium hydroxide is consumed through reaction with condensed silica fume yielding calcium-silicate hydrated phases via the reaction given below.

$Ca(OH)_2 + SiO_2 = CaSiO_3 * H_2O$ (chemical reaction derived from the text of Neville, 1996, p. 669) (Note that this reaction is based on a 1:1 mole ratio of calcium to silica. As is discussed below this ratio may be variable.)

A further complication is that the reaction between the silica fume (represented by SiO_2) and the calcium hydroxide may not proceed to completion. The exact amount of calcium hydroxide that may be consumed is dependent on the unknown degree of reaction efficiency of the silica fume (Neville, 1996, p. 669). Reportedly, up to 75 percent of silica fume may be consumed through reaction with calcium hydroxide after 90 days of curing. There is also a question as to the composition of the calcium silicate hydrate formed through this reaction, although Neville (1996,

p. 670) reports that calcium to silicate ratios of these hydrates may be as low as 1.0, although this is acknowledged to be variable.

Neville (1996, p. 498) further notes that carbonation of all calcium-bearing phases is possible, even at low concentrations of carbon dioxide.

Considering all of these uncertainties, the basis for a bounding calculation will be that all of the calcium present within the grout will be available for carbonation. Based on *Longevity of Emplacement Drift Ground Support Materials* (CRWMS M&O, 2000a, Table 4, p. 35) a value for CaO of 61.9 percent, by weight, will be used.

4.1.2 Diffusion Coefficient of Carbon Dioxide

The diffusion coefficient of carbon dioxide in air is 0.160 cm^2/s.

[Incropera and DeWitt, 1996, Table A.8, p. 849)]

4.2 CRITERIA

The specific issue to be addressed during this analysis was raised in the issue resolution status report pertaining to the reaction of concrete with dissolved carbonate, bicarbonate, and gaseous carbon dioxide, leading to a depletion of the dissolved and gaseous phases of carbon dioxide. [NRC 1999, Section 3.2.1]

4.3 CODES AND STANDARDS

This AMR was prepared to comply with the DOE interim guidance (Dyer, 1999), which directs the use of specified Subparts/Sections of the proposed NRC high-level waste rule, 10 CFR Part 63 (64 FR 8640). Subparts of this proposed rule that are applicable to data include Subpart B, Section 15 (Site Characterization), and Subpart E, Section 114 (Requirements For Performance Assessment). The subpart applicable to models is also outlined in Subpart E, Section 114.

5. ASSUMPTIONS

The specific assumptions used in this analysis are listed below. The basis for each assumption is included as part of the assumption. Where the assumption is used in this analysis is also identified.

5.1 A non-depletable reservoir of carbon dioxide is present at a constant partial pressure (fugacity) during carbonation for this bounding analysis (used in Section 6.1).

The justification of this assumption is that the atmosphere in contact with the grouted rockbolt will be able to freely exchange with the atmosphere residing within the rock mass forming the Yucca Mountain range. This massive gas repository will not be materially affected by the minimal consumption of carbon dioxide by the limited number of rockbolts proposed for use within the emplacement drifts.

5.2 Partial pressure is assumed to be equal to the fugacity, with a total pressure equal to 1.0 atmosphere, and the equilibrium fugacity of carbon dioxide in contact with the grout, specifically, portlandite [$Ca(OH)_2$] is essentially zero. This assumption indicates that all of the carbon dioxide is consumed upon contact with portlandite or other reactable calcium-bearing cementitious minerals as long as reactable calcium-bearing phases exist (used in Section 6.1).

As noted above, this analysis assumes a total pressure of 1.0 atmosphere. The actual pressure at the potential Yucca Mountain repository may be 10 to 15 percent less than this value, which would tend to increase the duration of time needed for carbonation to occur, under otherwise identical conditions, by a proportional amount, therefore the use of 1.0 atmosphere total pressure is considered to be conservative.

The justification for the assumption regarding carbon dioxide fugacity in the grout is that thermodynamic calculations reveal that the equilibrium fugacity of carbon dioxide in contact with calcium hydroxide is approximately 10^{-13} atmospheres. For the purposes of this bounding analysis, this very low value can be regarded as essentially zero. This calculation is reported below.

The thermodynamic data of Weast (1979, p. D-69 and D-71) provide the ability to calculate the equilibrium fugacity of carbon dioxide in equilibrium with calcium hydroxide.

