



**Scientific Analysis/Calculation
Administrative Change Notice**

QA:QA
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Complete only applicable items.

1. Document Number:	ANL-EBS-MD-000074	2. Revision:	01	3. ACN:	01
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6. Approvals:	
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7. Affected Pages	8. Description of Change:
4-20	Removal of indirect input DTN: LL041001423121.046 by deletion of the 2 nd to last paragraph in Section 4.1.7. This unqualified DTN (CR 9163) was corroborative and its removal does not affect any product output or product conclusions. CR 11039 corrective action is satisfied by the removal of above DTN.
6-5	As result of removal of DTN: LL041001423121.046 as input, Figure 6.1-1 B is removed along with its associated callouts.
6-55	Correction to parenthetical example of decomposition gasses from NH ₄ NO ₃ .
8-18	Removal of reference to LL041001423121.046 [DIRS 173688].
E-21	Callout to Figure 6.1-1 is corrected to be Figure E-1.

kinetic rate law (Equation 6.1-1) and associated ammonium nitrate kinetic parameters (Section 6.1.2.3).

Vyazovkin et al. 2001 [DIRS 172842]—*Description of Data:* Rate law and parameters describing sublimation/dissociation kinetics of ammonium nitrate. *Qualification Status:* Justified for intended use in this analysis. *Extent to Which the Data Demonstrate the Properties of Interest:* This paper determines the thermal dissociation kinetics of ammonium nitrate using a thermogravimetric method, examining both the solid and liquid phases. Data were acquired isothermally and non-isothermally and used to determine the best fit for the parameters of a rate equation describing ammonium nitrate dissociation. The methodology adopted in this study provides a detailed characterization of the sublimation/vaporization kinetics, allowing for a thorough characterization of these two processes. These kinetic parameters are the property of interest used in this report as input, and include the kinetic rate law and parameters for decomposition of ammonium nitrate. *Qualification of Personnel and Organization:* Dr. Sergey Vyazovkin has published over fifty papers in the scientific literature within the past ten years. Most of his body of work is in the specific area of calorimetry and kinetics of thermally induced processes (e.g., decomposition, crystallization and degradation). *Reliability of Data Source:* These data were published in *Chemical Materials*, which is a respected journal of the American Chemical Society. Its articles are peer-reviewed, i.e., reviewed by other experts in the pertinent technical field, individuals with experience in the subject matter who typically use such information in the course of their work. Technical issues are raised during the review process and either resolved prior to publication or the article is rejected. This process provides an appropriate level of confidence that the data are suitable for use in the types of analyses for which it was intended.

For Section 6.1.2.2, the file *Boiling_temperatures_R1c-1.doc* (“Figure 1”) supplies information regarding the dryout temperature of the NaCl–KNO₃ assemblage being below 160°C (DTN: LL040901831032.008 [DIRS 173659]). Also, Figure 6.1-1 uses data boiling point measurement data from this same file (*Boiling_temperatures_R1c-1.doc*, “Figure 3”).

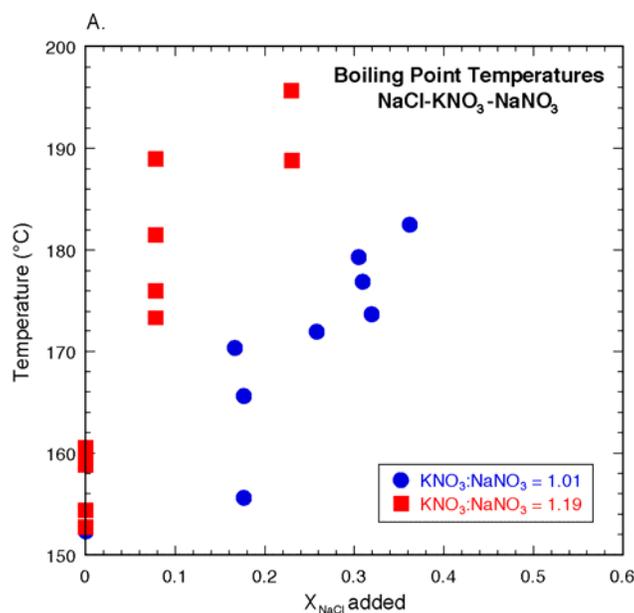
4.1.8 Input Data for Preclosure Temperature and Relative Humidity Analyses

Appendix A presents preclosure temperature and relative humidity analyses. Preclosure ventilation is analyzed to estimate the average waste package temperature at various times; individual waste package temperatures based on waste package output; partial pressure of water vapor based on meteorological data; and the relative humidity at individual waste packages. Preclosure temperature and relative humidity are not predicted by the multiscale model that describes postclosure conditions for TSPA-LA (BSC 2005 [DIRS 173944]); the analysis in Appendix A is an application of the validated analytical version of the ventilation model (BSC 2004 [DIRS 169862], Section 6.4.2) that describes a wider range of spatial and temporal variability than the original ventilation model output.

