Model Error Resolution Document

Complete only applicable items.

INITIATION

1. Originator: Carlos Jove-colon/David C. Sassani	2. Date: 02/26/2008	3. ERD No. ANL-EBS-MD-000045 ERD 01
4. Document Identifier: ANL-EBS-MD-000045 Rev 03	5. Document Title: In-Drift Precipitates/Salts Model	

6. Description of and Justification for Change (Identify applicable CRs and TBVs):

Description:

This ERD evaluates issues in the following Condition Reports and provides corrections to errors that have been identified by the Condition Reports listed below, or identified in the document during the corrective actions being performed. The specifics of the issues for each CR can be found in the attached pages as follows:

CR 11022 is addressed in the first section of the attached pages;
CR 11044 is addressed in the second section of the attached pages;
CR 11100 is addressed in the third section of the attached pages;
CR 11101 is addressed in the fourth section of the attached pages;
CR 11616 is addressed in the fifth section of the attached pages.

As part of these corrections, updates were also made to:
DTN MO0701EQ36IDPS.000 (changes made to "readme.doc" editorial and the following files to correct figures)
File "Linke binary1.zip", workbook "cacl2ev.xls" (Fig. 7-5 of the AMR)
File "Linke binary2.zip", workbook "mgno32ev.xls" (Fig. 7-24 of the AMR)
File "Linke ternary1.zip", workbook "caclnev.xls". (Figs. 7-46, 7-47 of the AMR)
File "Linke ternary1.zip", workbook "cacln25n.xls" (Figs. 7-48, 7-49 of the AMR)
File "Linke ternary1.zip", workbook "nacanev.xls" (Fig. 7-40 of the AMR)
DTN SN0609T0502404.012 (editorial changes made to "readme.doc"only)

GLOBAL: All figures with source notes that read as "Output DTN:" are corrected to read "Source: Output DTN:".

Revisions to the DIRS report were made based on changes documented in the attachment.

Justification:

In the attached materials it has been determined that none of the corrections affect the conclusions of the original product and have no impact to the downstream work that has been performed. There is no impact to the conclusion of this AMR and this ERD sufficiently corrects the issues for the CR listed above as detailed below.

CONCURRENCE

	Printed Name	Signature	Date
7. Checker	William F. Downs		3/28/08
8. QCS/QA Reviewer	Robert E. Spencer		3/28/08

APPROVAL

9. Originator	Carlos Jove-colon/David C. Sassani	FOR	3/28/2008 3/28/2008
10. Responsible Manager	Paul R. Dixon		3-31-08

Outline Information

Condition Report Number(s) and TBV's (if applicable)

This Error Resolution Document (ANL-EBS-MD-000045 ERD 01) is for the model report *In-Drift Precipitates/Salts Model* (ANL-EBS-MD-000045 Rev 03) to correct errors reported by the Condition Reports listed below, or identified in the document during the corrective actions being performed.

These condition reports are addressed sequentially below (note that where a figure is corrected to address more than one CR, it appears within the section of the first that is addresses with *all* corrections included):

CR 11022;

CR 11044;

CR 11100;

CR 11101; and

CR 11616.

CR 11022 Report Information

I Background Information Summary

The condition description for this CR is reproduced here as follows:

> **CR Title:** *"Minor documentation issues for ANL-EBS-MD-000045 Rev 03 and potential effects on model limitations."*
>
> **CR Description:** *"This CR identifies several documentation errors regarding model results of binary and ternary (Ca-Cl-NO3, in particular) systems (Section 7.1.1 and 7.1.2). These errors potentially affect the limitations of the IDPS model, which, as clarified in CR 11044, might affect a downstream document ANL-EBS-MD-000033 REV 06 and TSPA-LA. The errors include:*
>
> - *Figures with incorrect source file names*
> - *Figures with incorrect captions or text boxes*
>
> *Because CR 11044 is strongly related to CR 11022, it is also addressed in this extent of condition evaluation. CR 11044 calls for an evaluation of the potential effect of errors in the results of Ca-Cl-NO3 simulations on IDPS model limitations."*

The following is a list of the errors identified:

- Figure 7-23 cites file kcano32ev.xls instead of cano32ev.xls. This is a typographical error.

- Figure 7-47 cites file kcln91.xls instead of caclnev.xls. This is the wrong file from the DTN.

- Figures 7-48 through 7-51 have incorrect captions. The captions for 7-48 and 7-49 should have been switched with those for 7-50 and 7-51 (or the figures switched).

- Figures 7-48 and 7-49 include notes that say the model reaches saturation with respect to $Ca(NO_3)_2$ at 1.4 molal. These notes are incorrect. Instead, the model terminates at 1.4 molal prior to saturation with respect to this phase.

- Excel spreadsheets in MO0701EQ36IDPS.000 reference superseded DTN as input.

- Spreadsheet "cacln25.xls" tab "Data" contains a note "Note: The $CaCl_2$ value may be erroneous" This note comes off the source DTN (LL031106231032.007) but appears to be incorrectly applied as a general statement within the spreadsheet.

II Inputs and/or Software

No software or any types of calculations are used to evaluate the extent of conditions in this CR. No assumptions were used in this analysis.

III Analysis and Results

In the validation sections where simulations are performed and results are plotted (sections 7.1 through 7.4) there are 100 figures and 8 tables documenting validation simulations. These figures and tables were fully rechecked during this process for caption, note, and source file errors. No additional caption errors were found; however, three additional note errors and one additional source file error were found:

i. The line segment connecting the symbols for the 120°C and 140°C results in Figure 7-5 should not be present because the solubility limit was not achieved in the 120°C result. This is a note error because a note in the figure states "solubility limit not reached where x's are not connected."

ii. The note in Figure 7-24 that the solubility limit was not reached over the entire temperature range is wrong; it was reached at 140°C.

iii. There should be a line segment connecting the symbols for the 20°C and 40°C results in Figure 7-40 to indicate saturation with respect to $Ca(NO_3)_2$ at 20°C and 40°C. The note in the figure should state that "Solubilities are not reached where symbols are not connected."

iv. The source file for Figure 7-50 should be cacln25.xls.

All noted errors for the figures within the document are also in the in the source files in the DTN. None of these errors affects the validation of the model or its limitations. The source file error

name is easily discerned from the figure and the information in the DTN readme file. No errors were found in the tables. The corrections for these errors are given below the fixes for those errors originally identified in the CR.

The following is the list of errors identified in the CR, the corrections for those, and the assessment of their potential impact to the model results and conclusions:

- The note below Figure 7-23 cites file kcano32ev.xls instead of cano32ev.xls. This is a typo. The correct file is now cited in the corrected figure (included below). Because the data did not change, this issue does not affect the report or its conclusions. This is corrected to read "cano32ev.xls" in the note under the Figure 7-23 as shown below.

- The note below Figure 7-47 cites file kcln91.xls instead of caclnev.xls. This is the wrong file from the DTN; however, the correct file from the DTN can be discerned from the figure and the DTN readme file. The correction to the footnote of Figure 7-47 is shown below. The fix is replacing the file name 'kcln91.xls' with 'caclnev.xls'. This does not affect the report or its conclusions. The correction to the footnote of Figure 7-47 is shown below.

- Figures 7-48 through 7-51 have incorrect captions. The captions for 7-48 and 7-49 should have been switched with those for 7-50 and 7-51 (or the figures switched). This can be discerned from the descriptions in the figures themselves and can be confirmed by the sources listed. This error does not affect the report conclusions since premature termination of the run is acceptable in accord with validation purposes and validation criteria. The fix to switched captions for figures 7-48 through 7-51 is shown below.

- Figures 7-48 and 7-49 include notes that say the model reaches saturation with respect to $Ca(NO_3)_2$ at 1.4 molal. These notes are incorrect. Instead, the model terminates at 1.4 molal prior to saturation with respect to this phase. However, premature termination is acceptable for validation purposes (p. 7-8 ANL-EBS-MD-000045 REV 03). Model validation includes comparisons of experimental data to model results regardless of how the simulations terminate. As long as the differences between simulated end points and experimental data are within validation criteria (which they are in this case), validation criteria are met. Therefore, this does not affect the report or its conclusions. To correct this, the notes is Figures 7-48 and 7-49 stating the model reaches saturation with respect to $Ca(NO_3)_2$ at 1.4 molal have been removed, and the statements in these notes have been replaced with the following "Model run terminates prior to attaining saturation with respect to $Ca(NO_3)_2$". The corrected Figures 7-48 and 7-49 are shown below and in the revision to DTN MO0701EQ36IDPS.000.

- Excel spreadsheets in MO0701EQ36IDPS.000 reference superseded DTN as an input. This is true, but the readme file identifies this issue. The readme file flags all relevant spreadsheets with the following footnote: "**Some spreadsheets reference superseded DTN: LL031006231032.006 as a source for data. This DTN has been superseded by DTN: LL031006231032.007 however, the data used in the

spreadsheets is the same as the data in the new DTN." Therefore, because the data utilized from the DTN have been compared and found to be the same and this cross comparison is noted in the readme file, this does not affect the report or its conclusions. No correction is needed in this case.

