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Scientific Analysis/Calculation Administrative Change Notice

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Complete only applicable items.

1. Document Number:	ANL-EBS-MD-000074	**2. Revision**:	01/AD 01	**3. ACN**:	02
4. Title:	Analysis of Dust Deliquescence for FEP Screening				
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6. Approvals:		
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7. Affected Pages	8. Description of Change:
5-1, 6-4	CR 11180 identified the need to reference the control of dust from cement sources in the ventilation.
6-48	Deleted the description of Waste Package Localized Corrosion model implementation that is no longer correct. Related to CR 10670.
8-4	Included the new reference to BSC 2008, used on p. 5-1 and 6-4.
1-2, 6-19, and 7-1 (AD 01)	Potential for corrosive deliquescent brines considered as "not expected" rather than "unlikely".
4-1 (AD 01)	Clarified usage of Pitzer database and IDPS model per DOE comments.
6-1 (AD 01)	Deleted references to Figure 6.1-1B since it is not in the current report.
6-2 (AD 01)	Second reference to Table 4-2[a] corrected to refer to Table 4-3[a] per DOE comment. Added background information to clarify why removal of ammonium salts is justified for postclosure system.
6-3 to 6-5 (AD 01)	Provided further explanations to explain that convergence problems do not affect the quality of the subsequent postclosure dust brine analyses per DOE comment. Brief clarification (p. 6-5) on Pitzer database usage and link back to information in 4.1.1[a] per DOE comment.
6-19 (AD 01)	Clarified conclusion to 6.3.3[a].

5. ASSUMPTIONS

5.1 UNIFORMITY OF DUST COMPOSITION

It is necessary to assume that the dust is compositionally homogeneous, regardless of particle size. Although some data exist to indicate that the smaller size fraction holds more soluble salt content, the lack of size-specific chemical data precludes utilizing this information. This assumption is conservative because salts in the small size fraction (on the order of 1 µm and less) would be transported through the drift without depositing on the waste packages (see Table 6.4-2); thus, assuming compositional homogeneity maximizes the salt load deposited.

5.2 RELEVANT SOURCES OF DUST

This report assumes that the main source of dust that is of concern to the waste package corrosion performance comes from atmospheric dust brought in during the preclosure ventilation period. Dust generated by the comminution of the host rock (so called rock flower) during excavation, repository operation or closure, or seismic events is also considered. Concrete liners within the ventilation flow path are not considered a source of dust because controls will limit the occurrence of cementitious dust so its effects are insignificant (BSC 2008 [DIRS 183627], Table 1, parameter 02-03). This assumption and its implications with respect to brines formed by dust deliquescence is applied throughout this report and discussed further in Section 6.1.1.

deliquescence documented in *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier* (BSC 2004 [DIRS 161237]) and *Engineered Barrier System: Physical and Chemical Environment* (BSC 2004 [DIRS 169860], Section 6.10). That evaluation is based on incomplete chemical analyses of the dust leachates; more recent experimental work has identified ammonium as a significant component of the dusts, and the calculations presented in the reports cited above do not include ammonium.

It has also been recognized that samples of tunnel dust are probably not representative of dust that will be deposited during the ventilation period. The emplacement ventilation will flow from areas with concrete liners, however controls will keep cement dust generation to a minimum (BSC 2008 [DIRS 183627], Table 1, parameter 02-03), and therefore removes that source from further consideration (Assumption 5.2). The existing tunnel dust samples consist mostly of crushed rhyolite, generated by excavation and other support activities underground, and contain only a small amount (typically < 0.5% by weight; see BSC 2004 [DIRS 161237], Section 6.7.2.10, p. 6-65) of total soluble salts. However, dust deposited during ventilation will probably be more similar to atmospheric dusts and aerosols, with a greater soluble salt content (10 to 15%; see Table 4.1-9) and different composition. The composition of potential atmospheric dusts is evaluated using measured rain-out data collected by the National Atmospheric Deposition Program at a Nevada sampling site (Section 4.1.3), which reflects contributions of both atmospheric aerosols and windblown dust in the Yucca Mountain area.

6.1.2 Analyses Based on Tunnel Dust Samples

In this section, the deliquescence behavior of dust on the waste package, as predicted by thermodynamic analysis and experimental studies of tunnel dusts and dust leachates, is presented, and the potential effects of ammonium in the dust are evaluated. Although the tunnel dusts are probably not representative of repository dust composition, as stated above, the following subsections show that the effects of ammonium salts are limited because they decompose. The same salt assemblages analyzed in the reports cited above (BSC 2004 [DIRS 161237]; BSC 2004 [DIRS 169860]) can then be used to represent multiple-salt deliquescence at elevated temperature.

6.1.2.1 Thermodynamic Analysis Results

In *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier* (BSC 2004 [DIRS 161237], Table 6.7-11) three major assemblages of deliquescent salts are identified as controlling the deliquescence RH for tunnel dust, based on analysis of dust leachates (not including NH_4). These salt assemblages were not directly observed in the dusts, but are inferred from a normative approach verified by simulation of evaporative evolution, and the analysis is representative of the soluble dust compositions with the exception of ammonia (see discussion in Section 6.1). The three assemblages are:

- Assemblage A: $NaCl–KNO_3$
- Assemblage B: $NaCl–KNO_3–NaNO_3$
- Assemblage C: $NaCl–KNO_3–NaNO_3–Ca(NO_3)_2$.

