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## **CHEMICAL DEGRADATION ASSESSMENT FOR THE H-AREA TANK FARM CONCRETE TANKS AND FILL GROUTS**

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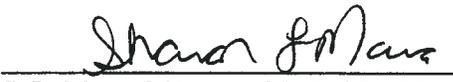
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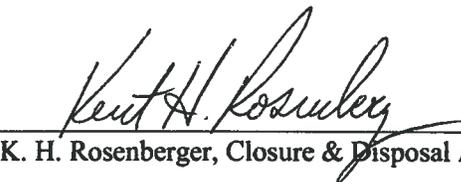
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## LIST OF ABBREVIATIONS

<b>AAR</b>	<b>Alkali Aggregate Reaction</b>
<b>ACI</b>	<b>American Concrete Institute</b>
<b>ASTM</b>	<b>American Society for Testing and Materials</b>
<b>AFm</b>	<b>(Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-mono) phases<sup>1</sup></b>
<b>AFt</b>	<b>(Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-tri) phases<sup>2</sup></b>
<b>C-S-H</b>	<b>Calcium silicate hydrate</b>
<b>DEF</b>	<b>Delayed Ettringite Formation</b>
<b>ERDMS</b>	<b>Environmental Restoration Data Management System</b>
<b>FTF</b>	<b>F-Area Tank Farm</b>
<b>g</b>	<b>gram</b>
<b>HLW</b>	<b>High Level Waste</b>
<b>HTF</b>	<b>H-Area Tank Farm</b>
<b>INEEL</b>	<b>Idaho National Engineering and Environmental Laboratory</b>
<b>K<sub>isat</sub></b>	<b>Initial Saturated Hydraulic Conductivity</b>
<b>LLW</b>	<b>Low Level Waste</b>
<b>mL</b>	<b>milliliter</b>
<b>NIST</b>	<b>National Institute of Standards and Testing</b>
<b>Pa</b>	<b>Pascal</b>
<b>PA</b>	<b>Performance Assessment</b>
<b>PS&amp;E</b>	<b>Process Science and Engineering</b>
<b>psi</b>	<b>pounds per square inch</b>
<b>RH</b>	<b>Relative Humidity</b>
<b>SRNL</b>	<b>Savannah River National Laboratory</b>
<b>SRS</b>	<b>Savannah River Site</b>
<b>TS</b>	<b>Total Solids</b>
<b>WSRC</b>	<b>Washington Savannah River Company</b>
<b>Wt</b>	<b>Weight</b>
<b>Wt%</b>	<b>Weight percent</b>

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<sup>1</sup> General formula is [Ca<sub>2</sub>(Al,Fe)(OH)<sub>6</sub>]·X·xH<sub>2</sub>O where X denotes one formula unit of a singly charged anion or ½ of a doubly charged anion.

<sup>2</sup> General formula is [Ca<sub>3</sub>(Al,Fe)(OH)<sub>6</sub>·12H<sub>2</sub>O]<sub>2</sub>·3X·xH<sub>2</sub>O where X is < or = 2 and represents one formula unit of a doubly charged anion or 2 formula units of a singly charged anion.

## 1.0 SUMMARY

The objective of this task was to provide estimates of the effects and extent of chemical degradation of the cementitious barriers used or planned to be used in the Savannah River Site (SRS) H-Area Tank Farm closure concept. Results from this work will be applied to the cementitious barrier performance predictions in the H-Area Tank Farm (HTF) Performance (PA).

This work was requested by K. H. Rosenberger, Savannah River Remediation, Closure and Disposal Assessment [SLA, 2009]. The specific request was to update Table 6.1 in WSRC-STI-2007-00607 Revision 0, which was prepared to support the F-Area Tank Farm PA, to include saturated exposure conditions [SLA, 2009]. The need for updating the earlier work for H-Area Tank Farm was because some of the H-Area Tank Farm high-level waste tanks or portions of tanks are in a saturated environment [Jones, Millings, and Rambo, 2010].

Background information on chemical degradation mechanisms and the methodology used to evaluate the effects of chemical degradation on the F-Area Tank Farm cementitious barriers is provided in WSRC-STI-2007-00607 Revision 0 [1]. The methodology applied to the F-Area Tank Farm chemical degradation analysis was based on the methodology in the INEL Tank Closure PA and based on work by Walton, et al., 1990 [INEEL PA Appendix E, 2003 and Walton, 1990, respectively].

Based on this review, the current SRS H-Area Tank Farm disposal environment was found to be benign with respect to chemical degradation of the reinforced concrete vaults and the tank fill grout material. Consequently, the degradation due to chemical processes will progress at a very slow rate. Simple empirical relationships or single phase diffusion equations were used to calculate distance of transport of the potentially corrosive species. This approach can over or under estimate the rate of loss of intact material because it does not take into account non deleterious binding reactions, activation energies, threshold values for initiation of corrosion, etc. It does not take into account coupled effects.

The penetration depth of the chemical species responsible for the degradation was assumed to be equivalent to the depth of degradation. The consequences of the degradation depended on the material porosity and whether or not the material contained steel reinforcing because carbon steel rebar introduces an additional degradation process, i.e., concrete cracking due to formation of expansive metal corrosion products.

Porosity and diffusivity data for two representative materials were used in calculations to predict the depth of penetration of the various forms of chemical attack. These materials were a surrogate base mat concrete (3000 psi concrete from P-Area, SRS which was poured in 1978) which represented the vault concrete/base mat and a tank fill reducing grout which represented all of the fill grout in the tanks and the annulus spaces.

For saturated concrete and grout, acid leaching (i.e., decalcification) was the most aggressive degradation mechanism. The depth of severe decalcification at 1000 years exposure was 6.5 and 8.2 cm for the surrogate vault concrete and tank fill grout, respectively. The impact of decalcification is to increase porosity and permeability and to decrease the pH of the pore

solution from about 12.5 to lower values depending on the evolution of the mineral phase assemblages as a function of calcium concentration in the pore solution [Langton, 2009].

For unsaturated vault concrete and tank fill grout in the vadose zone (exposed to air in the soil pores), the most extensive attack was from carbonation. Carbonation of unsaturated concrete was found to result in the greatest penetration depth (assumed to correspond to depth of degradation) as a function of time. For material with the porosity of the surrogate base mat concrete, 16.8 volume percent, the depth of penetration from carbonation was estimated to be 21 cm after 1000 years. The estimated depth of penetration for the representative fill grout from carbonation reactions was 36 cm after 1000 years. (The source of carbonate was assumed to be the atmosphere.) For saturated vault concrete and tank fill grout (in the water table) the depth of penetration of the carbonation front was about 80 times less than that calculated for unsaturated conditions.

The impact of carbonation on the permeability of the cementitious barriers in the HTF closure concept depends on whether the barrier contains steel. Carbonation in itself may actually reduce permeability by plugging pores with calcium carbonate. However, it will affect the permeability of reinforced concrete because the concrete will crack due to formation of expansive iron hydroxide phases which form when steel corrodes. Steel passivation is lost when the pH of the pore solution is in equilibrium with calcium carbonate (pH~8.4) rather than calcium hydroxide (pH~12.5).

The consequences of carbonation with respect to the permeability of the cementitious barriers in the HTF depend on the assumptions made to link depth of penetration with formation of expansive iron hydroxide phase from associated rebar corrosion and the assumptions linking corrosion with concrete cracking.

For the reinforced vault concrete, the assumption that cracking occurs simultaneously with carbonation is unrealistic. Cracking will lag the carbonation by a considerable time especially in the absence of other corrodents such as chloride ions. When cracking from expansion does occur, the permeability will increase. Permeability values for degraded HTF vault concrete have not been measured but are assumed to be the same as the infill soil above the tank. This is a reasonable assumption (100 times increase) given the lack of data.

Because the annulus fill grout and fill grout in the tanks without cooling coils do not contain rebar or steel, the overall effect of carbonation should be minimal regardless of the depth of penetration. The permeability of these materials is not expected to change significantly as the result of carbonation. This is the case even though the rate of carbonate penetration is faster due to the higher porosity of the fill grout (26.6 volume percent).

Carbonation of the tank fill grout will not commence until the tank is breached due to corrosion or development of a fast pathway. Based on calculated tank corrosion rates [Subramanian, 2007 and Garcia-Diaz, 2010] a lengthy lag time is anticipated before carbonate actually contacts the grout and the carbonation front advances to the cooling coils. The corrosion rate is expected to be very slow in the absence of additional corrodents.