- Spreadsheet "cacln25.xls" tab "Data" contains a note "Note: The $CaCl_2$ value may be erroneous" This note comes off the source DTN (LL031106231032.007) but appears to be incorrectly applied as a general statement within the spreadsheet. In fact, this note should not be in the "cacln25.xls" spreadsheet, but its presence does not affect the use of the data in the validation. These data are plotted in the AMR and used in the validation without any notes to the effect that they may be erroneous. Therefore, this note does not affect the report or its conclusions. The note about erroneous $CaCl_2$ data in the spreadsheet "cacln25.xls", worksheet "data", was incorrectly applied in this case. This is corrected by removing the statement from the spreadsheet "cacln25.xls", worksheet "data" in the DTN MO0701EQ36IDPS.000. Because the use of the data contained there is not affected by this for its use in the model validation, it therefore does not affect the report conclusions.

Note that CR 11044 (evaluated below) identifies an additional issue with the model results plotted for the Ca-Cl-NO_3 system in Figures 7-46 and 7-47. This resulted in an additional note being added to the figures and this is shown on the corrected Figure 7-47 in this section, but the correction is discussed in the next section on CR 11044. This additional issue does not affect the validation or limitations of the IDPS model, as explained in the resolution of CR 11044.

1. The line segment connecting the 120°C and 140°C results in Figure 7-5 should not be present because the solubility limit was not achieved in the 120°C result. This is a note error because a note in the figure states "Solubility limit not reached where x's are not connected." To correct this, the line segment connecting the symbols for the120°C and 140°C results in Figure 7-5 has been removed consistent with the note in the figure about not reaching solubility limits. The corrected Figure 7-5 is shown below and in the revision to DTN MO0701EQ36IDPS.000.

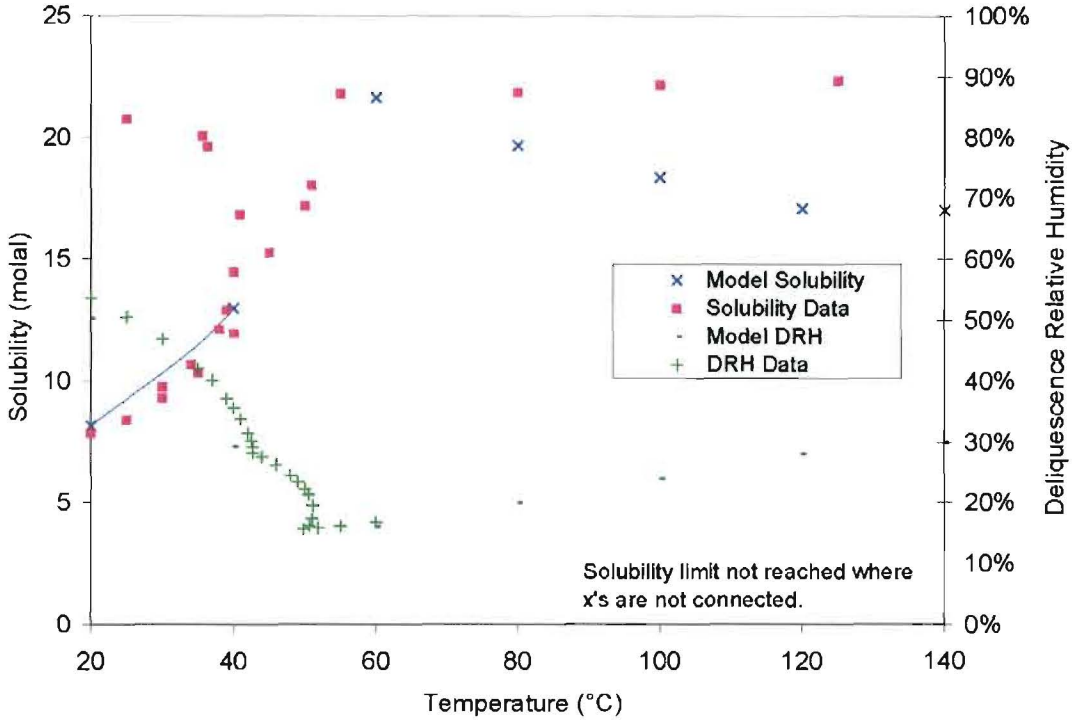
2. The note in Figure 7-24 that the solubility limit was not reached over the entire temperature range is wrong; it was reached at 140°C. The notation is corrected to read "Solubility limit only reached at 140°C". The corrected Figure 7-24 is shown below and in the revision to DTN MO0701EQ36IDPS.000.

3. There should be a line segment connecting the symbols for the 20°C and 40°C model results for $Ca(NO_3)_2$ in Figure 7-40 to indicate saturation with respect to $Ca(NO_3)_2$ at 20°C and 40°C. The note in the figure should state that "Solubilities are not reached where symbols are not connected." Figure 7-40 has been modified to correctly depict the data representing saturation conditions. The note in the figure has been modified to reflect this as well and is shown in the corrected Figure 7-40 below and in the revision to DTN MO0701EQ36IDPS.000.

4. The source file for Figure 7-50 should be "cacln25.xls". The caption in Figure 7-50 for the source spreadsheet file has been corrected to read "cacl2n25.xls" as shown below.

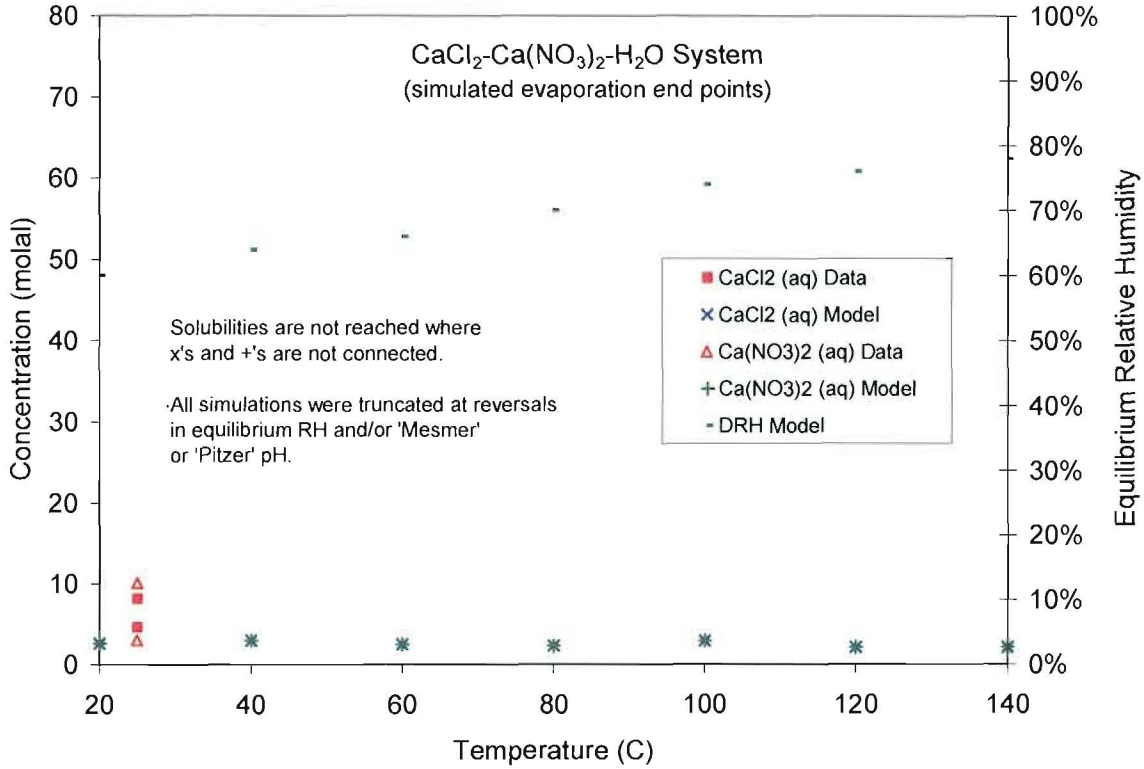
IV Impact Evaluation

Each of these errors is minor and does not affect the validation of the model, the limitations of the model, or the report's conclusions. While the errors in the source file names are a traceability issue, they are considered minor because the true source files were able to be discerned from the figures and the files listed in DTN MO0701EQ36IDPS.000. Because these errors are corrected here, they do not affect traceability and there is no impact from these corrections in downstream documents.