Simulations using the EQ3/6 V8.0 software code and Pitzer parameters developed for the in-drift precipitates/salts (IDPS) model (BSC 2004 [DIRS 169863]; as implemented in *data0.ypf.R0* from DTN: SN0302T0510102.002 [DIRS 162572]) predicted that maximum temperatures of deliquescence at 0.90 bars for the first two assemblages would be 126.1°C and 135.8°C, at its measured boiling point of nominally 112°C to 113°C, or where the relative humidity is nominally 70 to 75%.

Under conditions of low relative humidity, carbonate-type brines are rich in Cl^--NO_3^- with low carbonate content. The SSW test solution has characteristics of this type of brine.

Sulfate Brines—These have near-neutral pH and no significant carbonate or calcium content. Calcium precipitates as carbonates and possibly sulfates. In addition, brines typically have only a small amount of magnesium, though some surface brines have been observed to have high magnesium (Drever 1997 [DIRS 147480], Table 15-1, p. 333, brines 1 through 3). The dominant cation is typically Na^+. In brines formed by dust deliquescence, K^+ may be more significant than Na^+, and Mg^{2+} is predicted to be insignificant. As shown in Table 6.3-3, the sulfate-type brines are the most common type predicted to form by dust deliquescence.

As with the other brine types, the dominant ions in sulfate brines vary with relative humidity. At low relative humidity, the solutions will be dominated by Cl^- and NO_3^- anions, with NO_3^- ions dominating at the lowest relative humidity. At moderate relative humidity (>70%), Cl^- ions may dominate. However, unlike the carbonate brines, these brines are expected to have near-neutral to slightly acidic pH because of the lack of a carbonate component. Significant amounts of dissolved carbonate and sulfate are not predicted until the relative humidity is greater than 85%.

The corrosion test solutions corresponding to sulfate-type brines include SAW, SSW, and sodium chloride. The SSW has characteristics of water at low relative humidity, where sulfate is not a major brine component. Sodium chloride test solutions simulate the scenario where Cl^- is the dominant anion under moderate relative humidity conditions. The SAW test solutions have characteristics of solutions in equilibrium with nominally 90% relative humidity.

6.3.1.2 Experimental Evaluation of the Effect of Nitrate–Chloride Ratio

Cyclic polarization data were used for developing the localized corrosion initiation model, described in *General Corrosion and Localized Corrosion of the Waste Package Outer Barrier* (BSC 2004 [DIRS 169984]). The experimental conditions considered include electrolyte composition (including chloride and nitrate ion molal concentrations), nitrate–chloride ion ratio, pH, and temperature (BSC 2004 [DIRS 169984], Table 6-8).

Results from tests conducted by the Center for Nuclear Waste Regulatory Analyses (CNWRA) (Cragnolino et al. 2002 [DIRS 173552]) in aqueous environments at exposure temperatures of 95°C corroborate the nitrate inhibition effect, and indicate that a nitrate–chloride ratio of 0.1 is sufficient to inhibit localized corrosion of welded Alloy 22 in 0.5 M NaCl-based solutions.

173944 BSC 2005. *Multiscale Thermohydrologic Model.* ANL-EBS-MD-000049 REV 03. Las Vegas, Nevada: Bechtel SAIC Company.

174269 BSC 2005. *Q-List.* 000-30R-MGR0-00500-000-002. Las Vegas, Nevada: Bechtel SAIC Company. ACC: ENG.20050805.0006.

174995 BSC 2005. *Screening of Features, Events, and Processes in Drip Shield and Waste Package Degradation.* ANL-EBS-PA-000002 REV 05. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20050817.0003.

174965 BSC 2005. *Technical Management Review Board (TMRB) Decision Proposal.* TMRB-2005-047. Las Vegas, Nevada: Bechtel SAIC Company. ACC: MOL.20050809.0101.

183627 BSC 2008. *Postclosure Modeling and Analyses Design Parameters.* TDR-MGR-MD-000037 REV 02. Las Vegas, Nevada: Bechtel SAIC Company.

173255 Byrne, R.H. and Luo, Y.-R. 2000. “Direct Observations of Nonintegral Hydrous Ferric Oxide Solubility Products: $K^*_{S0} = [Fe^{3+}][H^+]^{-2.86}$.” *Geochimica et Cosmochimica Acta, 64,* (11), 1873-1877. New York, New York: Elsevier. TIC: 257121.

168006 Byrne, R.H.; Luo, Y.-R.; and Young, R.W. 2000. “Iron Hydrolysis and Solubility Revisited: Observations and Comments on Iron Hydrolysis Characterizations.” *Marine Chemistry, 70,* (1-3), 23-35. New York, New York: Elsevier. TIC: 255717.

163817 Campbell, A.N. and Smith, N.O. 1951. *The Phase Rule and its Applications.* 9th Edition. New York, New York: Dover Publications. TIC: 254360.