The Gibbs' Free Energy of Formation for the following compounds is presented:

Compound	Gibbs' Free Energy of Formation (at 25° C) (in kilocalories per mole)
$Ca(OH)_2$	-214.33
CO_2	-94.26
$CaCO_3$ (calcite)	-269.78
H_2O (l)	-56.690

For the reaction:

$$Ca(OH)_2 + CO_2 = CaCO_3 \text{ (calcite)} + H_2O \text{ (l)}$$

The following Gibbs' Free Energy of Reaction is calculated:

$$\Delta G \text{ (reaction)} = \Sigma \text{ (free energy of products)} - \Sigma \text{ (free energy of reactants)}$$

$$\Delta G \text{ (reaction)} = (-269.78 \text{ kcals} + -56.690 \text{ kcals}) - (-214.33 \text{ kcals} + -94.26 \text{ kcals}) = -17.88 \text{ kcals}$$

$$-1.364 \log K = \Delta G \text{ (reaction)} = -17.88 \text{ kcals}$$

$$\log K = 13.11$$

$$K = 10^{13.11}$$

$K = 1/P_{CO2}$

Therefore:

$1/P_{CO2} = 10^{13.11}$

or

$P_{CO2} = 10^{-13.11}$

(For clarification of the units being used for the reporting of the fugacity (or concentration on a volume basis) of carbon dioxide, at one atmosphere of pressure equals 1,000,000 ppmv. Therefore 1,000 ppmv equals 10^{-3} atmospheres, 100 ppmv equals 10^{-4} atmospheres, and 1 ppmv equals 10^{-6} atmospheres.)

5.3 All carbon dioxide diffusing into the grout matrix is available for the carbonation reaction, and no other internal source of carbon dioxide is available for carbonation of the grout (used in Section 6.1).

This assumption is based on the absence of any other carbon dioxide source, with the exception of atmospheric carbon dioxide.

5.4 As discussed above all calcium present within the grout will be subject to carbonation (used in Section 6.1).

This assumption is justified because of the impossibility of establishing that only calcium hydroxide will react with carbon dioxide and determining the amount of calcium hydroxide that might be present. Further, as reported by Neville (1996, p. 498) all calcium-bearing cementitious phase are subject to carbonation reactions.

5.5 Design of the rockbolting system has not been completed. For the purposes of this bounding analysis, the grouted rockbolts are assumed to be 200 cm long and have a diameter of 2.54 cm and are surrounded by 1.27 cm of grout (used in Section 6.1).

In the absence of definitive information, it was understood that industry-standard rockbolts, approximately 200 cm in length, would be used. These nominally 1-in.-diameter rockbolts would be emplaced in a 2-in.-diameter drilled hole and surrounded by grout. These are industry-standard dimensions and have been reported by Williams Form Engineering Corporation (1997, p. 8), a rockbolt supplier.

5.6 The Type K grout proposed for use has a specific gravity of 1.91 g/cm^3 *Rockbolt Grout Density* (CRWMS M&O, 2000b, p. 1 of 1) (used in Section 6.1).

6. ANALYSIS/MODEL

For this analysis, a diffusion-based equation (typically, this is referred to as Fick's First Law of Diffusion) was used to estimate both the amount of carbon dioxide that can be provided by

diffusive processes under the stated conditions and the relationship between the degree of depletion of the atmospheric carbon dioxide and the distance to a rockbolt undergoing carbonation. The amount of aqueous-phase carbon dioxide available for reaction was also estimated for this analysis.

6.1 MASS BALANCE CALCULATIONS

Given the current understanding of geochemical carbonation processes, mass balance calculations can define the mass of carbon dioxide required to quantitatively transform a given amount of calcium-bearing cementitious minerals into calcite. Given that diffusion-controlled processes predominate regarding the transport of the atmospheric gasses into the grout matrix, one can use a diffusion-based equation to estimate the time required for the conversion process. (This is detailed in Neville, 1996, pp. 485-487). A diffusion-based equation takes the following form for one-dimensional models (Neville, 1996, p. 486, equation [14-2]):

$$J = -D\ dc \div dL \qquad \text{(Eq. 1)}$$

where

J	=	mass flux per unit area per unit time
D	=	"effective" diffusion coefficient (a constant value derived from the data of Neville (1996) will be used as is discussed in Section 6.3)
dc	=	the concentration gradient that exists relative to the "initial" concentration of CO_2 and the "final" or equilibrated concentration of CO_2 (Which is zero per Assumption 5.2)
dL	=	the distance over which diffusion is occurring