The impact of carbonation on cracking when it does occur is expected to be the same as described above. The permeability of the degraded concrete could increase as much as 100

times. However, the possibility exists that expansive reactions occurring under the somewhat constrained conditions of the buried tank could result in very little change in permeability. This can be further evaluated by requesting a mechanical analysis be performed by the appropriate personnel in the SRS design integration organization or by a qualified subcontractor.

A more sophisticated approach would require additional material characterization data and advanced multi ionic transport codes specially designed for concrete long-term service life predictions. (Although current performance prediction codes are limited in that they have only been validated over relatively short performance times of 20-50 years, the chemical reactions and effects for the mechanisms responsible for degradation can be extrapolated. Evolution of the boundary conditions over time is more difficult to predict.)

## 2.0 INTRODUCTION

### 2.1 Objective and Approach

The objective of this task was to provide estimates of the effects and extent of chemical degradation for the cementitious barriers used or planned to be used in the Savannah River Site (SRS) H-Area Tank Farm closure concept. These estimates are intended to be used in the SRS H-Area Tank Farm Closure Performance Assessment (PA).

The approach used to evaluate the effects of chemical degradation for the H-Area Tank Farm cementitious barriers was to update Table 6.1 in WSRC-STI-2007-00607 Revision 0 to include saturated conditions because some of the H-Area Tank Farm high-level waste tanks or portions of tanks are in a saturated environment [Rosenberger, 2010 and Jones, Millings, and Rambo, 2010]. This approach was specified by K. H. Rosenberger, C & DA / SRR in a Service Level Agreement, SLA-WSTD-0015-Rev.1 [SLA, 2009].

Simple empirical relationships or single phase diffusion equations were used to calculate distance of transport of the potentially corrosive species. These equations and approach were developed by Walton, et al, 1990, and were used in the INEEL PA Appendix E, 2003 and the SRS F-Area Tank Farm PA. Coupled effects are recognized as important but literature data were insufficient to assess coupled effects. Given the limited amount of material-specific information, no uncertainty analysis was performed for this report.

### 2.2 Background: SRS HLW Tanks and Closure Concept

Conceptual drawings of the four types of SRS high-level waste (HLW) tanks are provided in WSRC-STI-2007-00607 Revision 0 [Rosenberger, 2007, Robinson, 2007, and Langton, 2007] and HTF-IP-03, Revision 0 (Type II waste tanks) [SRR, 2010]. A list of the cementitious materials used and planned to be used as fill materials in the H-Area Tank Farm (HTF) closure is provided in Table 2-1.

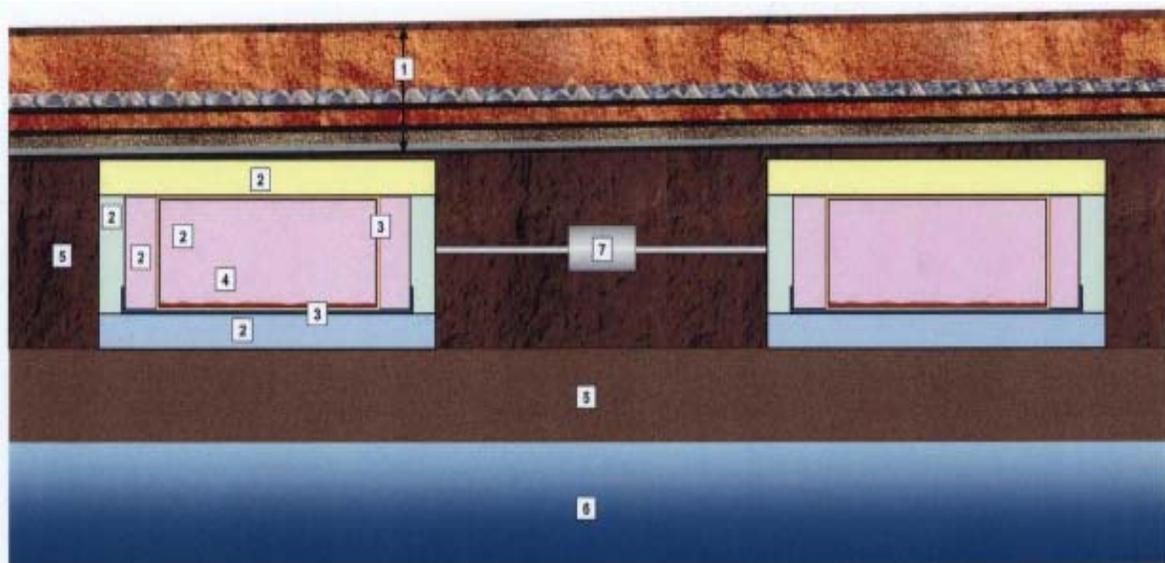
The H-Area Tank Farm conceptual closure model is the same as that for the F-Area Tank Farm and is illustrated in Figure 2-1. It involves:

- Removing as much waste as practical from the tank
- Completely filling the emptied tank with cementitious material to physically and chemically stabilize any remaining radionuclides.
- Completely filling the annulus space between the steel tank and concrete vault (Types I, II, III, and IIIA tanks) and the riser accesses in the top of the tanks to eliminate voids and pathways for water.
- Filling cooling coils in the Type I, II, III, and IIIA tanks to minimize fast pathways for infiltration water.

**Table 2-1. Summary of cementitious material used to construct and close the H-Area Tank Farm [K. Rosenberger and T. Robinson, 2007, R. Deshpande, 2007].**

APPLICATION	MATERIAL	REINFORCEMENT	THICKNESS	
			(inches)	(m)
<b>VAULT</b>				
<b>Type I</b>				
<i>Roof</i>	Concrete DuPont Spec. 3019 Section B	Yes	22	0.56
<i>Wall</i>		Yes	22	0.56
<i>Floor/ Base Mat</i>		Yes	30	0.76
<b>Type II</b>				
<i>Roof</i>	DuPont Spec Class C Concrete	Yes	45	1.14
<i>Wall</i>		Yes	33	0.84
<i>Floor/ Base Mat</i>		Yes	42	1.07
<b>Type III</b>				
<i>Roof</i>	DuPont Spec Class C Concrete	Yes	48	1.22
<i>Wall</i>		Yes	30	0.76
<i>Floor/ Base Mat</i>		Yes	42	1.07
<b>Type IIIA</b>				
<i>Roof</i>	DuPont Spec Class C Concrete	Yes	48	1.22
<i>Wall</i>		Yes	30	0.76
<i>Floor/ Base Mat</i>		Yes	41	1.04
<b>Type IV</b>				
<i>Roof</i>	Class C Concrete	Yes	7	0.178
<i>Wall</i>	Type I Portland Cement	Yes	7	0.178
<i>Floor/ Base Mat</i>	Class C Concrete	Yes	6.9	0.175
<b>FILL</b>				
<b>Type I</b>				
<i>Tank</i>	TBD	No	Cylinder 24.5 ft high, 75 ft diameter	Cylinder 7.47 m high, 22.86 m diameter
<i>Annulus</i>	TBD	No	Cylindrical shell 30 ft high, OD ~ 77.5ft ID ~ 75ft	Cylindrical shell 9.14 m high, OD ~ 23.62 m ID ~ 22.86 m
<i>Cooling Coil</i>	TBD	No	2 ID	0.05
<i>Riser</i>	TBD	No		
<b>Type II</b>				
<i>Tank</i>	TBD	No	Cylinder 27 feet high 85 feet in diameter	Cylinder 8.23 m high 25.9 m in diameter
<i>Annulus</i>	TBD	No	Cylinder ~28 ft high OD ~ 90 ft ID ~ 85 ft	Cylinder ~8.5 m high OD ~ 27.4 m ID ~25.9 m
<i>Cooling Coil</i>	TBD	No	2 ID	0.051
<i>Riser</i>	TBD	No		
<b>Type III, IIIA</b>				
<i>Tank</i>	TBD	No	Cylinder 33 feet high, 75 ft diameter	Cylinder 10.06 m high, 22.86 m diameter
<i>Annulus</i>	TBD	No	Cylindrical shell 30 ft high, OD ~ 77.5ft ID ~ 75ft	Cylindrical shell 9.14 m high, OD ~ 23.62 m ID ~ 22.86 m
<i>Cooling Coil</i>	TBD	No	2 ID	0.051
<i>Riser</i>	TBD	No		
<b>Type IV</b>				
<i>Tanks 17 and 20</i>	Reducing Grout (contact with residual waste), Bulk Fill, Strong Grouts (top layer, intruder barrier)	No	Cylinder 34.25 feet high, 85 ft diameter	Cylinder 10.44 m high, 25.91 m diameter
<i>Tanks 18 and 19</i>	Reducing Grout (contact with waste and bulk fill) Strong Grout (top layer, intruder barrier)*	No	Cylinder 34.25 feet high, 85 ft diameter	Cylinder 10.44 m high, 25.91 m diameter
<i>Annulus</i>	NA	No	0	0
<i>Cooling Coil</i>	NA	No	NA	NA
<i>Riser</i>	5000 psi Grout	No	NA	NA