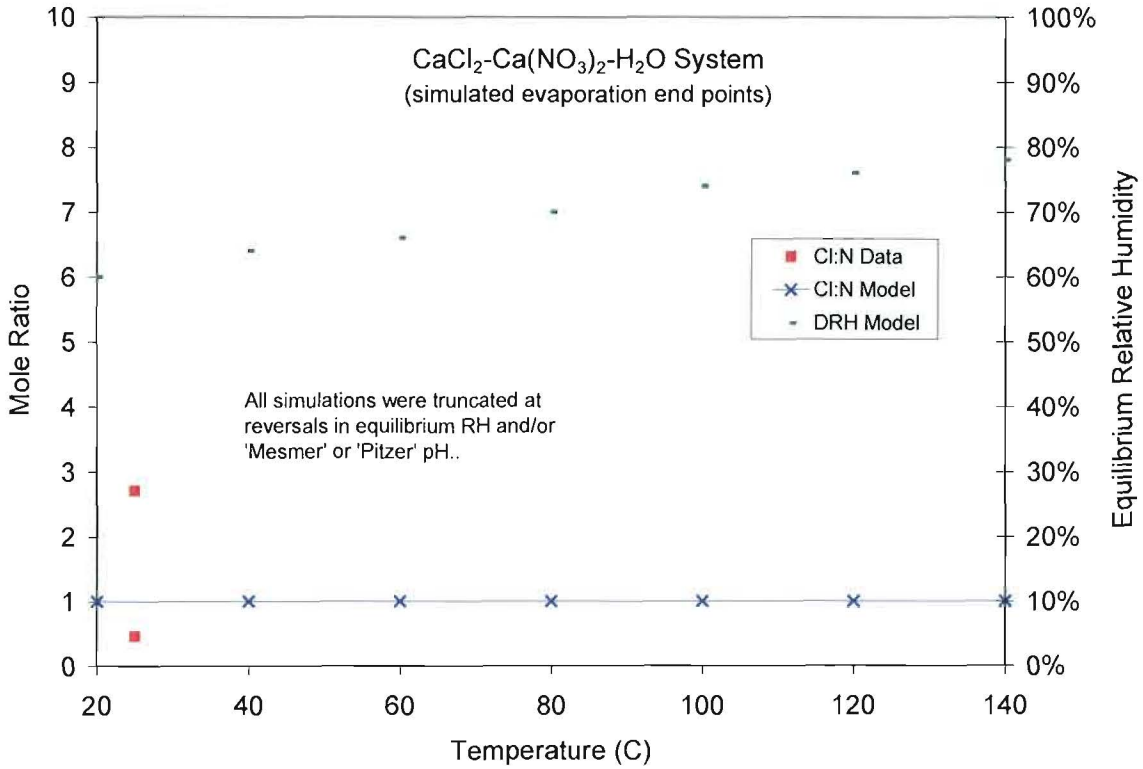
Output DTN: MO0701EQ36IDPS.000, file: *Linke binary1.zip*, *cano32ev.xls*.

Figure 7-23. Solubility and Deliquescence *RH* Predictions vs. Data for $Ca(NO_3)_2$



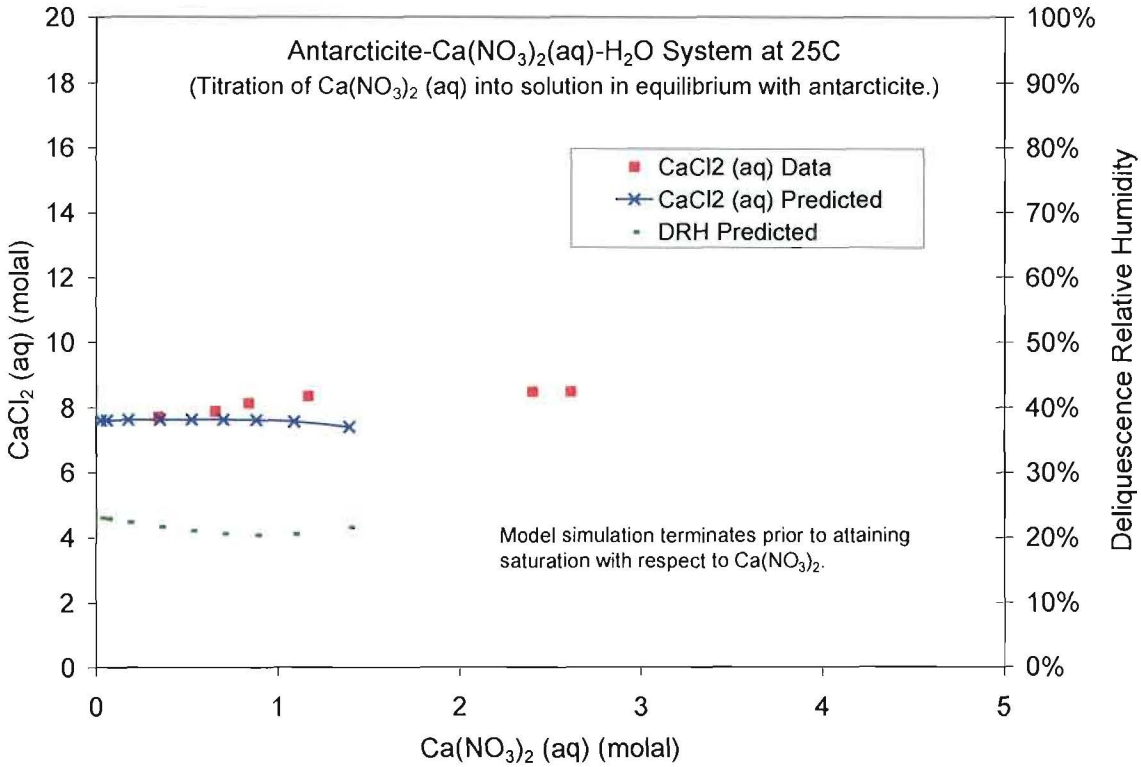
Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip*, *caclnev.xls*.

Figure 7-46. Model Predictions vs. Data for Ca-Cl-NO_3 Eutectic System



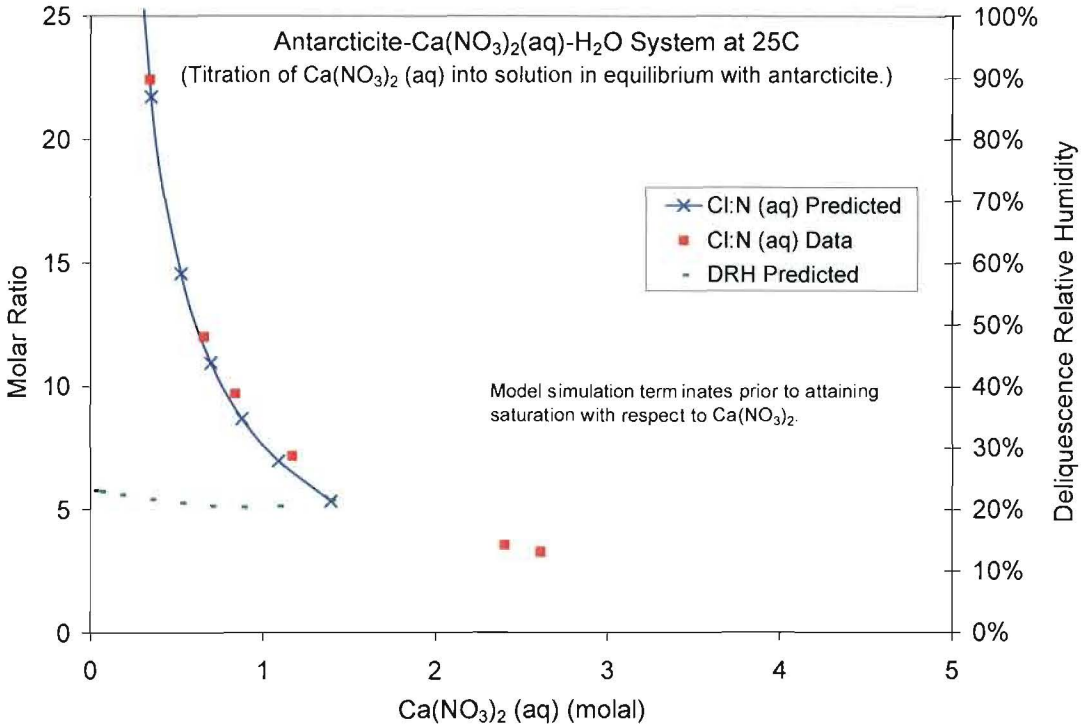
Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip*, *caclnev.xls*.