respectively (BSC 2004 [DIRS 161237], Tables 6.7-21 and 6.7-22). Because of limitations in the available thermodynamic data for the calcium-nitrate system, the third assemblage was not explicitly modeled, and a boiling temperature of 155°C (slightly higher than the boiling temperature of a pure $\text{Ca}(\text{NO}_3)_2$ solution at 1 bar) was assumed (BSC 2004 [DIRS 161237], Table 6.7-23). However, the IDPS model uncertainties in the calculated deliquescence RH values at these higher temperatures or lower relative humidities are large (e.g., $\pm 15\%$ for predicted RH values less than 40%; BSC 2004 [DIRS 169863], Table 7-8) and correspond to large uncertainties in the predicted boiling temperatures for these assemblages. As discussed in the next section, experimental data acquired subsequently show that the predicted boiling (dryout) temperatures for these assemblages are too low.

6.1.2.2 Results of Experimental Deliquescence Measurements

Experimental work has been performed with the three salt assemblages described above to evaluate the potential for deliquescence at high temperatures and low relative humidities. Experimental work with the NaCl-KNO_3 assemblage at 1 bar confirmed that dryout occurred at temperatures below 160°C, with the highest measured temperature at which deliquescent liquid was present being approximately 134°C (DTN: LL040901831032.008 [DIRS 173659], *Boiling_temperatures_Rlc_1.doc*, Figure 1). Deliquescence salt Assemblage B, the $\text{NaCl-KNO}_3\text{-NaNO}_3$ assemblage, has also been examined experimentally. Boiling-point experiments suggest that $\text{NaCl-KNO}_3\text{-NaNO}_3$ brine can form at temperatures in excess of 190°C (Figure 6.1-1). By inference, salt Assemblage C, $\text{NaCl-KNO}_3\text{-NaNO}_3\text{-Ca}(\text{NO}_3)_2$, of which Assemblage B is a subset, must also deliquesce at temperatures greater than 190°C.



NOTES: A. Boiling point measurements at fixed $\text{KNO}_3:\text{NaNO}_3$ mole ratios versus the mole fraction of NaCl salt added; from DTN: LL040901831032.008 [DIRS 173659], *Boiling_temperatures_Rlc_1.doc*, Figure 3.

Figure 6.1-1. Deliquescence of the $\text{NaCl-KNO}_3\text{-NaNO}_3$ System at Elevated Temperature

6.3.4 Summary

Initial brines formed by deliquescence are expected to be near-neutral pH, nitrate-rich, and chloride-poor (BSC 2004 [DIRS 169860], Section 6.10), and therefore to be benign with respect to localized corrosion. Experimental corrosion studies used to develop the localized corrosion model have verified that corrosion will not be initiated by brines high in nitrate, such as those formed by dust deliquescence, at temperatures below 120°C. Newer, higher-temperature data have verified that nitrate inhibition of corrosion can continue to be effective at temperatures up to 220°C.

Based on thermodynamic principles, brines potentially forming at temperatures above 140°C, the validation limit of the IDPS model, can only be more nitrate-rich (BSC 2004 [DIRS 169863], Section 7; BSC 2004 [DIRS 169860], Section 6.15.1.1) than brines that form at lower temperatures, within the range of validation. Analyses presented here show that processes occurring after deliquescence, acid degassing and reactions with silicate minerals, cannot result in brines that are corrosive with respect to localized corrosion. Acid degassing will raise the nitrate–chloride ratio of the remaining solution, and even small degrees of degassing will result in increases in the brine pH, to values ranging from near neutral to as high as approximately 10.3. Brine interactions with silicate minerals may buffer the pH to near-neutral values, and may lead to dryout and precipitation of a less-deliquestent salt assemblage. Initiation of localized corrosion is unlikely in these exposure environments (BSC 2004 [DIRS 169984], Section 6.4.4).

Uncertainty Discussion—The corrosivity part of the screening arguments for dust deliquescence emphasizes the inhibiting effect of the nitrate–chloride ratio on initiation and extent of localized corrosion in Alloy 22. However, other anionic species including carbonate and sulfate also provide some inhibition (BSC 2004 [DIRS 169984], Section 8.3.1) that is not considered quantitatively.

Nitrate in repository dust will be contributed by atmospheric aerosols, from host rock pore waters, from fossil-fuel operated equipment upstream of the emplacement areas, and other sources (Section 6.1.3). The chemical form of that nitrate is uncertain and may include NH_4NO_3 , NaNO_3 , and KNO_3 . To the extent that nitrate exists as NH_4NO_3 , it may volatilize from the waste package surface (e.g., as $\text{NH}_3(\text{g})$ and $\text{HNO}_3(\text{g})$). This behavior is taken into account in the qualitative description of dust (Section 6.1.2.3), and this report includes an analysis of the effects of ammonium salts on deliquescent brine (Section 6.1.2.4). However, lacking direct observations of the soluble salts present in dust, the partitioning of nitrate to ammonium and other salts remains an uncertainty in the analysis of corrosivity.