\* SRS Specification C-SPP-F-00047, Revision 2, 2003 identifies Reducing Grout. However, the specification may be revised prior to closing Tanks 18 and 19. NA = Not Applicable



[NOT TO SCALE]

- 1 Closure Cap - Provides water flux to the top of tank from infiltrating rainwater.
- 2 Vault Concrete and Tank Fill Grout - Provides degradation description of the concrete and grout based materials in the tank system.
- 3 Carbon Steel Tank Liner (Primary and Secondary) - Provides degradation description of the carbon steel liners in the tank system.
- 4 Contamination Leaching - Provides waste contamination release rates of residual waste heel based on solubility and sorption rates per nuclide.
- 5 Vadose Zone and Backfill - Provides hydraulic related values for the unsaturated undisturbed soil beneath the tanks and the backfill soil surrounding the tanks.
- 6 Hydrogeology - Provides hydraulic related values for the saturated soil beneath the tanks.
- 7 Ancillary Equipment - Provides waste contamination release rates of residual waste associated with ancillary equipment.

**Figure 2-2. H- and F-Area Tank Farm conceptual closure model** [K. Rosenberger and T. Robinson, 2007].

### 2.2.1 Vault Concrete and Cementitious Fill Properties for SRS PA Modeling

For the PA modeling all of the concrete materials used in construction of the tanks in the HTF are consolidated into two generic materials, surrogate reinforced concrete and representative reducing grout. Since the actual tank vault concrete is not readily accessible, a surrogate material was used to obtain property data. The surrogate material was collected from a slab constructed in 1978 in P-Area. This material is a 3000 psi reinforced concrete containing Type I Portland cement and local aggregates [Dixon, 2007]. The slab was constructed on grade such that the bottom was exposed to unsaturated soil and the top surface was exposed to ambient outdoor conditions. Hydraulic properties and sorption properties of this surrogate material are reported elsewhere [Dixon, 2007 and Kaplan, 2006, 2007, 2008, respectively].

The tank fill materials including the cooling coil fill material are reducing formulations. The tank fill material, Mix No. OPDEXE-X-P-0-BS, is described in SRS Specification C-SPP-F-00047, Revision 2, Section 03311, paragraph 2. The recommended cooling coil grout, Mix MF816 + 10 BFS, respectively is described elsewhere [Harbour et. al, 2008]. Hydraulic properties of these materials are provided in Table 2-2.

**Table 2-2. Properties of the cementitious barriers applicable to the H-Area Tank Farm Closure [Dixon, 2007 and Harbour, 2008].**

<b>Cementitious Barrier</b>	<b>Ave. Permeability (cm/s)</b>	<b>Ave. Bulk Density (g/cm<sup>3</sup>)</b>	<b>Ave. Water Exchangeable Porosity (fraction)</b>
<b>Tank Vault Concrete</b> Surrogate 3000 psi reinforced concrete from [DuPont, 1978]	3.4E-08	2.06	0.168
<b>Tank Fill</b> Reducing Grout Mix No. OPDEXE-X-P-0-BS [WSRC, 2003]	3.6E-08	1.81	0.266
<b>Cooling Coil Fill</b> MF816 + 10 BFS [Harbour et. al, 2008]	1E-10	2.07	0.35

### 2.2.2 PA Environmental Scenarios and Cementitious Barrier Degradation Scenarios

Several environmental scenarios were assumed in the H-Area Tank Farm PA. Three scenarios are illustrated in Figure 2-3. These scenarios were selected to illustrate the range of conditions that are considered in the analysis. They include an intact tank unit (concrete vault, steel tank, and fill grout) in unsaturated soil, a closed tank that develops fast flow paths in unsaturated soil, and a closed tank in saturated soil assuming a rise in the water table.

The properties of degraded vault concrete, fill grout, and cooling coil grout have not been measured. For the PA modeling, all of the cementitious barriers were assumed to degrade to material with the properties of soil used as infill above the tanks and are listed in Table 2-3 [M. Layton, 2007, Dixon and Phifer, 2007].

**Table 2-3. Properties assumed for degraded SRS tank farm cementitious barriers used in PA analyses [Layton, 2007, Dixon and Phifer, 2007].**

<b>Cementitious Barrier</b>	<b>Ave. Permeability (cm/s)</b>	<b>Ave. Bulk Density (g/cm<sup>3</sup>)</b>	<b>Ave. Water Exchangeable Porosity (fraction)</b>
<b>Degraded Cementitious Barrier (Vault Concrete and Fill grouts)</b>	3.60E-06	1.81	0.266

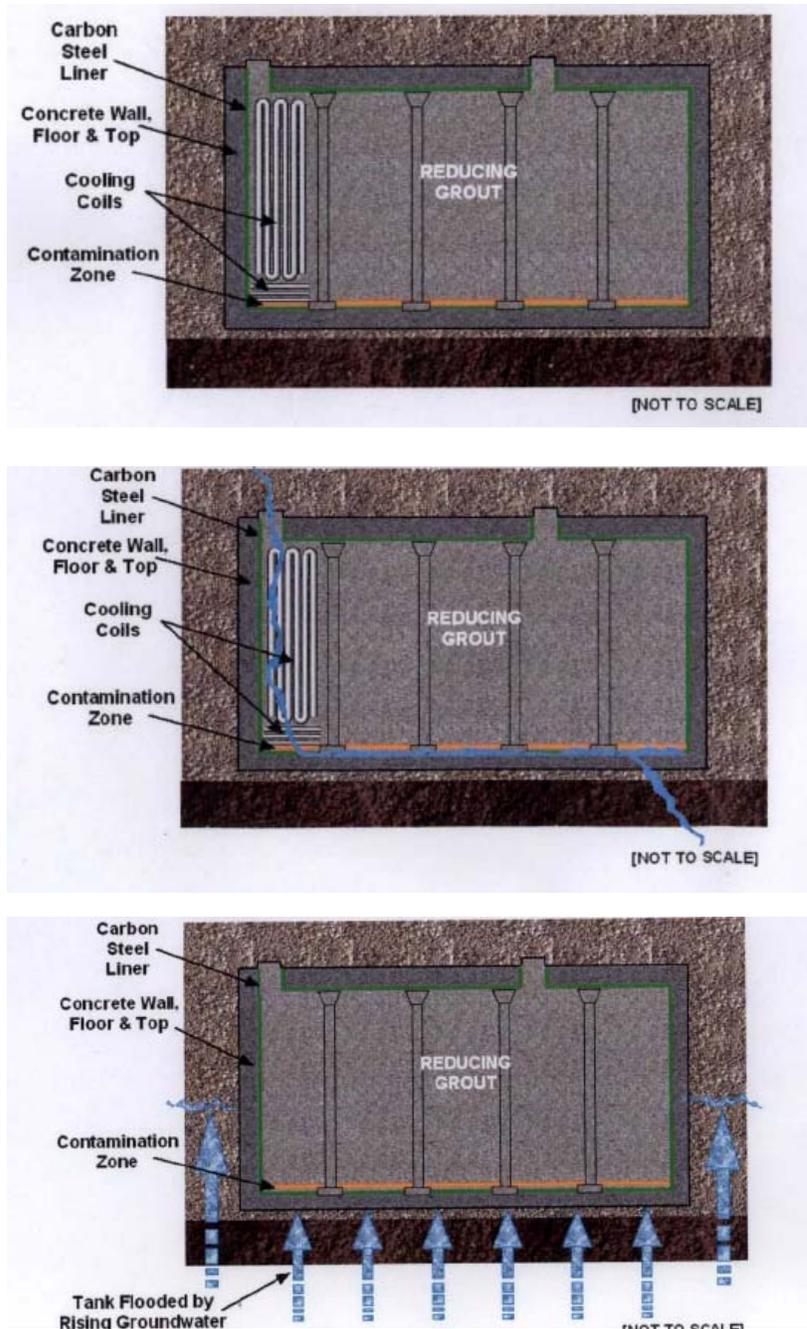


Figure 2-3. Examples for degradation scenarios for closed tanks [K. Rosenberger and T. Robinson, 2007].