Figure 7-47. Cl:NO_3 Mole Ratio Predictions vs. Data for Ca-Cl-NO_3 Eutectic System



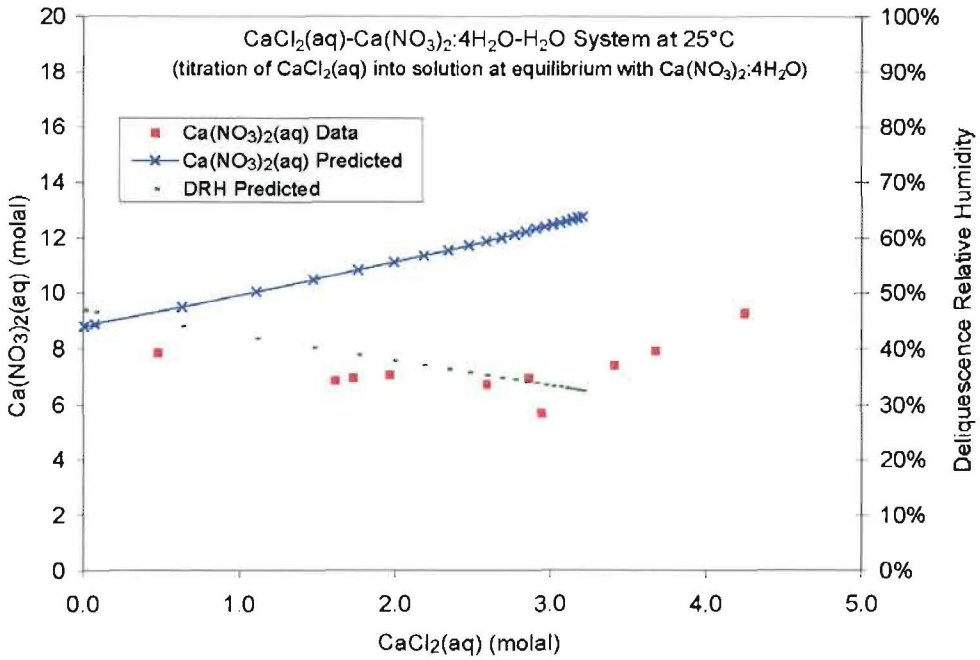
Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip, cacln25n.xls.*

Figure 7-48. $CaCl_2$ Solubility Predictions vs. Data as a Function of $Ca(NO_3)_2$ Concentration at 25°C



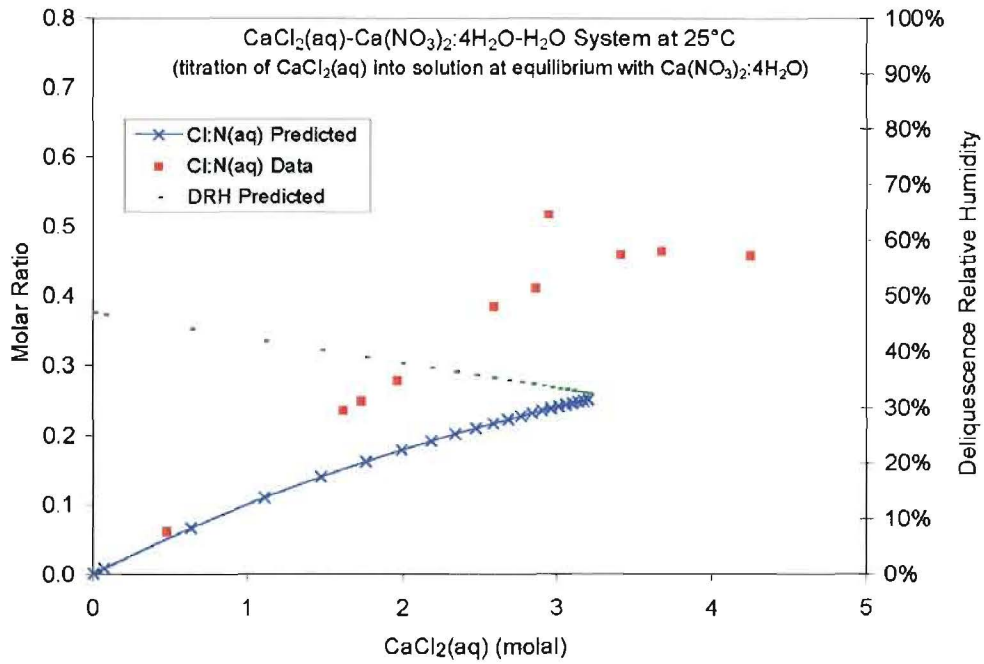
Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip*, *cacln25n.xls*.

Figure 7-49. $Cl:NO_3$ Mole Ratio Predictions at $CaCl_2$ Saturation vs. Data as a Function of $Ca(NO_3)_2$ Concentration at 25°C.



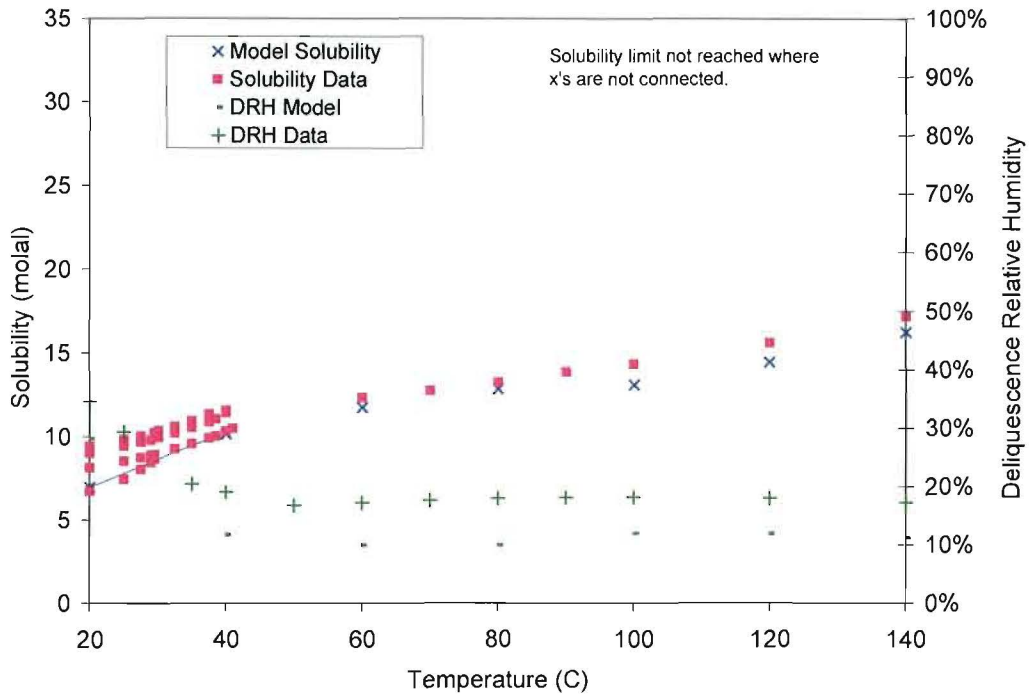
Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip*, *cacln25.xls*.

Figure 7-50. $Ca(NO_3)_2$ Solubility Predictions vs. Data as a Function of $CaCl_2$ Concentration at 25°C



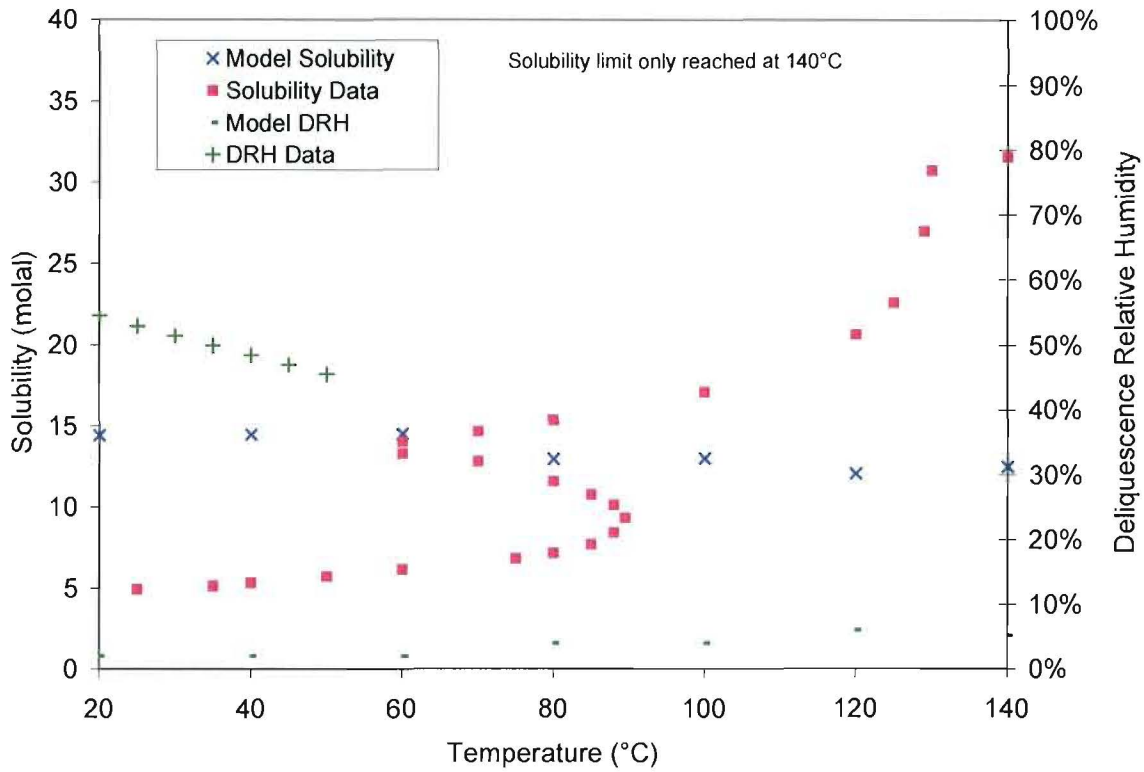
Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip, cacln25.xls.*

Figure 7-51. $Cl:NO_3$ Mole Ratio Predictions at $Ca(NO_3)_2$ Saturation vs. Data as a Function of $CaCl_2$ Concentration at 25°C