166275 Canori, G.F. and Leitner, M.M. 2003. *Project Requirements Document.* TER-MGR-MD-000001 REV 02. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20031222.0006.

173681 Chaiken, R.F.; Sibbett, D.J.; Sutherland, J.E.; Van De Mark, D.K.; and Wheeler, A. 1962. “Rate of Sublimation of Ammonium Halides.” *The Journal of Chemical Physics, 37,* (10), 2311-2318. College Park, Maryland: American Institute of Physics. ACC: 257269.

173233 Chen, Z. and Sverjensky, D.A. 1991. “Partitioning of F-Cl-OH between Minerals and Hydrothermal Fluids.” *Geochimica et Cosmochimica Acta, 55,* 1837-1848. Elmsford, New York: Pergamon Press. TIC: 257103.

172846 Chow, J.C. 1995. “Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles.” *Journal of Air & Waste Management Association, 45,* (5), 320-382. Pittsburgh, Pennsylvania: Air and Waste Management Association. TIC: 256900.

- CR 7820 identified a software problem with EQ3/6 V. 8.0 (STN: 10813-8.0-00 [DIRS 162228]) that affects output DTN: MO0506SPAEQ36F.002 and Figure 6.3-1 in the parent report; the DTN calculations and figure are updated with acceptable unaffected data in Section 6.3.2[a].
- CR 8391 noted that input DTN: GS050408313000.001 [DIRS 173724], described in Section 4.1.9 and used in calculations in Section 6.1.2.4 of the parent report, has been superseded by the qualified DTN: GS060208313000.001 [DIRS 181404]. Data from this new qualified DTN are presented in Section 4.1.3[a], and the calculations from Section 6.1.2.4 of the parent document are updated with the qualified data in Section 6.1.2[a] of this addendum.

Deviations from the work plan documentation are the following:

- This update is being implemented as an addendum, whereas the TWP indicated that updates to the parent report would be accomplished by a document revision (SNL 2007 [DIRS 179287], Section 1.2.5); as such, not all of the EQ3/6 calculations in the parent report have been rerun, but only those either affected by CR 7820 or needed to analyze new dust leachate data.
- CR 8508, relating to thermogravimetric analysis results and the interpretation of acid gas volatilization presented in Appendix E, is addressed in Section 6.2.1[a].
- CR 9163, which had resulted in the change in qualification status of a DTN that was a direct input to the parent document (DTN: LL041001423121.046 [DIRS 173688]) prior to ACN 01; this issue is discussed concurrently with CR 7702 in Section 6.1.1[a].

The first deviation noted above has occurred because the addendum process was not procedurally available in SCI-PRO-005 at the time the TWP was approved. The scope of updates and additions required for the parent report are limited enough that an addendum is more appropriate than a full document revision at this time. The second and third deviations above are due to these CRs being issued after the approval of the controlling TWP; as such they are appropriate to include in the work scope of this addendum.

No modification to the screening process has occurred in this addendum. However, the relative strengths of the individual screening questions have changed as follows: (1) if deliquescent brine forms, it is now considered as “not expected” to be corrosive; (2) if potentially corrosive brine forms, additional information further supports the Project position that localized corrosion will not initiate; and (3) if localized corrosion initiates, stifling of the process prior to penetration of the waste package corrosion barrier is now more strongly supported, based upon new information.

4[a]. INPUTS

4.1[a] DIRECT INPUT

Direct inputs that are used in this addendum are specified and discussed here.

4.1.1[a] Thermodynamic Database and Use of EQ3/6 V. 8.0

Sections 6.1.2.1[a] and 6.1.2.2[a] of this addendum use the most recent Pitzer project database (DTN: SN0609T0502404.012 [DIRS 179067], file *data1.yp2*). This database is an updated version of that which was utilized in the parent report. This most recent database is also used as the foundation for updating with ammonium additions. Table 4-1[a] lists the qualified input data that are used as direct feeds to produce the modified Pitzer thermodynamic database (output DTN: SN0706AMMONIUM.001, file *Database YPD\data0.ypd*) that is then suitable for partitioning the removal of ammonium from the systems.

Table 4-1[a]. Input Sources to "YPD" Database

Data Description (Used In)	Data Source
EQ3/6 Pitzer database, used directly for geochemical modeling of dust leachate, also modified with dust-specific changes	DTN: SN0609T0502404.012 [DIRS 179067], file *data0.ypf.R2*
EQ3/6 B-dot database, selected portions extracted to modify dust-specific database (details below)	DTN: SN0612T0502404.014 [DIRS 178850], file *data0.ymp.R5*
Database parameters for ammonia and ammonium in solution	Section 4.1.1.1 of parent report
Database parameters for solids (ammonium solids, fictive Alloy-22, layered double hydroxides, and akaganeite)	Section 4.1.1.2 of parent report