### 2.3 Background: Chemical Degradation Mechanisms

Chemical degradation mechanisms discussed in this report include: acid attack (decalcification), carbonation, sulfate attack, alkali aggregate reaction, and reinforcing steel corrosion. These processes result in an increase in porosity and cracking which in turn result in an increase in the advective and diffusive transport of moisture and dissolved chemical species. Cracking associated with wet-dry cycling and freeze thaw cycling was not discussed because the cementitious barriers in the H-Area Tank Farm closure concept will be located in the sub surface environment and will not be subjected to these conditions.

Descriptions of chemical degradation mechanism and approaches to modeling chemical degradation processes are provided in the F-Area Tank Farm report on chemical degradation of cementitious barriers [Langton, 2007] and also in a summary report prepared by the DOE sponsored Cementitious Barriers Partnership Project [CBP, 2009].

Structural degradation (cracking) in response to thermo mechanical forces was not considered in this analysis. However the HTF PA analysis does include fast pathways [Rosenberger, 2010]. The response of degraded material to mechanical forces is also not considered in this report.<sup>3</sup>

Cementitious barriers used for LLW isolation have additional chemical durability requirements involving pH and Eh of the barrier system (CO<sub>2</sub> and O<sub>2</sub>, respectively). The effects of chemical reactions which result in changes in oxidation state and alkalinity on contaminant leaching are described elsewhere [Kaplan, 2006, Kaplan and Coates, 2007, Kaplan et al, 2008, and Denham, 2007]

### 2.4 Background: H-Area Tank Farm Groundwater Analyses

H-Area Tank Farm well water data from 1990 to 2009 was obtained from the SRS Environmental Restoration Data Management System (ERDMS) data base [ERDMS, 2010]. The wells were screened over 20 ft intervals. The shallowest top screen depth was 20 feet, the deepest was 58 feet. The highest Mg<sup>2+</sup> concentration reported was 2.4 mg/L in well HTF15 screened between 40 and 60 feet.

The highest concentration of SO<sub>4</sub><sup>2-</sup> in HTF well water was 52 mg/L for a sample collected from well HTF 34 screened between 60 and 80 feet. HRT wells 7, 14, 19, 22, and 23 had elevated SO<sub>4</sub><sup>2-</sup> concentrations between 3.4 and 13.2 mg/L. The water sample collected from HTF well 27 had a concentration of 33 mg/L.

Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations of 2.4 and 52 mg/L, respectively, were assumed in the sulfate degradation calculations in Section 3 of this report.

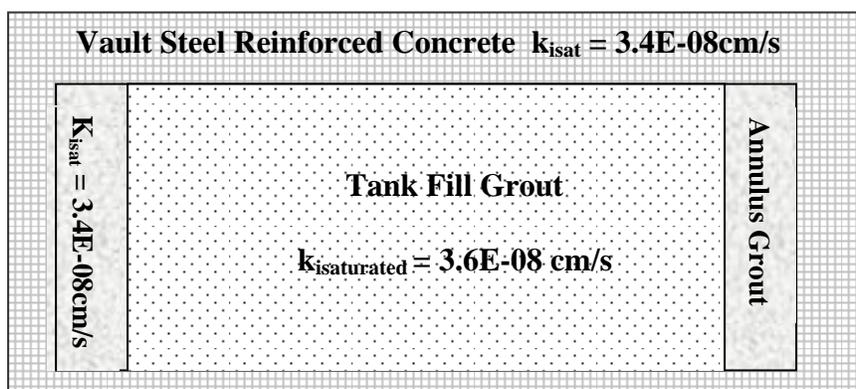
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<sup>3</sup> It is assumed that the response of a degraded structure to overload, creep, and/or seismic events will be more severe than that of an intact structure.

### 3.0 MODELS and RESULTS

#### 3.1 Chemical Degradation Model for H-Area Tank Farm Cementitious Barriers

The cementitious barriers identified in the HTF closure concept are either reinforced concrete (tank vault and base mat) or non reinforced grout (annulus and tank fill grouts). A schematic drawing of the HTF cementitious barriers is provided in Figure 3-1. The hydraulic conductivities of the initial state (not degraded) material were obtained from a concrete sample collected from a slab constructed in 1978 that was used as a surrogate for the vault and base mat concrete and a laboratory prepared sample of reducing grout that is in the current specification for closing the HTF tanks. The saturated hydraulic conductivities of the concrete barriers after degradation by the various mechanisms were estimated. In some cases, the saturated hydraulic conductivity was unaffected by the chemical changes. In other cases in which the chemical changes resulted in the formation of expansive phases, the saturated hydraulic conductivity was assumed to increase due to cracking. In this analysis no credit was given to the metal tank or the metal secondary liner.



**Figure 3-1. Intact SRS H-Area Tank Farm cementitious barriers (not to scale).**

This report is limited to a discussion of chemical degradation processes that are known to affect the physical durability which is defined as changes in the microstructure and crack network. Structural degradation (cracking) in response to thermo mechanical forces was not considered in this analysis. However the HTF PA analysis does include fast pathways [Rosenberger, 2010]. Evolution of the stabilization chemistry (pH and Eh) of the vault concrete and the fill are also discussed elsewhere [Kaplan, 2006 and 2007 (a), (b), (c) respectively]. Assumptions and treatment of macro cracking (fast pathways) and the evolution of the stabilization chemistry are described in detail in the HTF Performance Assessment.

#### 3.2 Sulfate Attack (External)

A linear empirical relationship between the depth of attack and the amount of tricalcium aluminate plus the concentration of  $Mg^{2+}$  and  $SO_4^{2-}$  in the groundwater was used to calculate the depth of penetration of attack by sulfate and magnesium [INEEL Appendix E, 2003].

The depth of penetration was assumed to be the depth of degradation. See Equation 1 derived from empirical relationships [Atkinson and Hearne, 1984 and Walton, 1990] and used in the INEEL PA [INEEL, 2003] and F-Area Tank Farm PA [SRS, 2007]. An explanation of the values used in this calculation is provided in Table 3-1.

The depth of degradation was calculated to be 1.729 E-03 cm/year for the vault concrete which was made with Type I Portland cement (maximum C<sub>3</sub>A content in Type I portland cement =12wt%) and 1.153E-03 cm/year for the annulus and tank fill grouts (maximum C<sub>3</sub>A content in Type I/II cement = 8 wt%).

$$\text{Equation 1. } x = 0.55 C_{C3A} (Mg^{2+} + SO_4^{2-}) t$$

where:

$x$  = depth of concrete degradation (cm)

$C_{C3A}$  = weight percent of tricalcium aluminate in the unhydrated cement

$Mg^{2+}$ ,  $SO_4^{2-}$  = concentrations of these ions in bulk solution (moles/L)

Penetration rates calculated from Equation 1 and inputs in Table 3-1 did not take into consideration sulfate ion binding by the cement matrix (formation of phases that are not expansive). In addition, the tank fill grout contains fly ash (pozzolan) and slag cement, both of which are routinely used to improve resistance to sulfate attack [ACI 201, 2005]. Consequently, from these two aspect (binding capacity and bulk mineralogy), the calculated rates may be somewhat conservative.

**Table 3-1. Values used to calculate rate of sulfate attack and depth of degradation.**

Parameter	SRS Vault Concrete	SRS Annulus and Tank Fill Grouts
<b>Inputs</b>		
C <sub>3</sub> A (wt %)	12*	8*
Mg <sup>2+</sup> (moles/L)	9.88 E-05 (2.4 mg/L)**	9.88 E-05 (2.4 mg/L)**
SO <sub>4</sub> <sup>2-</sup> (moles/L)	5.31 E-04 (52 mg/L)**	5.31 E-04 (52 mg/L)**
<b>Output</b>		
Estimated Penetration Rate (cm/year)	4.157E-03	2.771E-03
Estimated Depth of Degradation after 1000 years	4.2 cm	2.8 cm

\* The maximum tricalcium aluminate content in Type I cement of 12 wt. % was assumed for the vault concrete. The maximum tricalcium aluminate content in Type I/II cement of 8 wt. % was assumed for the annulus and tank fills [ASTM C-150, 2007].