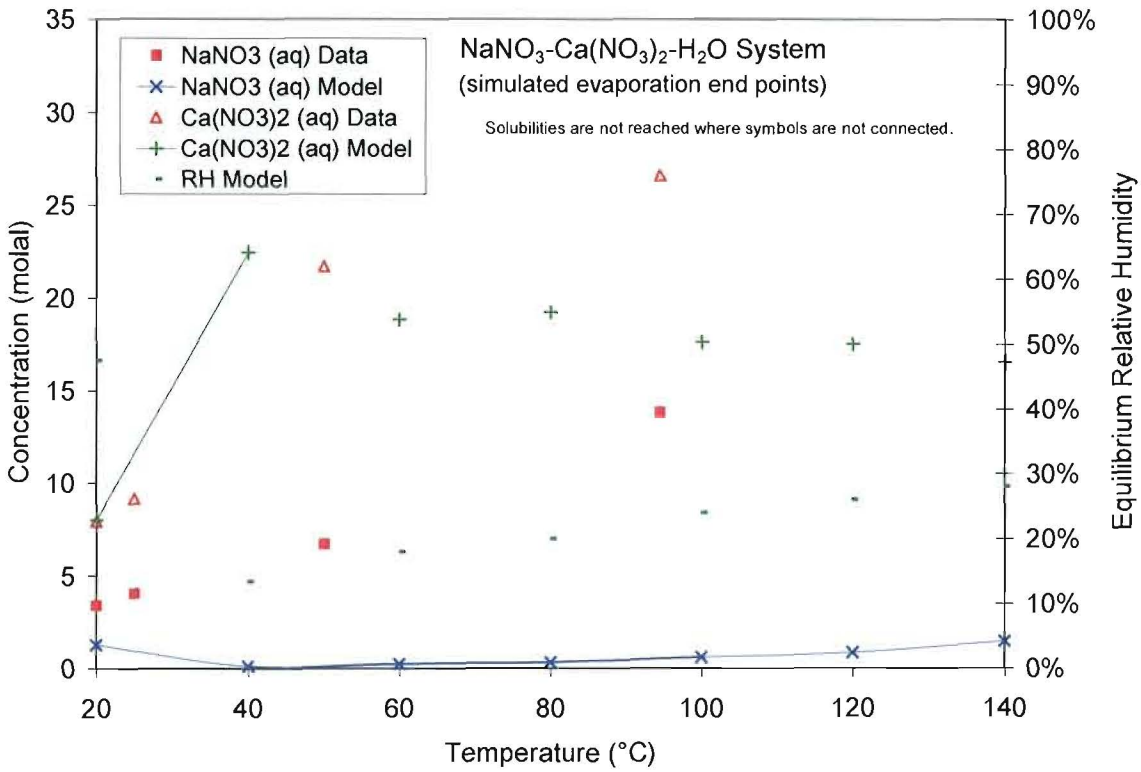
Output DTN: MO0701EQ36IDPS.000, file: Linke binary1.zip, cacl2ev.xls.

Figure 7-5. Solubility and Deliquescence *RH* Predictions vs. Data for $CaCl_2$.



Output DTN: MO0701EQ36IDPS.000, file: *Linke binary2.zip*, *mgno32ev.xls*.

Figure 7-24. Solubility and Deliquescence *RH* Predictions vs. Data for $Mg(NO_3)_2$.



Output DTN: MO0701EQ36IDPS.000, file: *Linke ternary1.zip, nacanev.xls.*

Figure 7-40. Model Predictions vs. Data for Na-Ca-NO_3 Eutectic System

CR 11044 Report Information

I Background Information Summary

The condition description for this CR is reproduced here as follows:

> **CR Title:** *"CR-11044: IDPS (ANL-EBS-MD-000045 REV 03) Pitzer Database (DTN SN0609T0502404.012) Area to Improve and Potential Limitation."*
>
> **CR Description:** *"This CR calls for further evaluation of the Ca-Cl-NO_3 system in the IDPS model to determine if this is an area in need of improvement and if it constitutes an additional model limitation. Use of the Pitzer database, per the IDPS model, in Ca-Cl-NO_3 systems has produced results that are not well behaved and do not seem reliable. For example, most of the EQ3/6 results presented in IDPS file Linke ternary1.xls in DTN MO0701EQ36IDPS.000 had their water activity reverse direction twice during evaporative evolution (this is usually taken as a sign that the activity model has reached a limit); specifically, in EQ3/6 output file caclne.6o a local minima of water activity is observed at about 0.72, after which it goes backup to 0.78, then continues downward. This first inflection occurs at the point where the new aqueous specie $CaCl^+$ becomes the dominant chloride species. This $CaCl^+$ species is relatively undeveloped with regards to Pitzer interaction parameters for mixed systems; in particular it does not contain any interaction for $CaCl^+$ with NO_3^-, which is a very important binary term in this type of mixture. Even at 25C the database model does not appear to be able to predict simultaneous saturation of $CaCl_2$ and $Ca(NO_3)_2$ as was (inaccurately) indicated by Figures 7-48 and 7-49 (addressed in CR 11022). This system should be further evaluated to see if the solubility remains within 1 order of magnitude per the validation criteria. If it does not then a model limitation is warranted."*

II Inputs and/or Software

No software or any types of calculations are used to evaluate the extent of conditions in this CR. No assumptions were used in this analysis.

III Analysis and Results

It is noted that the reversal of the activity of water (a(w)) in the CR for Ca-Cl-NO_3 ternary system happens in simulations at 20, 40, 60, 80, 100, and 120°C but not at 140°C. Although there was no reversal, there is an inflection in the activity of water for the run at 140°C and there is a sharp reversal in pH ('Pitzer' and 'Mesmer' pH; not NBS) at a(w)~0.78. Reversals in 'Pitzer' and 'Mesmer' pH values strongly correlate with reversals in the activity of water in all affected evaporation simulations. Therefore, it is very likely that this instance also reflects this issue. Further, NBS pH values for simulations at 60-140 °C tabulated in the spreadsheet 'caclnev.xls', worksheet 'Model', file: "Linke ternary1.zip", appear to be unreasonably large (i.e., pH>>14). Therefore, this could also be considered as an indicator of expanded uncertainty

in results at the evaporation endpoints. The reversals are minor (i.e., they were not persistent) because a(w) increased for only a short period of the simulation and then decreased again, ending at a much lower a(w) than the values where the reversals occurred.

It has been customary to truncate evaporation simulations whenever a(w) begins to increase because there is no clear reason why this should occur when water is being removed from the system. There is no physical or theoretical explanation for an increase in a(w) during evaporation; thus, such an occurrence indicates that the simulation is being affected by numerical issues. Although there is no *a priori* explanation for the reversal, this unexpected result may be due to the incomplete set of explicit Pitzer interaction parameters involving the aqueous species $CaCl^+$, NO_3^-, Cl^-, and Ca^{++}. The Pitzer database used in these simulations has binary interactions parameters for $CaCl^+ - Cl^-$, $Ca^{++} - Cl^-$, $Ca^{++} - NO_3^-$, and $NO_3^- - Cl^-$. The first three pairs can be used over a wide range of temperatures whereas the last one applies only at 25°C and 1 bar. There are no set of Pitzer parameters for ternary interactions such as $CaCl^+ - Cl^- - NO_3^-$, and $Ca^{++} - Cl^- - NO_3^-$ and their absence may cause the unexpected behavior of the evaporation calculations. Most of the parameters for the system $CaCl^+ - NO_3^- - Cl^- - Ca^{++}$ are based on studies of binary salts. Usage of these to analyze multi-component solutions at certain conditions of temperature and composition where binary and ternary interactions could be substantial may produce these unexpected results. Another potential cause is the capability of Pitzer parameters currently available in the thermodynamic database to accurately represent the behavior of the relevant electrolyte in the composition and temperature conditions of the simulations. Although significant accomplishments have been made in generating data to quantify Pitzer parameters for highly soluble salts as a function of temperature and solute concentration, there is uncertainty in the evaporation simulations, particularly in multi-component systems. These uncertainties may be within the range of validation of the model, however, truncation of the results is also a viable approach because the increased uncertainty in the results for these conditions is within the validation range as shown below.

Truncating the Ca-Cl-NO_3 ternary system simulations at the point where a(w) reverses directions results in different end points except for the simulation at 140°C, which showed no a(w) reversal but showed an unexpected inflection at a(w)~0.78 and a reversal in 'Pitzer' and 'Mesmer' pH values. Plotting the truncated model results would show different values than those in the original Figures 7-46 and 7-47. However, even with these values, there is very little difference in the model predictions at 20°C when compare to experimental data at 25°C. Thus, agreement between model simulations and experimental data is sufficient to satisfy model validation criteria and there is no impact on model validation or limitations.