It is acknowledged that the effective diffusion coefficient may change during the carbonation process. In fact, due to the consumption of void space and the generation of liquid water during the reaction, (please see the representative carbonation reaction in Assumption 5.2) one could argue that the effective diffusion rate must change. However, for the purposes of this analysis, the use of the "average" effective diffusion rate will suffice, in that we are concerned with the time required for total carbonation of the grout cylinder, rather than the time required for its incremental carbonation.

Examination of Equation 1 shows that a number of parameters can be determined by assigning values to the remaining variables. For example, one can calculate the time duration required to supply the necessary carbon dioxide, given a fixed length of diffusion of the carbon dioxide from a non-depleteable atmospheric reservoir (Assumption 5.1). This equation takes on the form (again, on a unit area basis):

$$t = m \div D\,(dc \div dL) \qquad \text{(Eq. 2)}$$

where

t	=	time
m	=	mass of CO_2 supplied by diffusion

The estimating process assumes that each grouted rockbolt contains 5.8 kilograms of grout based on results of Equation 3 below.

Mass of grout per rockbolt = length of grout × area of grout × density of grout

Mass of grout per rockbolt = 200 cm × (pi(or 3.14) × $(2.54)^2$ – pi (or 3.14) × $(1.27)^2$) × 1.91 g/cm^3 = 5,807 g

(Eq. 3)

The grout contains 61.9 percent, by weight, calcium-bearing cementitious minerals, which is reported as CaO (Parameter 4.1.1). Therefore, each grouted rockbolt cylinder contains 5.8 kg × 0.619 or 3.59 kg of calcium-bearing cementitious minerals (or 3590 g).

Given the reaction:

$$CaO + CO_2 = CaCO_3$$

(Eq. 4)

one can calculate that the mass of carbon dioxide required to carbonate 3.59 kg of calcium-bearing cementitious minerals is equal to

$$44 \text{ kg/mole } CO_2 \times 3.59 \text{ kg CaO} \div 56 \text{ kg/mole CaO} = 2.82 \text{ kg of } CO_2 \text{ (or 2,820 g)}$$

(Eq. 5)

Therefore, the next step is to establish the relationship between the initial carbon dioxide concentration versus duration to supply 2,820 grams of carbon dioxide over a diffusion length (or radius) of 1.27 cm (½ in., the thickness of the grout shell) through a cross-sectional area of 1,596 cm^2 (200 cm × pi (or 3.14) × 2.54 cm).

The only remaining data item is the appropriate effective diffusion coefficient.

6.2 EFFECTIVE DIFFUSION COEFFICIENT

Since transport of carbon dioxide into the matrix of the grout will likely involve both gaseous and aqueous phase diffusive transport, one would expect that the "average" effective diffusion coefficient prevailing during carbonation would occur between these two bounding values.

6.3 RATE OF CARBONATION

Neville (1996, p. 501) writes that the fundamental factor controlling carbonation is the diffusivity (or diffusion coefficient) of the hardened cement paste. Examination of Equation 1 shows that the flux is a linear function of the diffusion coefficient. Linearity of the result may not be a concern when an input is well constrained, or even when the factors that effect the input are well understood. A problem that arises for this analysis is that neither of these features is achieved. The diffusion coefficient for carbon dioxide in air is 0.16 cm^2/s . This contrasts with a diffusion coefficient for aqueous phase carbon dioxide that is four orders of magnitude less (Neville, 1996, p. 499). Typically for bounding case analyses one takes the possible extreme input values to estimate the bounds that will result. The problem is that use of these "extreme"

diffusion coefficients results in such a tremendous range of time estimates as to be rather useless, especially since empirical evidence from industry suggests that the actual rate of carbonation of cementitious products lies between the extreme ranges that would be estimated.