The thermodynamic EQ3/6 calculations in Section 6.1.2.1[a] involving ammonium utilize a modified version of the Pitzer database that is based upon the current *data0.ypf.R2* (DTN: SN0609T0502404.012 [DIRS 179067]). This ammonium-containing EQ3/6 "YPD" database (output DTN: SN0706AMMONIUM.001, file *Database YPD\data1.ypd*) has inputs described here in Section 4.1.1[a], several of which are identical in their entirety to Sections 4.1.1.1 and 4.1.1.2 of the parent report. Several database changes unique to this addendum are copied from the latest B-dot database (DTN: SN0612T0502404.014 [DIRS 178850]) and include the following items:

- Updated Cr^{3+} aqueous species ($CrOH^{2+}$, CrO^{+}, and CrO^{2-})
- Deactivated polynuclear Cr(III) species $Cr_2O_2(OH)_4^{2-}$
- Updated to Eskolaite logK values
- Added the $NiMoO_4$ and $NiCO_3{:}5.5H_2O$ solids
- Updated solid $Fe_2(MoO_4)_3$ in file *data0.ymp.R5*.

Note that none of these items listed from the B-dot database are used by any calculations within this addendum as this scope of work had been removed after the creation of the YPD database.

The validated model of *In-Drift Precipitates/Salts Model* (SNL 2007 [DIRS 177411], Section 8.1) is used with its corresponding product output Pitzer database

(DTN: SN0609T0502404.012 [DIRS 179067], file *data1.yp2*) in the evaporative evolution of potential repository dust brine (Sections 6.1.2.2[a] and 6.1.2.3[a]). This usage is both consistent with the stated purpose and within the defined component system of the validated IDPS model (SNL 2007 [DIRS 177411], Section 1).

The analyses to provide a quantitative partitioning of the ammonium salts in Section 6.1.2.1[a] do not use the IDPS model. The ammonium component of dust has been determined to be unstable within the heated repository environment (Section 6.1.2.3 of the parent report) and is therefore not a relevant to the postclosure system. The purpose of Section 6.1.2.1[a] is to develop a set of repository representative input conditions which then implement the IDPS model as previously discussed and is only one of two methods examined for this purpose (the other being a less-conservative and simplistic removal of all ammonium as the common atmospheric component ammonium sulfate).

6[a]. DISCUSSION

6.1[a] MULTI-SALT DELIQUESCENCE AT ELEVATED TEMPERATURE

Some amount of deliquescence will likely occur in dust on the waste packages under emplacement drift environmental conditions. The purpose of this section is to describe the expected chemical composition of aqueous brine that would result from such deliquescence. New and more repository-relevant project data are available for this analysis and include atmospheric dust collected at a repository location. The discussion focuses on three salt mixtures composed as follows:

- Assemblage A: a two-salt mixture of $NaCl + KNO_3$
- Assemblage B: a three-salt mixture of $NaCl + NaNO_3 + KNO_3$
- Assemblage C: a four-salt mixture of $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2$.

6.1.1[a] Deliquescence Activity of Salt Assemblages (CR 7702 and CR 9163)

Section 6.1.2.2 of the parent document had used DTN: LL041001423121.046 [DIRS 173688] to provide data confirming the deliquescence of the three-salt assemblage at temperatures of at least 180°C. However, the qualification status of DTN: LL041001423121.046 was downgraded to unqualified (see CR 9163) due to a lack of proper calibration of relative humidity probes (see CR 7702) and its usage as input was re-evaluated.

The project data from this now-unqualified DTN had provided some direct evidence of the deliquescent process occurring for a three-salt mixture. This DTN was an indirect input, providing a confirmation that deliquescence occurs at temperatures similar to the observed boiling points measured for similarly composed salts (Figure 6.1-1A). That deliquescence confirmation demonstrated that the process was reversible and that the solutions were not metastable either as a superheated solution or supersaturated gels (Staggs 2005 [DIRS 181516], p. 65 of Supplement I).

Deliquescent activity is additionally confirmed by recent observations of the deliquescence of the four-salt mixture (Assemblage C) at 180°C, based on both parallel electrode conduction and visual observation (Rard and Barish 2007 [DIRS 181640], pp. 8 and 9 of record). The exact relative humidity at which deliquescence occurred in this experiment is not important; the fact that the experimental conditions were not pressurized and deliquescence was confirmed by parallel electrode conduction as humidity was increased is sufficient to confirm the relevance of potential dust deliquescence to repository conditions.

In addition, it appears that there is essentially no "temperature limit" to deliquescent activity that can be applied to either Assemblage B or Assemblage C as they both transition to salt melts at approximately 300°C and > 400°C, respectively (Rard et al. (2006 [DIRS 181457], Sections 3.1.4 and 3.1.5). However, the composition range of these salt mixtures that behave as such is quite narrow, and any deviation from that composition range can either strictly limit any deliquescence brine volume or prevent any detectable deliquescence.