\*\* Representative ground water concentrations are based on SRS well data. [Strom, 1992, SRS ERDMS, 2010].

### 3.3 Sulfate Attack (Internal)

Internal sulfate attack of concrete has not been observed at SRS. Consequently, it was not considered in this analysis of degradation of the vault concrete. However, sulfate is present in the residual waste that may be left in the tank. Reactions between the waste and the fill grout have not been studied. Literature data are insufficient to address the likelihood and consequences of this potential mechanism for degradation. Consequently, at this time there is no basis for determining whether reactions if they were to occur would be detrimental to the integrity of the material in the waste-fill zone.

### 3.4 Alkali-Aggregate Reaction

Alkali-aggregate (silica or carbonate) attack is a coupled diffusion/dissolution/hydration process which occurs when alkalis react with reactive aggregates to produce hygroscopic gel phases. The aggregates used in SRS concrete and planned for use in the tank fill grouts are not highly susceptible to this form of attack. In addition, the concentrations of alkalis in soil pore water and ground water are very low (typical value is less than 1ppm). Consequently this degradation mechanism was not considered for the tank vault concrete and base mat which are in contact with the environment.

Alkalis are present in the residual waste, which may be impossible to completely remove from the tanks. However, because reactions between the washed residual waste and the fill grout have not been studied to date, there is insufficient data to determine what reactions will occur in this unique chemical environment and to determine the consequences of these reactions with respect to degradation.

The chemical processes responsible for alkali aggregate reaction are similar to if not the same as the beneficial reactions between pozzolans and hydrated cement. The difference is the spatial distribution of the reaction products which are dispersed throughout the matrix in the case of beneficial pozzolans versus concentrated at matrix aggregate interfaces in the case of alkali aggregate degradation. Literature data are insufficient to address the likelihood and consequences of this potential mechanism for degradation. Consequently this degradation mechanism was not considered for the tank fill material due to lack of data on the waste-fill reactions and physical consequences of these reactions.

### 3.5 Acid Attack

The depth of penetration from acid attack on the vault concrete and fill was represented by ionic diffusion of calcium ions through aqueous pore water. Diffusion is driven by the concentration gradient between ions in the cementitious material versus ions in the environmental water.

In the penetration rate equation (Equation 2), the concentration of  $\text{Ca}^{2+}$  in the groundwater (soil pore water) was assumed to be zero, which maximizes the concentration gradient and consequently the penetration rate. The values used for the concentrations of  $\text{Ca}^{2+}$  in the cementitious pore water and in the cementitious solids were the same as those used in the

INEEL PA Appendix E and are reasonable for cement paste pore solution and the bulk composition of concrete with inert aggregates such as the quartz sand and granite and schist aggregates used for the SRS tank closures.

The INEEL equation was combined with SRNL diffusion data as presented in Phifer et al., 2006, to generate Equations 3 through 5. Results are provided in Table 3-2.

$$\text{Equation 2.} \quad X = \left( 2D_m \tau \Phi \frac{(C_l - C_{gw})t}{C_s} \right)^{1/2} \quad [\text{INEEL PA Appendix E, 2003}]$$

$$\text{Equation 3.} \quad X = \left( 2 \frac{D_m \Phi}{\tau'} \frac{(C_l - C_{gw})t}{C_s} \right)^{1/2} \quad \text{SRNL diffusion nomenclature [Phifer, et al., 2006]}$$

$$\text{Equation 4.} \quad D_e = \frac{D_m}{\tau'} \quad \text{SRNL diffusion nomenclature [Phifer, et al., 2006]}$$

$$\text{Equation 5.} \quad X = \left( 2D_e \Phi \frac{(C_l - C_{gw})t}{C_s} \right)^{1/2}$$

**where:**

- X = Depth of penetration
- $D_m$  = Molecular diffusion coefficient for  $\text{Ca}^{2+}$  ions
- $D_e$  = Effective diffusion coefficient for  $\text{Ca}^{2+}$  ions, ( $D_e = D_m / \tau'$ )
- $\tau$  = Tortuosity factor ( $\leq 1$ )
- $\tau'$  = SRNL Tortuosity factor ( $1/\tau \geq 1$ )
- $\Phi$  = Porosity (volumetric water content)
- $C_l$  = Calcium ion concentration in pores
- $C_{gw}$  = Calcium ion concentration in groundwater
- $C_s$  = Calcium ion concentration attributed to  $\text{Ca}(\text{OH})_2$  in bulk concrete
- t = Time

**Table 3-2 Values used to calculate rate of acid attack.**

Parameter	SRS Vault Concrete	SRS Annulus and Tank Fill Grouts
<b>Inputs</b>		
$D_e^{(a)}$ (cm <sup>2</sup> /sec)	8E-07	8E-07
$\tau^{(a)}$	Value included in $D_e$	Value included in $D_e$
$\Phi^{(b)}$ Water exchangeable porosity	0.168	0.266
$C_l^{(c)}$ (mol/cm <sup>3</sup> )	2.70E-06	2.70E-06
$C_{gw}^{(d)}$ (mol/cm <sup>3</sup> )	0	0
$C_s^{(e)}$ (mol/cm <sup>3</sup> )	5.4E-04	5.4E-04
<b>Output</b>		
Estimated Penetration Depth at 1000 years	6.5cm Rate is time dependent. This assumes that 100 % of the calcium hydroxide in the penetrated zone is leached.	8.2 cm Rate is time dependent. This assumes that 100 % of the calcium hydroxide in the penetrated zone is leached.

<sup>(a)</sup> The effective diffusivity,  $D_e$ , is documented elsewhere [Dixon and M. Phifer, 2007].  $D_e = D \div$  tortuosity, where  $D = D_{\text{molecular}}$ . Consequently, a separate tortuosity term was not included in the calculation. Diffusion coefficient definitions and terminology are presented elsewhere [Phifer, et al., 2006].

(The value for  $D_e$  is close to the value used for  $D/\Phi$  in the Idaho PA.)

<sup>(b)</sup> Porosity values vault and base mat concrete and for reducing grout were obtained from WSRC-STI-2007-00369 [Dixon, 2007].

<sup>(c)</sup> Pore solution data from Idaho PA

<sup>(d)</sup> Assigned value of 0 which results in the greatest concentration gradient and is the most conservative case. (The concentrations of calcium in HTF well water samples collected between 1990 and 2009 ranged from 0.5 to 54 mg/L.)

<sup>(e)</sup> Estimated value assumed that concrete contains 27.5 kmol/m<sup>3</sup> CaO and the 3000 psi concrete is only 13 % cement and of the cement, only 15% is hydrated to Ca(OH)<sub>2</sub>. The penetration value assumes it is all leachable.

The calculation contains the assumption that the acid component diffuses into the concrete via the aqueous phase and that the dissolution rate of solid phases is instantaneous. An improvement to the current model would include the solubilities of all calcium phases in the cementitious material plus new phases formed as the result of acid leaching.

### 3.6 Carbonation

In the carbonation process, carbon dioxide from the atmosphere or dissolved in contacting water (e.g. rain water or groundwater) reacts with ions dissolved in the cementitious barrier pore solution. For gaseous carbon dioxide, the process consists of several steps that can be summarized as follows: CO<sub>2</sub> gas penetrates the material and partitions in the aqueous phase in the solution as HCO<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> and CO<sub>2(aqueous)</sub> which react with dissolved calcium to precipitate calcite, CaCO<sub>3</sub> as well as other carbonate species. Depletion of calcium in the pore solution leads to dissolution of portlandite in the matrix material and an associated pH drop when the portlandite is depleted. Continued exposure results in incongruent dissolution

(decalcification) of the calcium silicate hydrate phase and another pH drop when this phase is depleted as more calcite other carbonate phases are precipitated.

Although the carbonation process has some effect on the physical properties of the cementitious materials the significant effects are on: 1) contaminant leaching and 2) steel rebar corrosion both of which are a function of pore solution alkalinity (pH). The effect of carbonation on contaminant leaching is addressed elsewhere [Kaplan, 2006].