Neville (1996, p. 486 and pp. 499 – 504) also discusses the factors that influence the actual diffusion coefficient that can apply to cementitious products. It is important to note that the Neville discussion focuses on concrete rather than specifically on rockbolt grout, but, in the absence of more specific information, this information will be used. Among the factors that he notes that can effect the actual diffusion coefficient include: relative humidity of the air, porosity of the hardened concrete, compressive strength, type of curing, water to cement ratio, and permeability. Neville (1996, p. 499 – 504) also discusses the effects of the "type" of exposure of the concrete and reagent composition as being important to the rate of carbonation. Given all of these factors it is both not surprising that a wide range of carbonation rates are noted and that specific data do not exist for the proposed grout formulation.

It is interesting to also note that certain parameters tend to conflict with the actual rate of carbon dioxide diffusion and carbonation. For example, effective carbonation requires a certain degree of saturation of the pore spaces, however, a high degree of saturation can impede the diffusion of carbon dioxide within the cementitious matrix. The specific relationship between these two parameters, for "intermediate" values (e. g., not saturated, but also not entirely dry) is unknown. Given insufficient water, CO_2 remains in a gaseous form and does not react with the hydrated cement with the highest rate of carbonation occurs at a relative humidity of between 50 and 70 percent (Neville, 1996, p. 499).

To demonstrate the effect of changes in one of the factors, Neville (1996, p. 486) reports that diffusion coefficients for oxygen gas (which is about 17 percent faster than carbon dioxide, Neville, 1996, p. 486) can vary by an order of magnitude simply due to changes in curing conditions of the concrete, from 5×10^{-8} m^2/s to 50×10^{-8} m^2/s (or converting to centimeters squared per second, from 5×10^{-4} cm^2/s to 5×10^{-3} cm^2/s).

Based on the above discussion it is clear that any assumed diffusion coefficient, used in the absence of grout-specific data, is subject to dispute. However, as noted above and upon a reexamination of Equation 1, since the flux rate is a linear function of the diffusion coefficient any difference in the "actual" diffusion coefficient versus the assumed value used herein is also a linear function. For example, if the actual diffusion coefficient is 5-times the diffusion coefficient value used herein, the results of the time required for total carbonation is one-fifth as great.

In spite of all of the acknowledged uncertainties noted above, this analysis is based on an "intermediate" diffusion coefficient of 1×10^{-3} cm^2/s, which is the geometric mean of the range of diffusion coefficients derived from the data reported by Neville (1996, p. 486). It is recognized the reported value pertains to oxygen rather than carbon dioxide, but reflecting the fact that this is a "rounded" estimate, no "correction" is made to adjust for the differing atomic weight between oxygen and carbon dioxide, which would amount to 17 percent, as noted above.

Since 2,820 g of carbon dioxide must be diffused through an area of 1,596 cm^2, adjusting to a unit area basis, (2820 g ÷ 1596 cm^2) equals 1.77 g of carbon dioxide per cm^2. Therefore, based on Equation 2, for a carbon dioxide concentration of 1 ppmv and a D_e equal to 1.0×10^{-3} cm^2/s, one can develop the following equation:

$t = 1.77\ g/cm^2 \div [1.0 \times 10\text{-}3\ cm^2/s \times \{(1 \times 10^{-6} \times 44\ g/mole)/(24.5\ l/mole \times 1{,}000\ cm^3/l) \div 1.27cm\}]$

$$t = 1.25 \times 10^{12}\ s \qquad \text{(Eq. 6)}$$

Converting to years, where $t = 1.25 \times 10^{12}$ s gives

$$t = 1.25 \times 10^{12}\ s \div 31{,}557{,}600\ s/yr = 39{,}663\ yrs\ (\text{round to } 39{,}700 \text{ years}) \qquad \text{(Eq. 7)}$$

Since the diffusion-media transport is linear with respect to carbon dioxide concentration, the time for 100 ppmv is 0.01 times the duration for 1 ppmv and is therefore 397 years. Similarly, the time required for total carbonation to result given a carbon dioxide concentration of 1,000 ppmv is 40 years. These predicted durations are shown in Table 1.

As noted above, the basis for the range of values used in this analysis stems from the carbon dioxide concentration of 1,000 ppmv in the unsaturated zone that is being used in another study (Engineered Barrier System: Physical and Chemical Environment (P&CE) Model (in progress) (CRWMS M&O 2000d, p. 1 of 1). This value was used to establish an upper bound. It is recognized that boiling would cause a decrease in the air-mass fraction and thereby a decrease in the concentration of carbon dioxide. Essentially this analysis assesses the rates of carbonation predicted at air-mass fractions of 0.001, 0.1, and 1.0.