6.1.2[a] Yucca Mountain Dust-Brine Analyses

This section re-evaluates the results of the dust analysis work from Section 6.1.2.4 of the parent report. As described in Section 6.1.2.2 of the parent report, the salt mineral assemblages that control the compositions of deliquescent brines on the waste package surface have previously been evaluated by evaporation of measured dust leachates to eutectic compositions. However, these previous calculations did not include ammonium as a measured species. Ammonia in the atmosphere primarily reacts to neutralize acidic substances (e.g., sulfuric acid, nitric acid and hydrochloric acid) to produce condensed or particulate salts of ammonium (Seinfeld 1986 [DIRS 102180], p. 377). Once these resulting ammonium minerals or condensates are exposed to the heat of waste packages they will decompose to the gas phase (Section 6.1.2.3 of the parent report) and be swept out of the emplacement drifts by ongoing ventilation. In order to model the evolution of potential dust deliquescent brines that may exist during the postclosure period, this process is taken into account.

As described in Section 6.1.2.3 of the parent report, ammonium chlorides and nitrates will rapidly decompose at elevated temperatures, and will not be present in the salt mineral assemblage on the waste package surface that will deliquesce during postclosure. Both ammonium and the anion that is mineralogically associated with it are lost during ammonium mineral decomposition, hence, some fraction of the nitrate and chloride that was present in the dust leachates would have been associated with ammonium and lost (for example, see Figure 6.1-2 of the parent report). While the decomposition of ammonium sulfate is not expected to result in loss of sulfate, the analysis here treats it as if it had fully decomposed to provide a bounding aggressive brine composition (i.e., one that is depleted in sulfate is more likely to allow concentration of calcium in the brine).

In Section 6.1.2.4 of the parent report, tunnel dust analyses including ammonium were used to evaluate the effect of this process. It is necessary to redo these calculations because the original DTN source for that data has been superseded by a DTN containing new data from duplicate analyses of the same leachate compositions (DTN: GS060208313000.001 [DIRS 181404], file *dust package.xls,* see Table 4-2[a]). Also, new dust leachate analyses of ECRB tunnel dust, with ammonium concentrations, are available in the same DTN. In addition, a new source of data for atmospheric dust compositions is available in the form of analyses of leachates from dust samples collected by the Torit Cyclone dust collector at the South Portal (Table 4-3[a]).

In order to determine the salt mineral assemblage remaining after ammonium mineral decomposition and to quantitatively describe the postclosure brine types that would develop by deliquescence of the minerals, ammonium and the anions that are mineralogically associated with it (which are also lost to the gas phase during ammonium mineral decomposition) must be subtracted from the dust leachate compositions. Then the resulting adjusted compositions are evaporated to dryness using EQ3/6 to determine the eutectic salt assemblage. To accurately determine the abundance of the remaining soluble components, it is necessary to apportion the ammonium present in the dust chemical analysis between the different anionic species present (i.e., NO_3^-, Cl^-, and SO_4^{2-}). This ammonium apportionment is based on EQ3/6 simulations of evaporative dryout of the ammonium-bearing dust samples collected by NADP and the dust leachate compositions collected by the Torit Cyclone. These simulations use the EQ3/6

YPD thermodynamic database because they are anticipated to represent the atmospheric dust component in the tunnel dusts.

To accomplish these analyses that include ammonium requires the modification of the EQ3/6 Pitzer database (DTN: SN0609T0502404.012 [DIRS 179067]), similar to the modification that was done for the parent report (Section 4.1.1). The database modifications are described in Section 4.1.1[a] and include input from the original parent report and selections from the EQ3/6 B-dot database (DTN: SN0612T0502404.014 [DIRS 178850]), per Table 4-1[a]. All EQ3/6 analyses in this addendum perform a charge balance with H^+ while maintaining a fixed partial pressure of carbon dioxide equal to $10^{-3.5}$ bar.

Simply evaporating the tunnel dust leachate compositions to dryness to determine the ammonium mineral partitioning would be incorrect, as it is assumed to be a mechanical mixture of the crushed tuff component, which contains an ammonium- and nitrate-poor salt assemblage, and the ammonium- and nitrate-rich atmospheric component. It is the atmospheric component that is likely to contain the ammonium minerals.

6.1.2.1[a] Disposition of Ammonium Salt Content

Two methods are employed to disposition the ammonium salts and are both used for the subsequent removal of ammonium from the postclosure-relevant system. Because ammonia in the atmosphere primarily reacts to neutralize acidic substances to produce condensed or particulate salts of ammonium (Seinfeld 1986 [DIRS 102180], pp. 377 and 378), and while preferring sulfate the major conjugate acid component of the local dust is nitrate. It follows that ammonium should associate with predominate nitrate in competition with sulfate, and then the residual chloride (also see discussion in Section 6.1.3 of the parent report). In addition, a sulfate-dominant case is analyzed because it is a commonly identified atmospheric dust component.

The first analysis is to corroborate the dominant ammonium nitrate presence and provide a numerical best-estimate partitioning of ammonium nitrate/chloride removal based upon the conceptual assumption of a completely deliquesced and mixed composition. This should result in the predominance of ammonium nitrate removal to be consistent with the literature information. The second is the removal of only ammonium sulfate, and while only a qualitative analysis process, it is based upon the atmospheric aerosol studies (Section 6.1.3 of the parent report) that indicate ammonium sulfate can be a significant aerosol component.