The downstream applications of the IDPS model are documented in *Engineered Barrier System: Physical and Chemical Environment* (ANL-EBS-MD-000033 REV 06) and *Analysis of Dust Deliquescence for FEP Screening* (ANL-EBS-MD-000074 REV 01 AD01). The originator of the latter discovered the reversal in the IDPS Ca-Cl-NO_3 ternary system and initiated this CR. Thus, the originator dealt appropriately with this condition in his report and therefore there is no impact on the report ANL-EBS-MD-000074 REV 01 AD01. The originator of the former report (ANL-EBS-MD-000033 REV 06) documented around 400 IDPS model evaporation simulations.

To evaluate any impact of this issue within the *Engineered Barrier System: Physical and Chemical Environment* (ANL-EBS-MD-000033 REV 06), each spreadsheet lookup table was examined for a(w) reversals. Reversals were found in six spreadsheets (20p2t1.xls, 20p3t30.xls, 20p4t1.xls, 20p4t30.xls, 2bp2t30.xls, and 2jp2t1.xls). In addition, a sharp uncharacteristic change was observed at the end of 2ip4t70.xls. (The README file in DTN: SN0701PAEBSPCE.001 needs to be updated noting that these a(w) reversals occur in spreadsheets 20p2t1.xls, 20p3t30.xls, 20p4t1.xls, 20p4t30.xls, 2bp2t30.xls, 2jp2t1.xls, and 2ip4t70.xls and that these simulations should be truncated where a(w) begins to increase. This should be done by ANL-EBS-MD-000033 ERD 01.) For these seven spreadsheets, none of these reversals/changes occurred at a(w) values greater than 0.66 (i.e. RH>66%). The seven lookup tables generated from these are used within TSPA to determine conditions for initiation of corrosion on the drip shield and waste package, and to determine the aqueous composition in the invert. Because the aqueous composition in the invert is only relevant at 95% RH or higher; these a(w) reversals have no effect on modeling in the invert. For use in corrosion evaluation, it is noted that none of the seven tables noted above were sampled in the RH range (<66%) of the condition except perhaps for a single time step that might have been used when the RH was right at 66% (See CR 11044 attached file "CR 11044 Zwahlen e-mail.pdf"). Therefore, this truncation does not affect results used by TSPA.

To address the above issues within the IDPS model report (ANL-EBS-MD-000045 REV 03), Figures 7-46 and 7-47 (ANL-EBS-MD-000045 REV 03) were modified with the results at the appropriate truncation points and to include a note that these simulations were to be truncated where a(w) reverses directions or where there is a reversal in pH. The updated figures are given above in the text, as well as in the DTN MO0701EQ36IDPS.000. Additionally, a specific note was added to the readme file for this DTN as listed below.

Truncating the Ca-Cl-NO_3 ternary system simulations at the point where a(w) reverses directions results in different end points on Figure 7-46, except for the simulation at 140°C, which showed no a(w) reversal but showed an unexpected inflection at a(w)~0.78 and a reversal in 'Pitzer' and 'Mesmer' pH values. However, even with these truncated results, there is very little difference in the model predictions at 20°C when compare to experimental data at 25°C. Thus, agreement between model simulations and experimental data is sufficient to satisfy model validation criteria and there is no impact on model validation or limitations. (The updated Figure 7-47 does not show any differences).

In the case of the simluation at 140°C, where there is no reversal in water activity, the run was truncated when there is a sharp reversal in 'Mesmer' or 'Pitzer' pH (excluding NBS). As noted previously, there is a strong correlation between reversals in the activity of water and sharp reversals in 'Mesmer' or 'Pitzer' pH for all these runs. Therefore, a reversal in 'Mesmer' or 'Pitzer' pH should also be considered as an indicator of the evaporation simulation yielding erroneous data beyond certain value of water activity. The resulting end-points from the simulations at low temperatures are expected to be a closer representation of the salt solubility given the abrupt termination of the higher temperature simulations at relatively large water activities. As a concluding remark, it should be emphasized that this condition does not affect the model validation or its limitations. The updated figures with new end-points and explanatory notes are given above.

The README file for DTN: MO0701EQ36IDPS.000 has been updated to note as follows:

"NOTE, there are instances where a(w) reversals have occurred in the Ca-Cl-NO_3 ternary system (see the simulations in the file 'caclnev.xls') and it should be standard practice that all the simulations should be truncated either (a) where a(w) begins to increase in evaporation simulations or (b) where there is a sharp reversal in 'Pitzer' or 'Mesmer' pH that reflects the same issue."

The readme file of SN0609T0502404.012 has been updated as follows:

"NOTE, usage of this datafile has shown that the Ca-Cl-NO_3 ternary system has been found to be more uncertain at low RH when $CaCl^+$ becomes a dominant species. Related to this are instances where a(w) reversals have occurred in the Ca-Cl-NO_3 ternary system, and it should be standard practice that all the simulations should be truncated either (a) where a(w) begins to increase in evaporation simulations or (b) where there is a sharp reversal in 'Pitzer' or 'Mesmer' pH that reflects the same issue."

In addition, the Section 8.4 (Uncertainties and Limitations) is modified at the end of the third paragraph of the section as follows:

"NOTE, the Ca-Cl-NO_3 ternary system has been found to be more uncertain at low RH when $CaCl^+$ becomes a dominant species. Related to this are instances where a(w) reversals have occurred in the Ca-Cl-NO_3 ternary system, and it should be standard practice that all the simulations should be truncated either (a) where a(w) begins to increase in evaporation simulations or (b) where there is a sharp reversal in 'Pitzer' or 'Mesmer' pH that reflects the same issue."

IV Impact Evaluation

Although the updates are needed to improve transparency and provide an additional caution regarding application of the model to specific ternary systems where uncertainties may be larger, there are no impacts to the model conclusions and there is no impact on TSPA-LA of the truncations made to files already generated within the Ca-Cl-NO_3 ternary system.

CR 11000 Report Information

I Background Information Summary

The condition description for this CR is reproduced here as follows:

CR Title: "Incorrect Documentation of 2 Inputs in ANL-EBS-MD-000045 REV 03"

CR Description: "The following 2 input documentation issues in ANL-EBS-MD-000045 REV 03 were taken from Audit LLQA-IA-07-08. Audit Issue#5. Section 6.4 of ANL-EBS-MD-000045, Rev. 03 (p. 6-10) references BSC, 2001 [DIRS 155640], Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier, ANL-EBS-MD-000001, Rev. 00. This reference was cancelled. It was used for indirect input. It was unclear where this reference was demonstrated to be suitable for intended use and justified within the technical product documentation. SCI-PRO-006, Rev. 5 no longer allows use of cancelled documents for providing input. Audit Issue #16. DTN SN0612T0502404.014 is described in Appendix I and in Section 9.3 as a source of data for the Pitzer database. This DTN is not identified in Table 4-1 as direct input as required by SCI-PRO-006."

II Inputs and/or Software

No software or any types of calculations are used to evaluate the extent of conditions in this CR. No assumptions were used in this analysis.

III Analysis and Results

Note that the "Issues" below are quoted from the CR documentation.

Issue #5: *(1) The use of the cancelled document ANL-EBS-MD-000001 Rev 00 ICN 02 and related* [sic] *is deferred to the assessment given for audit issue #9 of CR 11101. For completeness, the arguments use* [sic] *to resolve audit issue #9 of CR 11101 are repeated here. There are two general references to ANL-EBS-MD-000001 Rev 00 ICN 02 [DIRS 155640]. One is to Table 8 on p. 29 (Greenspan, 1977 [DIRS 104945]), which has to do with equilibrium relative humidity values for various pure salts (item 1 under audit issue #9 of CR 11101), and the other is to a 100x J13 evaporation experiment (item 2 under audit issue #9 of CR 11101). A search of the IDPS report for citations of DIRS 155640 indicates that the extent of condition is limited to these two general references. The only reference to Table 8 is the one noted in the CR (page 6-10 of Section 6.4). For the 100x J13 evaporation experiment, citations in addition to the one noted in the CR can be found in Table 4-5, Table 4-22, Section 7.2, and Section 7.2.2. It should also be noted that ANL-EBS-MD-000001 Rev 00 ICN 02 is a cancelled document but it was in the report as an indirect input.*

The corrections made to address these issues are:

(1) The citation of ANL-EBS-MD-000001 Rev 00 ICN 02 [DIRS 155640] is replaced with that of Greenspan (1977, p. 92, [DIRS 104945]) and it is noted that the salt is $MgCl_2$, not $CaCl_2$. This correction needs to be made in p. 6-10, 2nd paragraph, last

sentence. The modified sentence should read as: "If a magnesium chloride salt is the most soluble and hygroscopic salt deposited, the critical relative humidity would be around 22% (Greenspan (1977, p. 92, [DIRS 104945]) or lower depending on the abundance of additional soluble components."

A change in the DIRS report ANL-EBS-MD-000045 (REV 03) is also needed to reflect this modification.

(2) Concerning the 100x J13 evaporation experiments, the reference on page 7-56, Section 7.2.2, of the report ANL-EBS-MD-000045 (REV 03) should cite pages 39, 40, and 69 from ANL-EBS-MD-000001 Rev 00 ICN 02. However, because the report ANL-EBS-MD-000001 (Rev 00 ICN 02) is cancelled the citation for these evaporation experiments is being changed to DTN: LL000202905924.117 [DIRS 144913].