Table 1. Relationship Between CO_2 Concentration and Duration Required for Carbonation

CO_2 Concentration (in ppmv)	Corresponding Air Mass Fraction	Duration for Carbonation (years)
1	0.001	39,700
100	0.1	397
1,000	1.0	40

An analysis of the results reported in Table 1 indicates that a very long period of time is required to carbonate the rockbolt grout under a low (1-ppmv) concentration of carbon dioxide. Conversely, under more elevated concentrations of carbon dioxide the carbonation is predicted to be completed within a few tens to hundreds of years. This rate of carbonation is commensurate with carbonation rates that are observed under certain ambient conditions (see Neville, 1996, pp. 499 – 503) and is to be generally expected given that an "intermediate" diffusion coefficient as discussed above was used.

To show the sensitivity of these results to the diffusion coefficient recall that these are a linear function of the diffusion coefficient. Therefore if a diffusion coefficient of 1×10^{-5} cm^2/s (one approximately equal to the diffusion of carbon dioxide in water, per Neville (1996, p. 499)) were used as opposed to 1×10^{-3} cm^2/s value the time for carbonation at 100 ppmv would increase to 39,700 years (or the length of time reported in Table 1 for 1 ppmv). Conversely, if a diffusion coefficient of carbon dioxide in ambient air was used (0.16 cm^2/s, Section 4.1.2) instead of the 1×10^{-3} cm^2/s value the rate of carbonation would be 160 times faster than the values reported in Table 1. Therefore, total carbonation at a concentration of 100 ppmv could occur at this higher diffusion rate within about 2.5 years. At a 1,000-ppmv carbon dioxide concentration carbonation would be complete within about 3 months, or virtually during the time the grout is curing.

An explicit assumption of Equation 1 is that the atmospheric concentration of carbon dioxide is maintained at the initial value as carbon dioxide is consumed within the grout matrix. By negating this assumption, one can determine the gradient that will develop within the atmosphere if a constant concentration of carbon dioxide is not maintained.

If one assumes that a constant concentration of carbon dioxide is not maintained during carbonation, then as the concentration of carbon dioxide within the atmosphere decreases, so does the rate of diffusion of carbon dioxide into the grout. This latter scenario is based on the assumption that the carbon dioxide concentration within the grout is zero. Since the rate of diffusion depends on the concentration gradient between the atmospheric concentration and a zero concentration within the grout, any decrease of the atmospheric concentration must cause a decrease in the diffusion rate. At steady-state conditions, the gradient will decrease until the rate of carbon dioxide consumption within the grout is matched by the decreased diffusion rate to the grout surface.

This allows us to establish the relationship between the two diffusion-controlled rates:

$$\text{Flux within the grout } (J1) = D1(C1 - C2) \div x1 \qquad \text{(Eq. 8)}$$

where

J1	=	mass of CO_2 in moles per unit area per unit time
D1	=	effective diffusion coefficient (assumed to be 1.0×10^{-3} cm^2/s)
C1	=	concentration of CO_2 at the grout surface
C2	=	concentration of CO_2 within the grout (assumed to be zero)
x1	=	distance of diffusion within grout (assumed to be 1.27 cm)

Flux to the grout surface through the atmosphere will be:

$$J2 = D_e2(C3 - C1) \div x2 \quad \text{(Eq. 9)}$$

where

J2	=	mass of CO_2 in moles per unit area per unit time
D_e2	=	effective diffusion coefficient (assumed to be 0.160 cm^2/s)
C1	=	concentration of CO_2 at grout surface
C3	=	concentration of CO_2 away from grout surface
x2	=	distance of diffusion through atmosphere

At steady-state conditions, J1 must equal J2; therefore, one can develop the relationship J1 = J2, or:

$$D_e1(C1 - C2) \div x1 = D_e2(C3 - C1) \div x2 \quad \text{(Eq. 10)}$$

Substituting in the known values, one can develop the following equation:

$$(1.0 \times 10^{-3}\ cm^2/s)(C1) \div 1.27\ cm = (0.160\ cm^2/s)(C3 - C1) \div x2 \quad \text{(Eq. 11)}$$