This process is a degradation mechanism for reinforced concrete. Pore water in equilibrium with calcium hydroxide has a high pH (12.5) which stabilizes the oxide layer surrounding the steel and prevents active corrosion. On the other hand, pure water in equilibrium with calcium carbonate has a pH of 8.4 and fails to stabilize the oxide layer and allows active corrosion.

For non-reinforced cementitious material, carbonation has been reported to seal pores and create a protective layer (rind) on exposed surfaces. Consequently, carbonation was only considered as a degradation mechanism for the steel reinforced cementitious materials, i.e., base mat and concrete vault.

### 3.7 Carbonate-Induced Rebar Corrosion Unsaturated Conditions

The corrosion products formed when rebar oxidizes (corrodes) have a higher volume than the original metal. The resulting expansion can crack the surrounding concrete. In this analysis, the depth of penetration of CO<sub>2</sub> is calculated for unsaturated conditions with 50 percent of the pore volume filled with air. The carbonation depth was assumed to be equal to the depth to which rebar and steel in the structure is corroded (i.e., assumed to correspond to decrease in member thickness and loss of mechanical properties attributed to the reinforced concrete to the affected depth). This case applies to a scenario where the concrete is above the water table.

The depth of penetration of CO<sub>2</sub> into reinforced concrete is a gaseous diffusion controlled process. The external source of the CO<sub>2</sub> is the atmosphere (0.03 volume %). (The small amount of CO<sub>2</sub> dissolved in water in equilibrium with the atmosphere was ignored). This assumption maximizes the concentration gradient which in turn maximizes the depth of penetration.

Input values for Equations 6 and 7 were obtained from several sources. The binary diffusion coefficient for CO<sub>2</sub> in air was 9.60E-04 m<sup>2</sup>/min (505 m<sup>2</sup>/y) [Lide, 1995].<sup>4</sup> The bulk concentration of calcium hydroxide in hardened concrete was estimated to be 5.4E-01 kmol/m<sup>3</sup>. This value assumes that concrete contains 27.5 kmol/m<sup>3</sup> CaO. (The 3000 psi concrete is only 13 % cement and only 15% of the hydrated cement results in Ca(OH)<sub>2</sub>.) The penetration value assumes all of the Ca(OH)<sub>2</sub> is all leachable.<sup>5</sup>

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<sup>4</sup> This value is different than the value stated in the INEEL PA of 1.55 E-04 m<sup>2</sup>/y.

<sup>5</sup> This value is lower than that assumed in the Idaho PA and results in a greater depth of penetration, all other values being equal. Neither of these assumptions take into account the complex reaction fronts observed in actual carbonated material.

Tortuosity factors of 9.2E-03 and 1.7E-02 were used for vault concrete and cementitious tank fill grout, respectively. These values are calculated from the Millington-Quirk model, Equation 6 [Jin, 1996]. The difference in the tortuosity factor for the vault concrete and fill material is due to the difference in the porosities measured for surrogate tank vault concrete and reducing grout fill, 16.8 and 26.6 volume percent, respectively.

**Equation 6.**  $\tau = a^{10/3} / \Phi^2$

where:

$\tau$  = tortuosity

$a$  = volumetric air content assuming 50 % saturation (This allows for gas phase transport in the cementitious material.)

$\Phi$  = cementitious barrier porosity

**Equation 7**  $X = \left( 2D_{air} \tau \Phi_{air} \frac{(C_{atm})t}{C_s} \right)^{1/2}$

where:

$X$  = Depth of penetration

$D_{air}$  = Binary diffusion coefficient for air/CO<sub>2</sub>

$\tau$  = Tortuosity factor of gas in the concrete

$\Phi_{air}$  = Volumetric air content in concrete assuming 50 % saturation

$C_{atm}$  = Concentration of total inorganic carbon in air (present as CO<sub>2</sub>)

$C_s$  = Bulk Concentration of Ca(OH)<sub>2</sub> in concrete

$t$  = Time

**Table 3-3. Values used to calculate rate of carbonation for unsaturated conditions for tanks in the vadose zone.**

Parameter	SRS Vault Concrete	SRS Annulus and Tank Fill Grouts
<b>Inputs</b>		
$D_{\text{air}}^{(a)}$ (m <sup>2</sup> /yr)	5.05E+02	5.05E+02
$\tau^{(b, c)}$	9.2E-03	1.7E-02
$\Phi_{\text{air}}^{(c)}$	0.084	0.133
$C_{\text{atm}}^{(d)}$ (moles/cm <sup>3</sup> )	3.00E-05	3.00E-05
$C_s^{(e)}$ (moles/cm <sup>3</sup> )	5.4E-01	5.4E-01
<b>Output</b>		
Estimated Penetration Depth at 1000 years	20.8 cm Rate is time dependent This assumes that 100 % of the calcium hydroxide in the penetration zone is carbonated	35.6 cm Rate is time dependent. This assumes that 100 % of the calcium hydroxide in the penetration zone is carbonated

(a) Lide, 1995. The value used in this calculation is different than the value reported in the INEEL PA Appendix E which was 1.55E-04 m<sup>2</sup>/y but using the CRC value produces similar results as those presented in the Appendix E Figure E-4.

(b) Millington-Quirk Formula used to calculate tortuosity factor =  $a^{10/3}/\Phi^2$  where "a" equals the volumetric air content [Jin, 1996].

(c) WSRC-STI-2007-00369 for air volume plus the assumption of 50 % saturation from INEEL Appendix E

(d) INEEL used density of air 1.2 kg/m<sup>3</sup>.

(e) Assumed that 10 % of the calcium in concrete is CaOH<sub>2</sub> which is approximately 0.15g/cc of cementitious material.

### 3.8 Carbonate-Induced Rebar Corrosion Saturated Conditions

In this analysis, the depth of penetration of CO<sub>2</sub> is calculated for saturated conditions with 100 percent of the pore volume filled with water. The carbonation depth was assumed to be equal to the depth to which rebar and steel in the structure was corroded. This case applies to a scenario where the concrete is in the water table.

Input values for Equation 8 were obtained from several sources. The diffusion coefficient for carbonate ion  $\frac{1}{2} \text{CO}_3^{2-}$  in water was 0.923E-5 cm<sup>2</sup>/s (29.37 cm<sup>2</sup>/y) [Lide, 1995].<sup>6</sup> The bulk concentration of calcium hydroxide in hardened concrete was estimated to be 5.4E-01 kmol/m<sup>3</sup>. The estimated value assumes that concrete contains 27.5 kmol/m<sup>3</sup> CaO and the 3000 psi concrete is only 13 % cement and of the cement, only 15% is hydrated to Ca(OH)<sub>2</sub>. The penetration value assumes it can all be carbonated.<sup>7</sup>

<sup>6</sup> This value is different than the value stated in the INEEL PA of 1.55 E-04 m<sup>2</sup>/y.

<sup>7</sup> This value is lower than that assumed in the Idaho PA and results in a greater depth of penetration, all other values being equal. Neither of these assumptions takes into account the complex reaction fronts observed in actual carbonated material.

$$\text{Equation 8.} \quad X = \left( 2D_e \Phi \frac{(C_l - C_{gw})t}{C_s} \right)^{1/2}$$

where:

- X = Depth of penetration  
 $D_e$  = Effective diffusion coefficient for  $\text{Ca}^{2+}$  ions, ( $D_e = D_m / \tau'$ )  
 $\Phi$  = Porosity (volumetric water content)  
 $C_l$  = Carbonate ion concentration in pores  
 $C_{gw}$  = Carbonate ion concentration in groundwater  
 $C_s$  = Calcium ion concentration attributed to  $\text{Ca}(\text{OH})_2$  in bulk concrete  
t = Time

**Table 3-4. Values used to calculate rate of carbonation under saturated conditions for tanks in the water table.**

Parameter	SRS Vault Concrete	SRS Annulus and Tank Fill Grouts
<b>Inputs</b>		
$D_m \frac{1}{2} \text{CO}_3^{2- (a)}$ (cm <sup>2</sup> /sec) (cm <sup>2</sup> /y)	0.923E-5 cm <sup>2</sup> /s 29.37 cm <sup>2</sup> /y	0.923E-5 cm <sup>2</sup> /s 29.37 cm <sup>2</sup> /y
$D_e \frac{1}{2} \text{CO}_3^{2- (b)}$ (cm <sup>2</sup> /sec) (cm <sup>2</sup> /y)	9.3E-07 29.34	9.3E-07 29.34
$\tau^{(a)}$	Value included in $D_e$	Value included in $D_e$
$\Phi^{(c)}$ Water exchangeable porosity	0.168	0.266
$C_l^{(d)}$ (mol/cm <sup>3</sup> )	0	0
$C_{gw}^{(e)}$ (mol/cm <sup>3</sup> )	3.57E-08	3.57E-08
$C_s^{(f)}$ (mol/cm <sup>3</sup> )	5.4E-04	5.4E-04
<b>Output</b>		
Estimated Penetration Depth at 1000 years	0.26 cm Rate is time dependent. This assumes that 100 % of the calcium hydroxide in the penetrated zone is carbonated.	0.32 cm Rate is time dependent. This assumes that 100 % of the calcium hydroxide in the penetrated zone is carbonated.