Finally, the representation of the undissociated HCl and HNO_3 species in concentrated brines, upon which the calculated gas-phase partial pressures depend directly, may be subject to effects that are not represented in the EQ3/6 Pitzer calculations. In other words, whereas the partial pressure of HCl is predicted to be greater than that of HNO_3 , this has not been observed directly. The impact of this uncertainty is minor if the extent of degassing is minor, and the effects are limited to buffering the pH (Section 6.2).

- 166419 LL030808523122.035. Input and Output Files Supporting MSTHM Micro-Abstractions for LA Multi-Scale Analyses. Submittal date: 09/11/2003.
- 168767 LL030905931032.001. Sensitivity Studies for Evaluating the Impact of Thermal Conductivity and Percolation Rate on LA Multi-Scale Analyses. Lower Percolation Case, Low Thermal Conductivity in Hostrock. Submittal date: 09/16/2003.
- 168768 LL030906331032.004. Sensitivity Studies for Evaluating the Impact of Thermal Conductivity and Percolation Rate on LA Multi-Scale Analyses. Upper Percolation Case, High Thermal Conductivity in Hostrock. Submittal date: 09/16/2003.
- 172589 LL040502512251.099. Weight Loss Measurements and Weight Loss Corrosion Rates from Alloy 22 Foil Specimens. Submittal date: 06/11/2004.
- 173822 LL040702112251.112. Open Circuit Electrochemical Studies of Alloy 22 with High Temperature Pseudo Thin-Film (5MM) NACL Brine and PVDF (Polyvinylidene Fluoride) Crevice Formers. Submittal date: 11/17/2004.
- 171362 LL040803112251.117. Target Compositions of Aqueous Solutions Used for Corrosion Testing. Submittal date: 08/14/2004.
- 173659 LL040901831032.008. Results from Boiling Temperature Measurements for Saturated Solutions in the Systems NACL + KNO₃ + H₂O, NaNO₃ + KNO₃ + H₂O, and NACL + NANO₃ + KNO₃ + H₂O. Submittal date: 02/17/2005.
- 172593 LL040907112251.122. Weight Loss Measurements and Weight Loss Corrosion Rates from Alloy 22 Foil Specimens. Submittal date: 12/16/2004.
- 173131 LL050200212251.125. Constant Potential Tests for Alloy 22 in Chloride Plus Nitrate Brines. Submittal date: 03/09/2005.
- 174025 LL050205223121.048. Thermal Analysis of Ammonium Chloride and Ammonium Sulfate. Submittal date: 05/26/2005.
- 173175 LL050301723121.050. Thermal Analysis of Ammonium Chloride and Ammonium Sulfate. Submittal date: 03/15/2005.
- 173608 LL050302823121.051. X-Ray Diffraction Data of Alloy 22 Corrosion Products from Electrochemically Induced Localized Corrosion in 4M NACL and 5M CACL₂. Submittal date: 04/14/2005.
- 173790 MO0104SEPMARQ.001. Ambient Air Quality - 1998 Particulate matter Concentration. Submittal date: 04/23/2001.

Period II: The heat-up period begins after ventilation ceases and lasts for approximately 10 to 15 years. A thermal vaporization barrier forms when rock surrounding the emplacement tunnels reaches above-boiling temperatures. The thermal barrier works in conjunction with the capillary barrier effect and the drip shield to prevent seepage from dripping onto waste packages. Dust from external sources is no longer entering the drift, and only minor amounts of dust can be generated by drift degradation. Thus, the dust present on the waste package at cessation of ventilation represents the total amount present for deliquescence. Relative humidity also decreases during this heat-up period. Dust deliquescence is unlikely, and corrosion is negligible.

Period III: In this period, the thermal vaporization barrier is also effective. Drift wall temperatures exceed boiling, and seepage onto the waste package will not occur. The drift wall stays above boiling until approximately 750 years after closure (a median value; see Figure E-1). Condensation on the waste package will not generally occur because it is hotter than the drift wall. Dust deliquescence can occur, but deliquescence brines are nitrate-rich (calcium chloride brines are unlikely, and if present, unstable), and there is no significant corrosion (Figure E-12).

Period IV: Begins at approximately year 750 and lasts until the waste package surface has fallen below the critical temperature for corrosion—about year 1375 for a median waste package (Figure E-12). Drift wall temperatures are below boiling, and dripping onto waste packages could occur, although other barrier effects, capillary diversion and the drip shield, are still operative. Nevertheless, it is conceivable that seepage could contact the waste package (if the drip shield does not perform its function) and should the seepage be corrosive, localized corrosion could occur. The end of this time period is not well constrained, but corresponds to the condition that contacting solutions are sufficiently dilute, and other environmental factors (such as temperature) sufficiently benign, that localized corrosion is no longer a significant process.

Period V: The waste package surface has now fallen below the localized corrosion cutoff temperature. The localized corrosion cutoff temperature is a function of brine composition, and is not known exactly; however, expected repository brine compositions would not be corrosive below 90°C, the value assumed here. Passive corrosion rates (on the order of 1.0 to 0.01 $\mu\text{m}/\text{yr}$; see Section 6.4.4 for additional discussion and reference to the abstraction for TSPA-LA) apply.