From Equation 11, one can develop a relationship between C1 (the concentration of carbon dioxide at the grout surface) and C3 (the concentration of carbon dioxide within the atmosphere at a distance of x2, the distance over which the concentration gradient forms). This relationship solving for C3 is:

$$(7.87 \times 10^{-4})\ C1 = 0.160\ C3 - 0.160\ C1 \div x2$$

$$x2(7.87 \times 10^{-4})\ C1 = 0.160\ C3 - 0.160\ C1$$

$$0.160\ C3 = x2(7.87 \times 10^{-4})\ C1 + 0.160\ C1$$

or

$$C3 = C1\ (0.0049x2 + 1) \quad \text{(Eq. 12)}$$

Therefore, for any two input values of C1 and x2, the value of C3 is defined. For example, at a concentration (C1) equal to 500 ppmv and x2 equal to 300 cm, C3 equals:

$$C3 = (500)(0.0049)(300) + 500) = 1{,}235\ \text{ppmv} \quad \text{(Eq. 13)}$$

Since we will constrain C3 to a maximum value of 1,000 ppmv, at an x2 value of 100 cm, the C1 value will be:

$$C1 = C3 \div (0.0049x2 + 1)$$

or

$$C1 = 1{,}000 \div [(0.0049 \times 100) + 1] = 671 \text{ ppmv}$$

(Eq. 14)

One can show that:

$$2 = 204[(C3 \div C1)-1]$$

(Eq. 15)

It follows that where C1 equals 1 ppmv and C3 equals 1,000 ppmv:

$$x2 = 204\ [(1000 \div 1)-1]$$

$$x2 = 203{,}796 \text{ cm}$$

(Eq. 16)

Table 2 can therefore be developed, where C3 is maintained at 1,000 ppmv.

Table 2. Relationship Between CO_2 Concentration at Grout Interface and Distance of Atmospheric Diffusion Gradient with Atmospheric CO_2 Concentration of 1,000 ppmv

C1 (in ppmv)	x2 (in cm)
1	203,796
10	20,196
100	1,836
250	612
500	204
750	68
999	.2

Examination of Table 2 shows that an improbably long diffusion gradient is postulated in order to maintain a 1-ppmv carbon dioxide concentration at the grout surface. Rather, the results from Table 2 suggest that a relatively short gradient (measuring on the order of less than 1 m) might develop around the rockbolt grout column with a resulting carbon dioxide concentration that represents perhaps 75 to 99.9 percent of the ambient carbon dioxide concentration.

6.4 RATE OF AQUEOUS-PHASE CARBON DIOXIDE AVAILABLE FOR CARBONATION REACTION

The design analysis for the Engineered Barrier System: Physical and Chemical Environment (P&CE) Model (in progress) reports that the scaled water flow per rockbolt is 7.52×10^{-5} m^3/yr (CRWMS M&O 2000c, p. 2 of 2). Given a water density of 965.254 kg/m^3 (CRWMS M&O 2000c, p. 2 of 2) and total carbonate content of 128.9 mg/kg (CRWMS M&O 2000c, p. 1 of 2),

one can calculate the bounding rate of carbon dioxide that could be supplied from an aqueous source.

$$\text{Rate of } CO_2 \text{ supply} = \text{mass of water} \times CO_2 \text{ concentration}$$

$$\text{Rate of } CO_2 \text{ supply} = 7.52\times10^{-5}\ m^3/yr \times 965.254\ kg/m^3 \times 128.9\ mg/kg$$

$$\text{Rate of } CO_2 \text{ supply} = 9.36\ mg/yr \text{ per rockbolt}$$

(Eq. 17)

Therefore to supply 2,820 g of CO2 to a rockbolt at a rate of 9.36 mg/yr would require over 300,000 years. Clearly this is an extremely long period of time and suggests that carbonation of the rockbolt grout will be constrained by the supply of gaseous phase carbon dioxide, provided, for example, by diffusive processes, as opposed to carbon dioxide supplied as an advective aqueous phase.

7. CONCLUSIONS

This analysis has derived the time required for carbonation of the grout surrounding a hypothetical rockbolt by diffusive processes under a given (and acknowledged to be a highly sensitive) set of conditions. This analysis has also established the linear relationship between the time required for carbonation and the concentration of carbon dioxide. Examination of the diffusion equation (Equation 8) reveals that the time required for complete carbonation is also a linear function of the diffusion coefficient. As has been discussed throughout this report the sensitivity of these results relative to the input suggests that additional analyses are required to validate this parameter. Suggested information to be collected on the actual grout product is discussed below.