The soluble chemical analyses that potentially represent the salt load in atmospheric dust are available from the two sources described above in Section 6.1.2[a]. The first data set is from regional aerosols obtained from the NADP (see Section 4.1.2[a] and Table 4.1-8 of parent report) in the form of three average annual precipitation compositions representing the years 2000 to 2002[1]. The second is leachate data from atmospheric dust collected at the South Pad by the Torit Cyclone. Chemically, both the cyclone dust leachate and NADP rain-out samples are nitrate-rich; however, ammonium comprises a large fraction of the total soluble cations in the NADP data. Both sets of data provide compositional data for the soluble salts only—phase characterization was not carried out. The charge balancing on H^+ had the effect of raising the pH of all solutions from their measured values by: 1.04, 1.11, and 0.62 for years 2000 through 2002, respectively (output DTN: SN0706AMMONIUM.001, see **.3o* files in directory *EQ36 – ammonium partitioning/NADP runs*). While a relatively simplistic methodology, this is not considered to be too large a pH adjustment because this analysis is only to indicate the general partitioning of ammonium minerals, whose solubilities are not directly pH-dependent under these near-neutral conditions.

With respect to determining the partitioning of ammonium among the different salt phases, the evaporation of the cyclone dust leachate samples was unsuccessful. Upon evaporation, the samples evolved into concentrated Ca-Cl-NO_3 solutions, which are not well represented with the

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[1] Precipitation scavenges aerosols from the atmosphere and is often used to evaluate atmospheric aerosol compositions.

data0.ypd database. Specifically, it is found that under these concentrated compositions the aqueous species $CaCl^+$ becomes the dominant chloride-containing species, which delays or suppresses the prediction of chloride mineral formation. In those affected samples, the simulations failed to converge to a dryout composition, and all (except one at 0.59 activity of water) simulations reached water activity values lower than 0.3, with five below 0.1. In addition, some of the charge balancing indicated that the initial compositions may be slightly incomplete or uncertain, with one case (output DTN: SN0706AMMONIUM.001, *EQ36 – ammonium partitioning/cyclone dust/spc008.3o*) increasing the total carbonate from 6.5 to 38.9 millimolal, and two other carbonate-poor samples increasing by an order of magnitude. As a result of the poor simulation performance, this evaporative analysis is highly uncertain (output DTN: SN0706AMMONIUM.001, spreadsheet *Cyclone dust ammonium partitioning.xls*) and not utilized for ammonium partitioning.

The best-estimate numerical disposition of ammonium among different salt phases is based only upon analysis of the NADP results, which includes two cases where both ammonium chloride and ammonium nitrate precipitate (similar to the analyses performed in Section 6.1.2.4 of the parent report). The results for the NADP data were selected to represent the ammonium distribution because their EQ3/6 analyses resulted in appreciable ammonium mineral precipitation, and the results corroborate the expected result to predict predominance of ammonium nitrate over that of ammonium chloride. Although none of the South Pad ammonium-containing evaporative analyses are used, the two NADP results that are selected can adequately represent the conceptual partitioning of ammonium salts. There are two reasons why this analysis is acceptable for its use to indicate if such brines could be detrimental to the corrosion performance of Alloy 22. First, because the result partitions over ninety-percent to ammonium nitrate and as such should produce higher chloride-containing brine solutions. As such it provides nearly a bounding conservative look at the potential dust-brine corrosion environments. Second, this ammonium adjustment process on the South Pad dust leachate compositions does not greatly change those initial compositions due to the fact that they generally contain much less ammonium. Without much ammonium to remove the exact value of the ammonium chloride/nitrate partition has little effect on the resulting evaporative evolution of those brines.

While none of the NADP brines went entirely to a eutectic composition, the year 2000 and year 2001 samples did precipitate out an appreciable amount of ammonium nitrate and ammonium chloride. For the

NADP data from the year 2002, the simulation failed to converge, stopping before any chloride-bearing phase precipitated. The calculation results are summarized in Table 6-2[a]. With respect to NADP samples from the years 2000 and 2001, ammonium chloride was the only chloride phase present when the simulation stopped. Although nitrate dominantly precipitated as ammonium nitrate, niter and soda niter are also present and hence would remain after ammonium mineral decomposition.

Table 6-2[a]. Effect of Ammonium Salt Decomposition on Predicted Brine Compositions

Year at Site NV-00	2000	2001	2002[a]	Average
Analysis Temp (°C)	25	25	25	–
Brine pH (Pitzer)	6.70	8.10	8.05	–
Brine DRH (%)	26.3	37.9	–	–
NH_4 ppts formed	Cl^-, NO_3^-	Cl^-, NO_3^-, SO_4^{2-}	–	–
% nitrate bound to NH_4	82.3	96.9	–	–
% chloride bound to NH_4	100	100	–	–
% NH_4 bound to chloride	5.6	8.6	–	7.1
% NH_4 bound to nitrate	94.4	91.4	–	92.9
% NH_4 bound to sulfate	0.0	0.0	–	0.0

[a] EQ3/6 simulation did not converge; after reaching 35.6% RH, the activity of water began to rise. The results shown are for the lowest-RH point, at which point no ammonium minerals had formed.