<sup>(a)</sup>  $D_m$  or  $D_{\text{free}}$  is the diffusion of the ionic species at infinite dilution in water [Lide, 1995].

<sup>(b)</sup> The effective diffusivity,  $D_e$ , is documented elsewhere [Dixon and M. Phifer, 2007].  $D_e = D \div \text{tortuosity}$ , where  $D = D_{\text{molecular}}$ . Consequently, a separate tortuosity term was not included in the calculation. Diffusion coefficient definitions and terminology are presented elsewhere [Phifer, et al., 2006]. (The value for  $D_e$  is close to the value used for  $D/\Phi$  in the Idaho PA.)

<sup>(c)</sup> Porosity values vault and base mat concrete and for reducing grout were obtained from WSRC-STI-2007-00369 [Dixon, 2007].

<sup>(d)</sup> Pore solution data from Idaho PA

<sup>(e)</sup> Carbonate data were not available for HTF well water samples collected between 1990 and 2009. Given the pH of 5.5, the amount of carbonate in the well water was assumed to be less than 1 mg/L. As a conservative case, 1 mg/L was used in the calculations.)

<sup>(f)</sup> Estimated value assumed that concrete contains 27.5 kmol/m<sup>3</sup> CaO and the 3000 psi concrete is only 13 % cement and of the cement, only 15% is hydrated to  $\text{Ca}(\text{OH})_2$ . The penetration value assumes it is all leachable.

### **3.9 Chloride-Induced Rebar Corrosion**

Chloride-induced rebar corrosion was not considered in this analysis because the concentration of chloride ions in SRS ground water and soil pore water is low. The highest chloride concentration in the HTF well water samples collected between 1990 and 2009 was 11 mg/L [ERDMS, 2010]. Chloride in the cement used to construct the tank vaults is of interest, but data are not available. Samples of old 3000 psi concrete were collected, tested and used as surrogates for the vault and base mat concrete. This material was not analyzed for chloride. However, inspection of the rebar in this concrete showed no sign of corrosion.

**Table 3-5. Summary of chemical attack mechanisms relevant to tank concrete and fill.**

<b>Attack</b>	<b>Process</b>	<b>Control</b>	<b>Comments</b>	<b>Expression and Effect on Permeability</b>
Acid Attack (Leaching)	Coupled dissolution/diffusion/leaching	Acid concentration  Ionic Diffusion through water	Source of acid is infiltrating rain water. Potential acids are from atmospheric gas (CO <sub>2</sub> , NO <sub>x</sub> , SO <sub>x</sub> ) or Organic acids from overlying soil	Vault Concrete (Reinforced). Increase in permeability, porosity and strength loss.  Fill. Increased porosity and change in stabilization chemistry/mineralogy of the system from high pH of 13 to 8.5  Progression of reaction front inward from surfaces and fracture surfaces. Rate depends on acid concentration
Carbonation	Coupled diffusion / dissolution / precipitation process	Carbonate or CO <sub>2</sub>  Ionic Diffusion through water for 100 % Saturated Condition  Gas Diffusion for Unsaturated Grout	Air is the source of CO <sub>2</sub> .  Residual waste is a source of carbonate.	Vault Concrete: Increase in permeability and strength loss.  Fill: No or only slight change +/- in permeability due to CaCO <sub>3</sub> precipitation in pores and on surfaces  Progression of reaction front inward from surfaces and fracture surfaces. Rate depends gas or aqueous diffusion Gas phase transport is ~1000X faster than diffusion through water.  The carbonate front penetration depth for the input data used in this report was about 80X less for saturated vs unsaturated conditions with 50 % of the pore volume filled with air
Sulfate Attack	Coupled diffusion / dissolution / precipitation process	Sulfate (Internal and External)  Ionic Diffusion through water	Soil does not contain sulfate  Residual waste is a source of sulfate	Vault Concrete. NA Negligible soluble sulfate in soil  Fill: Calcium aluminosulfate-carbonate phases may form at the waste zone-fill contact at the bottom of the closed tanks. Data is required to evaluate consequences.
Alkali Aggregate Reaction	Coupled diffusion / dissolution / hydration process	Na <sup>+</sup> , reactive aggregate, water	Aggregates have low reactivity	Vault Concrete. NA Negligible source of alkali in soil  Fill: Potential reactions at the waste zone-fill contact at the bottom of the closed tanks. Data is required to evaluate consequences.
Reinforcing Steel Corrosion	Coupled diffusion / dissolution / precipitation process	Carbonation Corrodents (Cl <sup>-</sup> ) Oxygen, Water  Ionic Diffusion through water (CO <sub>2</sub> can also diffuse through air)	Soil does not contain soluble corrodents eg. Cl <sup>-</sup>	Vault Concrete. Cracking due to expansion which results in strength loss and increased hydraulic conductivity. Loss of passivation by carbonation, expansive from iron hydration products  Fill: Not Applicable

## 4.0 CONCLUSIONS

The SRS disposal environment is not aggressive with respect to chemical degradation of the reinforced concrete vaults and the tank fill grout material. Consequently, the degradation due to chemical processes will progress at a very slow rate.

The chemical degradation mechanisms evaluated in this study were: sulfate attack (internal and external), acid leaching (decalcification), carbonation, alkali aggregate attack, and cracking from rebar corrosion (carbonate-induced and chloride-induced corrosion). Two cementitious barrier materials were evaluated:

1. Surrogate Vault Concrete. 1978 vintage 3000 psi concrete cored from a slab on grade in P-Area.
2. Representative Tank Fill Grout. Reducing Grout prepared according to the mix in SRS Specification C-SPP-F-00047 Rev. 2.

For unsaturated vault concrete and unsaturated tank fill grout, carbonation was identified as the most aggressive chemical degradation mechanism. This case is conservative for concrete and tank fill grout buried in unsaturated soil and for tanks exposed to saturated and unsaturated conditions due to a fluctuating water table. For material with the properties of the surrogate vault concrete, the thickness of the carbonated zone was calculated to be 20.8 cm after 1000 years of direct contact with atmospheric air in the soil pores. For material with the properties of the tank fill reducing grout, the carbonation depth was calculated to be 35.6 cm after 1000 years for the same condition.

For saturated vault concrete and tank fill grout, the depth of the carbonation front was about 80 times less than for the unsaturated cases (0.26 and 0.32 cm at 1000 years) because the rate of carbonate diffusion through pore solution is several orders of magnitude slower than through pore air.

For saturated vault concrete and tank fill grout, calcium leaching was the most aggressive chemical degradation mechanism for tanks in the water table. The calcium leaching front, defined as loss of 100 % of the  $\text{Ca}(\text{OH})_2$  in the concrete matrix was calculated to affect the vault concrete and tank fill grout to a depth of 6.5 cm and 8.2 cm at 1000 years of exposure to groundwater.

In this analysis, the depths of penetration of the chemical corrodents were assumed to be equivalent to the depth of degradation. Diffusion transport of the corrodent species through the pores in the cementitious material was assumed. Equations for single species diffusion were used. This is a very simplistic approach. A more sophisticated approach requires additional material characterization data and advanced multi ionic transport codes specifically designed for concrete service life predictions.<sup>8</sup>

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<sup>8</sup> Advanced service life prediction models for concrete structures were not used for this analysis. These models require concrete-specific properties, such as, moisture, ionic, and gas diffusion coefficients, pore solution chemistry, porosity, pore size distribution, degree of saturation, cement chemistry and mineralogy, and thickness of rebar cover. They also required environment-specific characterization data.