As reported in Table 1, approximately 39,700 years are required for complete carbonation given a carbon dioxide concentration of 1 ppmv. Since the diffusion-media transport is linear with respect to carbon dioxide concentration, the time for 100 ppmv is 0.01 times the duration for 1 ppmv and is 397 years. Similarly, the time required for total carbonation, given a carbon dioxide concentration of 1,000 ppmv, is 40 years (see Table 1). The basis for the range of values used in this analysis stems from the carbon dioxide concentration of 1,000 ppmv in the unsaturated zone that is being used in another study (Engineered Barrier System: Physical and Chemical Environment (P&CE) Model (in progress) (CRWMS M&O 2000d p. 1 of 1). This value was used to establish an upper bound. It is recognized that boiling would cause in a decrease in the air-mass fraction and thereby a decrease in the concentration of carbon dioxide. Essentially this analysis assessed the rates of carbonation predicted at air-mass fractions of 0.001, 0.1, and 1.0.

This analysis also establishes the relationship between the depletion of the atmospheric concentration of carbon dioxide and the distance from the rockbolt grout undergoing carbonation, under steady-state conditions. As reported in Table 2, an improbably long diffusion gradient is suggested to be necessary in order to maintain low (1 ppmv) carbon dioxide

concentration at the grout surface. Alternatively it is suggested that relatively short diffusion gradients measuring less than 1m will develop with a commensurately high carbon dioxide concentration developing on the rockbolt grout column.

Lastly, this analysis reports the rate of aqueous phase carbon dioxide available for the carbonation process, which is 9.36 mg/yr. per rockbolt and requires the improbably longer period of time of greater than 300,000 years for complete carbonation of the rockbolt grout. This suggests that atmospheric carbon dioxide will dominate the carbonation of the rockbolt grout column.

It is acknowledged that this analysis is replete with assumptions that in many ways drive the results of the analysis. For example, if it is assumed that only calcium hydroxide reacts with carbon dioxide a lesser amount of time will be required to carbonate this more limited reactant mass. Conversely, if it is assumed that sufficient moisture exists within the pore spaces of the cementitious matrix to impede the diffusion of carbon dioxide gas then a significantly longer period of time would be required for effective carbonation. However, a thoroughly dry grout matrix will impede carbonation in that at least some moisture is required to provide for the dissolution of gaseous carbon dioxide and speed the carbonation reaction. As noted by Neville (1996, p. 499) if there is insufficient water in the pores of the grout, CO_2 remains in gaseous form and does not react with the hydrated cement. Modifications of the grout formulation, particularly in terms of changes to the total calcium content will also directly effect the time required for total carbonation.

In spite of these acknowledged caveats related to this analysis, the linearity of the results relative to the most significant inputs parameters (diffusion coefficient and mass of reactable calcium) allow these results to be used in assessing the effects of changes to either the diffusion coefficient or the mass of reactable calcium.

Uncertainties Associated with Analysis

Fundamentally, the mathematics of this analysis suggests that two parameters must be better quantified in order to improve the estimate of the time required for carbonation of the final grout product. These consist of the diffusion coefficient of the grout and the mass of reactable calcium subject to carbonation.

The diffusion coefficient of the grout, for different periods of time or degree of carbonation, should be obtained. Based on an understanding of the carbonation reaction it is probable that a decline of the diffusion coefficient of the grout will be measured as the carbonation reaction progresses. An understanding of the changes in the diffusion coefficient of the grout with time, if any, is important to allow refinement of the carbonation rate relative to commensurate changes in drift gas phase composition. As noted above, in the absence of grout-specific diffusion coefficient data, this analysis used an average diffusion coefficient value derived from the literature, providing a reasonable estimate as the time required for carbonation under the specified conditions. Ascertaining a grout-specific diffusion coefficient would improve the estimated time for carbonation of the rockbolt-related grout.