Table 4-5, 10th row, 1st column is corrected as follows:
The error "(BSC 2001 [DIRS 155640]; DTN: LL000202905924.117 [DIRS 144913])" is replaced with "(DTN: LL000202905924.117 [DIRS 144913])"

Table 4-22 the Title and its entry in the Table of Contents are corrected as follows:
The error "(BSC 2001 [DIRS 155640])" is corrected to read "DTN: LL000202905924.117 [DIRS 144913]"

Section 7.2, the 1st paragraph, 2nd sentence, is corrected as follows,
Delete the erroneous "the report Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier (BSC 2001 [DIRS 155640])."

In Section 7.2.2, the 1st paragraph, 1st sentence, needs to be modified to read as follows: "In another synthetic J-13 well water evaporation experiment, a synthetic 100-times concentrated (100x) average J-13 well water was dripped through a column of heated tuff into a Teflon beaker (DTN: LL000202905924.117[DIRS 144913])".

For Figures 7-70, 7-71, and 7-72, their captions and their entries in the Table of Contents are each corrected as follows:
The error "(BSC 2001 [DIRS 155640])" is corrected to read "DTN: LL000202905924.117 [DIRS 144913]"

Section 9.1, the erroneously listed reference BSC 2001 [DIRS 155640] is deleted.

A change in the DIRS report ANL-EBS-MD-000045 (REV 03) is also needed to reflect this modification.

Evaluation: These changes are of no impact on downstream documents or TSPA-LA. It should be noted that the report ANL-EBS-MD-000001 Rev 00 ICN 02 is cancelled, but the data from the experiments are in the unqualified DTN: LL000202905924.117, which is available for use and is already cited in Tables 4-5 and 4-22. It should also be noted that the IDPS conclusions,

limitations, validation, uncertainty, and use would be unchanged even if this validation simulation had not been included in the report. Removal of the cancelled reference is possible without impacting the conclusions obtained from the model results.

Issue #16: The DTN SN0612T0502404.014 which refers to the thermodynamic database *data0.ymp.R5* is used in Appendix I and in Section 9.3 as a data source for the Pitzer database developed in ANL-EBS-MD-000045 (REV 03). This DTN is not identified in Table 4-1 as direct input as required by SCI-PRO-006. (1) *Evaluation of this issue indicates that this is most likely a typo or an inadvertent omission in Table 4-1. The DTN SN0612T0502404.014 is qualified and its omission from Table 4-1 does not have any effect on the mode or its conclusions.*

An updated form of the row in Table 4-1 containing this input source information and to be inserted within the table section "Single-phase mineral thermodynamic data, mineral solubility data, and solubility product constants" is shown below.

Type of Input	Source	Qualifications
Single-phase mineral thermodynamic data, mineral solubility data, and solubility product constants	DTN: SN0612T0502404.014 [DIRS 178850]	Product output

A change in the DIRS report ANL-EBS-MD-000045 (REV 03) is also needed to reflect this modification.

Evaluation: The correct data were used and this is a correction of the documentation to indicate that usage in the Table 4-1. The database is qualified product output and there is no impact to the conclusions of the IDPS report ANL-EBS-MD-000045 (REV 03).

Issue #29: *There is a typo in in Eq. I-19 is related to a reversed sign in the second term of the right hand side of the equation when compared to Eq. 62 (p. 89) in the source Pitzer 1991 [DIRS 152709.*

The error in Equation I-19 as it appears in the current version of the IDPS report is given below:

$$\phi = 1 - (2/\sum_i m_i)[-A_\phi I^{3/2}/(1 + b\sqrt{I}) + \sum_c \sum_a m_c m_a \{ B^\phi_{ca}(I) + ZC_{ca}\}$$
$$+ \sum_{c \neq c'}\sum m_c m_{c'}[(\Phi_{cc'} + I\Phi_{cc'}') + \sum_a m_a \psi_{cc'a}] + \sum_{a \neq a'}\sum m_a m_{a'}[(\Phi_{aa'} + I\Phi_{aa'}') + \sum_c m_c \psi_{caa'}] \quad \text{(Eq. I-19)}$$

The above erroneous equation is corrected by changing the sign in the second term of the right hand side of Eq. I-19 so the corrected equation reads as:

$$\phi = 1 + (2/\sum_i m_i)[-A_\phi I^{3/2}/(1 + b\sqrt{I}) + \sum_c \sum_a m_c m_a \{ B^\phi_{ca}(I) + ZC_{ca}\}$$
$$+ \sum_{c \neq c'}\sum m_c m_{c'}[(\Phi_{cc'} + I\Phi_{cc'}') + \sum_a m_a \psi_{cc'a}] + \sum_{a \neq a'}\sum m_a m_{a'}[(\Phi_{aa'} + I\Phi_{aa'}') + \sum_c m_c \psi_{caa'}] \quad \text{(Eq. I-19)}$$

consistent with Eq. 62 in Pitzer (1991 [DIRS 152709]).

In addition, the review of equations within the Report indicated that Eq. I-15 needs to be corrected to include the last term on the right hand side of the equation inside the square brackets.

The erroneous equation is shown here:

$$\begin{aligned} G^{EX}/(n_w RT) = & -(4IA_\phi/b)\ln(1 + b\sqrt{I}) + (2\nu_M\nu_X)m^2[\beta^{(0)}_{MX} \\ & + 2\{\beta^{(1)}_{MX}/\alpha_1{}^2 I\}\{1 - (1 + \alpha_1\sqrt{I})e^{-\alpha_1\sqrt{I}}\} \\ & + 2\{\beta^{(2)}_{MX}/\alpha_2{}^2 I\}\{1 - (1 + \alpha_2\sqrt{I})e^{-\alpha_2\sqrt{I}}\}] \\ & + (\nu_M z_M)mC_{MX} \end{aligned} \qquad \text{(Eq. I-15)}$$

The corrected equation is given by:

$$\begin{aligned} G^{EX}/(n_w RT) = & -(4IA_\phi/b)\ln(1 + b\sqrt{I}) + (2\nu_M\nu_X)m^2[\beta^{(0)}_{MX} \\ & + 2\{\beta^{(1)}_{MX}/\alpha_1{}^2 I\}\{1 - (1 + \alpha_1\sqrt{I})e^{-\alpha_1\sqrt{I}}\} \\ & + 2\{\beta^{(2)}_{MX}/\alpha_2{}^2 I\}\{1 - (1 + \alpha_2\sqrt{I})e^{-\alpha_2\sqrt{I}}\} \\ & + (\nu_M z_M)mC_{MX}] \end{aligned} \qquad \text{(Eq. I-15)}$$

The form of Eq. I-15 needs to be consistent with Eqs. 47 through 49 in Pitzer (1991 [DIRS 152709]).

Evaluation: All Pitzer interactions terms in the governing equations are accurately taken into account in the EQ3/6 code and are therefore captured accurately in the model calculation results. There is no impact to the model calculations or conclusions given that the equations are correctly implemented into the EQ3/6 code. Correction of this documentation error does not impact any conclusions.

IV Impact Evaluation

All issues raised in CR 11100 have been carefully addressed. The changes made to address this CR are documentation corrections that have no impact on the conclusions originally documented in AMR *In-Drift Precipitates/Salts Model* (ANL-EBS-MD-000045 REV 03).

CR 11101 Report Information

I Background Information Summary

The condition description for this CR is reproduced here as follows:

CR Title: "Errors in Traceability in 4 References in ANL-EBS-MD-000045, Rev 03"

CR Description: "Audit Issue #9 Errors were found in the references to document ANL-EBS-MD-000001 Rev 00 ICN 02 (Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier) in the text of ANL-EBS-MD-000045 Rev 03 (IDPS Model).

1. Page 6-10 of the IDPS Model AMR references $CaCl_2$ data from page 29 of ANL-EBS-MD-000001 Rev 00 ICN 02; however, the table on page 29 of ANL-EBS-MD-000001 Rev 00 ICN 02 does not include CaCl2 data. Instead of $CaCl_2$ data the data used in the IDPS Model comes from $MgCl_2$ from page 29 of ANL-EBS-MD-000001 Rev 00 ICN 02. This does not affect development of the IDPS model.
2. Data used in Section 7.2.2 for validation of the IDPS Model is described in the IDPS AMR, page 7-56 as coming from pages 6-16 of ANL-EBS-MD-000001 Rev 00 ICN 02. These pages referenced do not correctly point to the actual pages that contain the data used for the IDPS Model validation. The pages containing the referenced information are actually 39 and 65 69 of ANL-EBS-MD-000001 Rev 00 ICN 02.

Audit Issue #11 A comparison of the data in DTN: SN0611T0509206.006 with two figures illustrating that data (Figures 6-4 and Figures 6-7 in ANL-EBS-MD-000045, Rev. 03) revealed that the figures did not exactly match the data in the DTN.

Audit Issue #29 Equation I-19 on p. I-8 of ANL-EBS-MD-000045 references Pitzer 1991 [DIRS 152709] as the source. Review of the source identified a similar equation on p.89 of the source as equation (62). Line personnel verified that a sign error exists in the equation I-19."