Each degradation mechanism was evaluated independent of the others. Coupled effects and the potential for non deleterious binding of the chemical species within the cement matrix phases were not considered. Results are summarized in Table 4-1. Each material was assumed to be in direct contact with the environment supplying the corrosive chemicals. However, in the H-Area Tank Farm PA model, the annulus grout will not begin carbonating until the vault concrete is degraded, because the geometry of the engineered barriers is one of contacting concentric cylinders. (The roof and base mat thicknesses must also be taken into account as well as the actual configuration which includes metal liners and tanks.)

The effect of chemical degradation on permeability of each of the three cementitious barriers in the HTF Closure concept depends on how the attack is expressed. The chemical degradation mechanisms and consequences of these processes are summarized as follows:

- The saturated permeability of the initial vault concrete was estimated to be  $3.4\text{E-}08$  cm/s. This value was obtained from measurements on 1978 vintage 3000 psi reinforced concrete which was used as a surrogate. Carbonation will result in loss of passivation and subsequent corrosion of rebar. The rebar corrosion products are expansive and will cause cracking. The time of cracking will be offset from the time the carbonation front reaches the rebar because sufficient corrosion products must be formed to exert force on the concrete. In this analysis, depth of carbonation is a time dependent function. In 1000 years it is estimated to penetrate the vault concrete 21 cm.
  - The permeability for cracked concrete resulting from rebar corrosion due to carbonation was estimated to be 100 times higher than the initial permeability.<sup>9</sup>
- The saturated permeability of the annulus concrete was estimated to be  $3.6\text{E-}08$  cm/s based on measurements of samples of the reducing grout prepared in the laboratory. The overall effect of carbonation will be precipitation of calcite,  $\text{CaCO}_3$  which seals surfaces and plugs pores. Consequently, with no potential for rebar corrosion, carbonation will have no or very little effect on the annulus grout.
  - The permeability will remain at about  $3.6\text{E-}08$  cm/s. The same holds for tank fill grout for tanks with no cooling coils.
- Tanks that contain cooling coils will experience carbonation after the tank has corroded or after fast path ways develop. The rate of carbonation will be slightly faster than that estimated for the vault concrete because the porosity of the grout is slightly higher. The depth of penetration after 1000 years exposure to the atmosphere was 36 cm.

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An example of software for service life prediction is the STADIUM code which is being developed by SIMCO Technologies, Inc.

<sup>9</sup> The saturated hydraulic conductivity of degraded concrete has not been measured. Based on discussions between C. Langton and G. Flach a value about the same as that of compacted soil backfill, i.e., about 1 to  $5\text{E-}06$  cm/s was assumed to be reasonable. [Flach, 2007].

- The saturated permeability of concrete and tank fill grout subjected to severe decalcification is expected to increase by several orders of magnitude based on literature data for decalcification of tricalcium silicate paste [Henocq, 2009].

This evaluation was limited to chemical degradation mechanisms which are known to affect the microstructure, mechanical and engineering properties of materials containing portland cement. It does not address degradation caused by mechanical forces or evolution of the stabilization chemistry (pH and Eh) of the material.

**Table 4-1. Summary of depth of penetration (thickness of affected material) for SRS tank closure cementitious barriers.**

Mechanism	Penetration Depth at 1,000 years (cm)	
	Vault Concrete Material	Tank Fill Grout Material
<b>Sulfate Attack (External)</b>	1.7	1.2
<b>Sulfate Attack (Internal)</b>	Not Applicable Basis: Lack of this type of degradation in SRS concrete since early 1950s.	Not Estimated Basis: Sulfates are present in the residual tank waste but data on tank waste-grout chemistry and physical consequences are not available.
<b>Alkali Aggregate Attack</b>	Not Applicable Basis: Low alkali content (~5mg/L) of soil and groundwater and use of resistant aggregate is SRS concretes and grouts.	Not Estimated Basis: Alkalis are present in the residual tank waste but data on tank waste-grout chemistry and physical consequences are not available.
<b>Acid Attack (Calcium Leaching)</b>	6.5 Basis: Diffusion controlled by concentration gradient. $\text{Ca}^{2+}$ in ground water assumed to be 0 mg/L which is less than typical values of 5 mg/L. Ca leaching was assumed to preferentially dissolve $\text{Ca}(\text{OH})_2$ . $\text{Ca}(\text{OH})_2$ in the vault concrete was estimated at $5.4\text{E}-04 \text{ mol/cm}^3$ . Porosity of vault concrete is 16.8 vol. percent	8.2 Basis: Same but porosity of Reducing Grout was 26.6 vol. %
<b>Carbonation Unsaturated Conditions</b>	20.8 Basis: Diffusion controlled by concentration gradient. Atmosphere is the source of $\text{CO}_2$ (0.03 vol. % $\text{CO}_2$ ). One mole of C from $\text{CO}_2$ reacts with 1 mole of $\text{Ca}(\text{OH})_2$ to form $\text{CaCO}_3$ . $\text{Ca}(\text{OH})_2$ in the vault concrete was estimated at $5.4\text{E}-01 \text{ kmol/m}^3$ . Porosity of vault concrete is 16.8 vol. percent.	35.6 Basis: Same but porosity of Reducing Grout was 26.6 vol. %
<b>Carbonation Saturated Conditions</b>	0.26	0.32
<b>Concrete Cracking due to Rebar Corrosion</b>		
<b>Carbonate-Induced Corrosion Unsaturated</b>	20.8 Basis: The depth of penetration of the carbonation front can be used as a conservative estimate for depth of deterioration (cracking) due to rebar corrosion since carbonation lowers the alkalinity of the pore solution and reduces the stability of the corrosion resistant oxide film on the steel.	Not Estimated Basis: The annulus and tank fill grouts do not contain rebar. Depth of penetration of carbonate does not correlate with active corrosion of steel. Additional chemical conditions are required for steel corrosion. These conditions are discussed elsewhere [Subramanian, 2007]. Rates and consequences of steel tank, liner and cooling coil corrosion were not evaluated.
<b>Carbonate-Induced Corrosion Saturated</b>	0.26	Same as above
<b>Chloride-Induced Corrosion</b>	Not Estimated Basis: The chloride concentration in the groundwater and soil pore water is very low (~1 mg/L). The chloride binding capacity and the initial chloride content in the concrete have not been determined.	Not Estimated Basis: Same as for carbonate-induced corrosion and for chloride induced-corrosion of the vault concrete.

## 5.0 RECOMMENDATIONS

As a result of this effort, several areas for further study were identified and are listed below:

- Service Life predictions for the surrogate vault concrete and representative tank fill grout should be determined using multi ionic models such as STADIUM®, developed by SIMCO Technologies, Inc. Predictions will be limited to common service lives of concrete structures of 50 to 100 years but this is useful information for extrapolation to longer times required for performance assessment of low level waste disposal facilities.
- Diffusion data, solubility data and pore solution chemistry data are required for the advanced multi ionic transport models used to predict service life. These data should be obtained for surrogate and representative materials.
- Prediction of the pore solution chemistry over long times and the effect of this chemical environment on rebar and tank steel corrosion should be investigated.
- The unsaturated soil-cementitious barrier interface should be characterized with respect to:
  - Development of chemical and microstructural zones in both media and
  - Moisture and gas transport across the interface.Laboratory testing and instrumented test beds are recommended to obtain the relevant parameters and relationships.
- The degree of saturation of the cementitious barriers in the disposal environment should be considered as a function of time and degradation scenarios. This information should be factored into transport processes and into sensitivity or uncertainty analyses.
- Fracture transport should be evaluated with respect to chemical degradation processes and also the chemical environment required for stabilization.
- Residual waste-cementitious material interactions should be investigated with respect to formation of new phases, potential for expansive reactions and consequences of these reactions, and leachability of the contaminants. The physical properties of the waste-cement material zone should be characterized.
- Permeabilities of samples of concrete and tank fill grout degraded by carbonation and the other chemical mechanisms described in this report should be measured. The current surrogate material is a sandy clay soil and the permeability of this soil is assumed to approximate the permeability of degraded concrete.
  - Consider computer simulations for the evolution of the microstructure and macrostructure of the concrete in response to the various forms of degradation.

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