The second datum requirement relates to a determination of the mass of calcium that is readily susceptible to carbonation. This analysis is based on carbonation of all calcium present within the grout. Whereas this is a valid, if bounding assumption, it is likely that rapid carbonation of the more labile calcium hydroxide may impede subsequent carbonation of the more recalcitrant silicate, aluminate and ferrate phases. Therefore from a practical point-of-view this determination will help constrain the actual amount of calcium that will undergo carbonation and complies with the restrictions of the diffusion-based model used for this analysis. This statement is not to suggest that all calcium may not eventually be carbonated. However, one could speculate that after carbonation of all of the labile calcium hydroxide that the mechanism of carbonation may change for the residual calcium phases. For example, it is possible that although carbonation is continuing the rate of the carbonation reaction is no longer constrained by the supply of carbon dioxide, but the kinetics of the carbonation reaction itself. This would negate assumption 5.2 used for this analysis in that the fugacity of carbon dioxide in contact with the grout matrix would no longer be zero. This change in the reaction process can be modeled, after consumption of the calcium hydroxide, but will be based only on the transformation rate, which is currently unknown, of the recalcitrant calcium-bearing phases to calcite.

The outputs from this document are unqualified and cannot be used for procurement, fabrication, or construction.

8. REFERENCES

8.1 DOCUMENTS CITED

CRWMS M&O 1999a. *Development Plan (DP) Checklist and Cover Sheet: Provide Sub-models for the Physical and Chemical Environmental Abstraction Model for TSPA-LA.* TDP-WIS-MD-000006 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990902.0450.

CRWMS M&O 1999b. *Conduct of Performance Assessment.* Activity Evaluation, January 18, 1999. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990316.0014.

CRWMS M&O 2000a. *Longevity of Emplacement Drift Ground Support Materials.* ANL-EBS-GE-000003 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000307.0382.

CRWMS M&O 2000b. *Rockbolt Grout Density.* Input Transmittal 00072.T. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000310.0080.

CRWMS M&O 2000c. *Rockbolt Grout Leachate and Leaching Conditions.* Input Transmittal 00073.T. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000310.0029.

CRWMS M&O 2000d. *Concentration of CO2 Gas in the Unsaturated Zone Gas Phase*. Input Transmittal 00084.T. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000310.0078.

DOE (U.S. Department of Energy) 2000. *Quality Assurance Requirements and Description.* DOE/RW-0333P, Rev 9. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.19991028.0012.

Dyer, J.R. 1999. "Revised Interim Guidance Pending Issuance of New U.S. Nuclear Regulatory Commission (NRC) Regulations (Revision 01, July 22, 1999), for Yucca Mountain, Nevada." Letter from Dr. J.R. Dyer (DOE/YMSCO) to Dr. D.R. Wilkins (CRWMS M&O), September 3, 1999, OL&RC:SB-1714, with enclosure, "Interim Guidance Pending Issuance of New NRC Regulations for Yucca Mountain (Revision 01)." ACC: MOL.19990910.0079.

Incropera, F.P., and DeWitt, D.P. 1996. *Fundamentals of Heat and Mass Transfer*. 4th Edition. New York, New York: John Wiley and Sons. TIC: 243950.

Mindess, S. and Young, J.F. 1981. *Concrete*. Englewood Cliffs, New Jersey: Prentice-Hall. TIC: 242878.

Neville, A.M. 1996. *Properties of Concrete. Fourth Edition.* New York, New York: John Wiley & Sons, Inc. TIC: 236567.

NRC (U.S. Nuclear Regulatory Commission) 1999. *Issue Resolution Status Report Key Technical Issue: Evolution of the Near-Field Environment*. Rev. 2. Washington, D.C.: U.S. Nuclear Regulatory Commission. ACC: MOL.19990810.0640.

Weast, R.C. ed. 1979. *CRC Handbook of Chemistry and Physics*. 60th Edition, 1979-1980. Boca Raton, Florida: CRC Press Inc. TIC: 245312.

Williams Form Engineering Corporation 1997. *Rock Anchor Systems*. No. 397. Grand Rapids, Michigan: Williams Form Engineering Corporation. TIC: 245370.

64 FR 8640. Disposal of High-Level Radioactive Wastes in a Proposed Geologic Repository at Yucca Mountain, Nevada. Proposed rule 10 CFR 63. Readily Available.

8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

AP-3.10Q, Rev. 2, ICN 0. *Analyses and Models*. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000217.0240.

NLP-2-0, REV. 5. *Determination of Importance Evaluations*. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19981116.0120.

QAP-2-0, Rev. 5. *Conduct of Activities*. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19980826.0209.

QAP-2-3, Rev 10. *Classification of Permanent Items*. Las Vegas, Nevada: CRWMS M&O. ACC: MOL 19990316.0006.