Source: Output DTN: SN0706AMMONIUM.001, EQ36 - ammonium partitioning*NADP ammonium partitioning.xls*.

NOTE: DRH = deliquescent relative humidity.

Since these samples did not go to a eutectic composition, the relative proportion of nitrate removed to chloride removed by ammonium mineral decomposition is not well constrained (i.e., it has significant uncertainty). This is especially true for the NADP year 2001 simulation, which still had more ammonium in solution than in solid phases when the simulation stopped (output DTN: SN0706AMMONIUM.001, *EQ36 - ammonium partitioning\NADP ammonium partitioning.xls*). Because of the incomplete distribution of ammonium into mineral phases, the data are equivocal with respect to the effect of ammonium mineral loss on the NO_3^-/Cl^- ratio in the brine. The average fraction of ammonium bound to nitrate (92.9%) is larger in this current analysis than in the results in Table 6.1-2 of the parent report (84.0%). Therefore, use of the ammonium partitioning in Table 6-2[a] is acceptable, both because it is corroborated by the available literature indications that ammonium nitrate should predominate and because it is conservative with respect to its increasing chloride relative to nitrate.

Again, as was done in Section 6.1.2.4 of the parent report, this analysis assumes that the NADP rain-out compositions represent a salt assemblage in thermodynamic equilibrium. Atmospheric aerosol studies (from Section 6.1.3 of the parent report) suggest that ammonium sulfate should be a significant component of atmospheric aerosols. If the NADP data mixtures of atmospheric aerosols and windblown dust closer to the ground surface are not in equilibrium with each other, then it is likely that ammonium would be associated more with sulfate, and less with chloride and nitrate. Thus, the second analysis only considers ammonium sulfate for removal.

The NADP data from years 2000 and 2001 in Table 6-2[a] are used below to estimate ammonium partitioning and the resulting chloride and nitrate loss due to the ammonium-phase decomposition. This method, along with the simple removal of ammonium sulfate method, is adequate to investigate potential postclosure repository dust brine compositions. This processing of dust composition data is necessary in order to perform the postclosure modeling of potential dust brines from South Portal dust (Section 6.1.2.2[a]) and ESF tunnel dust (Section 6.1.2.3[a]).

6.1.2.2[a] South Portal Dust

The South Portal dust compositions collected by the Torit Cyclone are presented in Table 4-3[a]. The removal of ammonium from this dust composition to model its postclosure evolution from Section 6.1.2.1[a] is done by using both the NADP results from Table 6-2[a] and by removal of ammonium sulfate. The modified dust leachate compositions were then evaporated with EQ3/6 at 25°C and atmospheric CO_2 partial pressure to determine the type of brine that might form by deliquescence of atmospheric dusts deposited on the waste package during the ventilation period. The EQ3/6 runs for this section use the current Pitzer database without modification (DTN: SN0609T0502404.012 [DIRS 179067]) and the IDPS model (SNL 2007 [DIRS 177411], Section 8.1) as described in Section 4.1.1[a].

None of the ammonium-modified EQ3/6 analyses reached a eutectic composition, and about half of them became mixed calcium-rich systems where the results are not quantitatively reliable. Others may be affected by the charge balancing issue, as was described in Section 6.1.2.1[a]. For these two reasons, the predicted compositions are not shown here, but the results are recorded in an output DTN: SN0506T0502205.014 (file *Cyclone dusts_Summary_NADP salts_ subtracted.xls*). In all cases, the final NO_3^-/Cl^- ratio is greater than unity. In this and any calculations done after ammonium removal, NO_3^-/Cl^- is determined from the total elemental molar concentrations in solution of all nitrogen- and chlorine-bearing species. This is done intentionally to include all nitrate and chloride that may be complexed with other cations (e.g., $CaCl^+$).

The results can in general be divided into two groups: one where the samples evolved into Na-K-(Ca)-NO_3-Cl brines, and the other where they evolved into Ca-(Na)-NO_3-Cl brines of very high ionic strength (several tens of molal). This appears to be due to the recently included $CaCl^+$ ion-pair species in the YPD database, and in particular its lack of interaction parameters for that species with mixed species (particularly a binary parameter for $CaCl^+$ and nitrate interaction). With evaporation, the $CaCl^+$ species becomes more and more dominant in solution and appears to inhibit the precipitation of any Ca-NO_3 solid phases that were observed with previous revisions of the Pitzer database. Once the solution concentrations reach several tens of molal, they are outside of the bounds of the current Pitzer activity model, and this represents a limitation of the database in dealing with $Ca(NO_3)_2$-$CaCl_2$ solutions.

As stated earlier, the speciation indicated by the evaporation of the NADP samples (Table 6-2[a]) of ammonium nitrate plus minor ammonium chloride is at odds with the atmospheric aerosol literature, which suggests that ammonium sulfate should be the significant ammonium component. If ammonium sulfate is present, then sulfate instead of nitrate or chloride would be lost by decomposition. However, for the present purposes of evaluating the potential brine compositions with respect to their ability to initiate localized corrosion on Alloy 22, loss of nitrate is a conservative way to proceed.

There is no impact to any other discussion or conclusions resulting from the removal of the aforementioned text from the parent report.

6.3.3[a] Summary

The new experimental results and literature discussed in Section 6.2.1[a] indicate that a high-temperature brine containing calcium is able to produce calcite while losing HX(g) (X = Cl and NO_3), and thereby become less corrosive. Furthermore, at the highest temperatures (above about 190°C) Assemblage C (the four-salt mixture) should evolve to Assemblage B (the three-salt mixture), and as a result that brine will decrease in volume and may dry out completely.

The new data directly investigating the corrosive nature of persistent brines at high temperatures (Section 6.4.2[a]) have demonstrated that nitrate continues to inhibit initiation of crevice corrosion. Nevertheless, the new test results at 180°C leave open a small possibility that at even higher temperatures nitrate may become a less effective corrosion inhibitor. However, such a change in nitrate effectiveness is not supported by any directly relevant test results. For example, experimental factors other than “corrosive nitrate brine” are considered to be the cause of the extensive localized corrosion observed in autoclave testing described in Section 6.4.2.1[a], and this is supported by the lack of any observable corrosion attack under similar, but non-creviced, conditions (Section 6.4.1 of the parent report). It is acknowledged in this addendum that while experiments to examine the issue of high-temperature nitrate corrosion inhibition were performed (Section 6.4.2.2[a]), they have not been investigated up to the highest potential waste package temperature. Due to this slight uncertainty, the screening conclusion for this section is changed from “no” to “not expected.”

6.4[a] POTENTIAL FOR LOCALIZED CORROSION FROM DUST BRINE

6.4.1[a] Atmospheric Dust-Loading at South Portal of Repository

Because of the location of the South Portal near where intake air will likely come from, the atmospheric dust samples collected there are the most representative of the materials that forced ventilation may deposit upon waste packages. The next closest location where total dust loading was monitored was at Site 5, which is at the entrance gate to the Nevada Test Site, at Jackass Flats along Fortymile Wash, on the order of ten miles away. This portion of the addendum is to evaluate the new dust information from the South Portal location and compare it to the values used in deriving the potential quantity of brine that may result (Section 6.4.1 of the parent report).

Ongoing dust-collection activity at the site of the proposed repository, with the primary purpose of obtaining dust samples for chemical analysis, has also produced some information that can be used to calculate atmospheric dust loads. While this analysis is built upon qualified mass and time measurements of dust captured in collectors (DTN: SN0705F3405507.001 [DIRS 181495] per Section 4.1.6[a]), the flow-rate information required to determine the mass loading in a volume of air is not a calibrated value. Therefore, these calculations are unqualified in nature and are only used as corroborative information in support of the existing qualified analysis in Section 6.4.1.1 of the parent report.

7[a]. CONCLUSIONS

The addendum to the dust screening analysis addresses all related open CR issues to date; in addition, it provides updates with regards to more recent experimental activity. During this process, three output DTNs were modified or created; they are described in Table 7-1[a].

Table 7-1[a] Output DTN Descriptions

Output DTN (Qualification Status)	Title	Section	New/Update
SN0706AMMONIUM.001 (Qualified)	Analysis of Ammonium Decomposition on Potential Dust Brine Compositions including data0.ypd	6.1.2[a]	New
SN0708BULKDUST.001 (Qualified)	Comparison of Bulk Compositions: DST Dust, ECRB Dust, and Host Rock	6.1.3[a]	New
MO0506SPAEQ36F.002 (Qualified)	EQ3/6 Input/Output Files and Summary Spreadsheets Modeling Dust Deliquescence and Evolution of Brines in Dust	6.3.2[a]	Update
SN0706F3405507.002 (Unqualified)	Dust Collection for the Purpose of Studying Deliquescence: Dust Loading	6.4.1[a]	New

7.1[a] SCREENING DECISION

The recommended screening decision of the parent report remains that localized corrosion due to dust deliquescence at any repository temperature is to be excluded from TSPA for the license application due to its low consequence. Only minor adjustments were made in this addendum to the individual decision tree answers and reasoning. The additional sources presented in Table 7-2[a] are considered to be in addition to those already in Table 7.1-1 of the parent report.

Table 7-2 [a]. Decision Tree Propositions and Addendum Data Sources Considered

Decision Tree Item	Addendum Data Sources Considered
1. Can multiple-salt deliquescent brines form at elevated temperature? **Yes**	• Tunnel dust and South Portal atmospheric soluble compositions (high nitrate relative to chloride) • NH_4 salt decomposition
2. If brines form at elevated temperature, will they persist? **Sometimes**	• Calcium-rich brines degas acid species and react with CO_2
3. If deliquescent brines persist, will they be corrosive? **Not Expected**	Data only come from the parent report; the decision is modified based upon reconsidering the extent of pre-existing information.
4. If deliquescent brines are potentially corrosive, will they initiate localized corrosion? **No**	• Confirmation of limited atmospheric dust-loading at repository • Conditions beyond those sustainable within the repository have produced localized corrosion • Nitrate inhibition of localized corrosion remains valid under repository conditions at up to 180°C • Example of long-term instability of most deliquescent (> 190°C) salt Assemblage C