II Inputs and/or Software

No software or any types of calculations are used to evaluate the extent of conditions in this CR. No assumptions were used in this analysis.

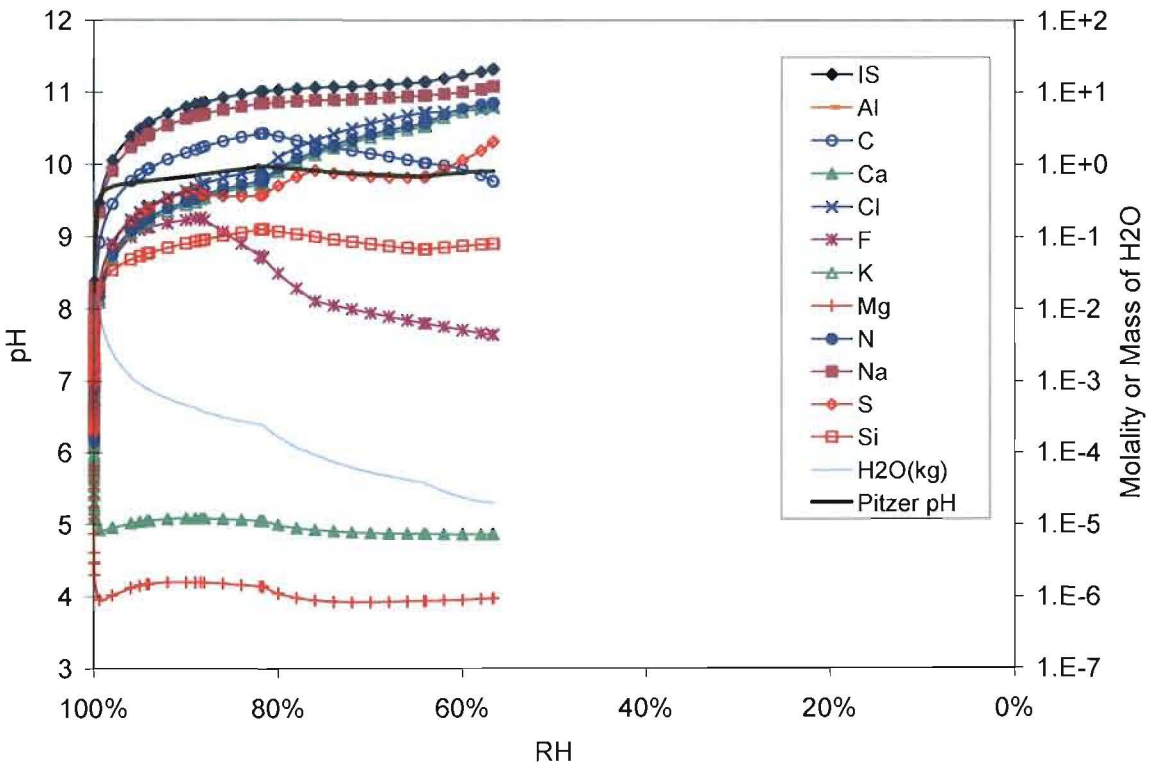
III Analysis and Results

Issue #9: *(1) There are two general references to ANL-EBS-MD-000001 Rev 00 ICN 02 [DIRS 155640]. One is Greenspan (1977, [DIRS 104945]) to Table 8 on p. 29, which has to do with equilibrium relative humidity values for various pure salts (item 1), and (2) the other is DTN: LL000202905924.117 to a 100x J13 evaporation experiment. A search of the IDPS report for citations of DIRS 155640 indicates that the extent of condition is limited to these two general references. The only reference to Table 8 is the one noted in the CR (page 6-10 of Section 6.4). For the 100x J13 evaporation experiment, citations in addition to the one noted in the CR can be found in Table 4-5, Table 4-22, Section 7.2, and Section 7.2.2. These experimental data is given in the unqualified DTN: LL000202905924.117 and is available for use.*

See above section covering CR 11100 for the corrections associated with Issue #9.

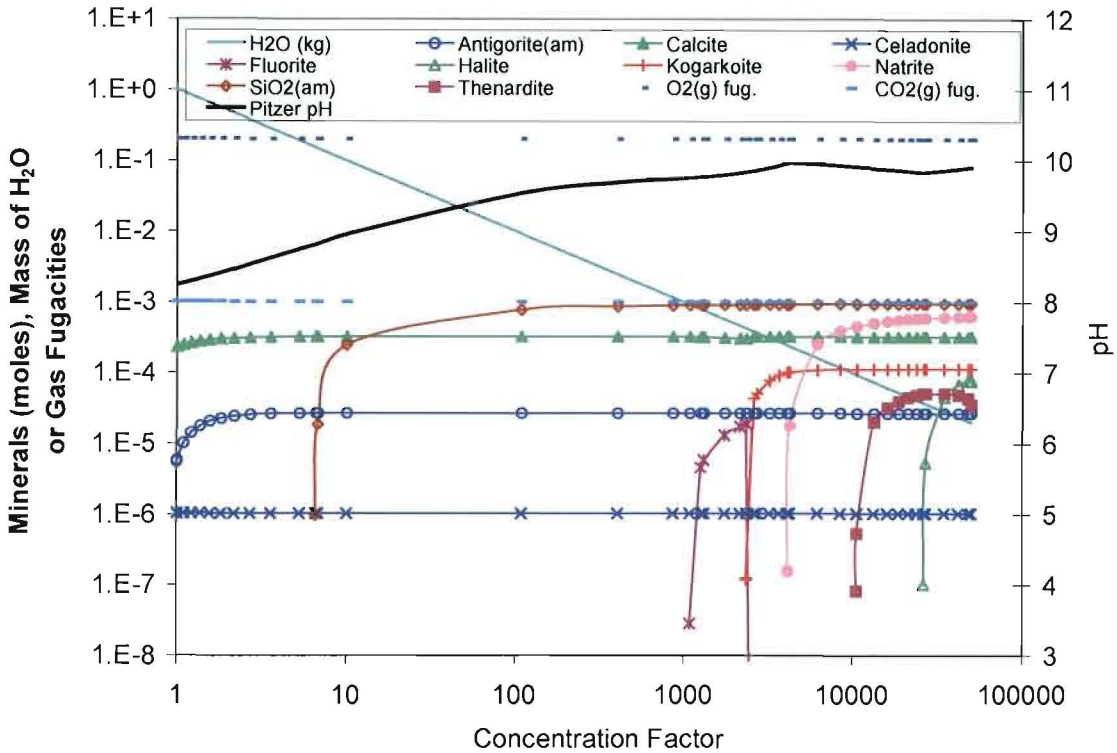
Issue #11: (1) *Evaluation of this issue indicates that each figure in Section 6.7 (Figures 6-4 and Figures 6-7 in ANL-EBS-MD-000045, Rev. 03) does not exactly match the values in the cited DTN. Accurate figures are provided in the DTN in the files containing the calculations. These figures are for demonstration only and do not have any effect on model validation, limitations, uncertainty, or use in TSPA-LA.*

(1) Figures 6-4 and 6-7 in Section 6.7 do not exactly match the data in the DTN but accurate figures can be found in the files in the DTN that contain the calculations. Therefore, this discrepancy does not impact the model results or the conclusions derived from them. The figures reflecting accurate representation of the data are already contained in DTN SN0611T0509206.006 and are shown below.



Output DTN: SN0611T0509206.006, file : *j13c3t7e.xls.*

Figure 6-4. Example Aqueous Composition Evaporation Predictions vs. *RH*



Output DTN: SN0611T0509206.006, file : *j13c3t7e.xls.*

Figure 6-7. Example Mineral Precipitation Evaporation Predictions vs. *CF*

Evaluation: It should be noted that DTN SN0611T0509206.006 already contains the correct figures and the figures in Section 6.7.1 are used only to provide a demonstration of the types of calculations that can be performed with the model. For these reasons, there is no need to perform any further analysis given the correct figures above, and the conclusions of the document are not affected by this issue.

Issue #29: *There is a typo in Eq. I-19 is related to a reversed sign in the second term of the right hand side of the equation when compared to Eq. 62 (p. 89) in the source Pitzer 1991 [DIRS 152709.*

See above section covering CR 11100 for the corrections associated with Issue #29.

IV Impact Evaluation

All issues raised in CR 11101 have been carefully addressed. The suggested changes made to address this CR have no impact on the conclusions originally documented in AMR *In-Drift Precipitates/Salts Model* (ANL-EBS-MD-000045 REV 03). No other documents are impacted by these changes made in this ERD.

CR 11616 Report Information

I Background Information Summary

CR Title: "Missing labels in two figures"

CR Description: "Figures 7-68 and 7-72 in ANL-EBS-MD-000045 REV 03 are missing labels to identify the elements for each data point. These labels apparently were lost during technical editing when converting the figures to pdf because they are not missing in the Word document drafts (at least through draft REV 03D).

The text in ANL-EBS-MD-000045 REV 03 associated with these figures clearly indicates which elements were well-predicted and which were the least well-predicted. Thus, with regard to ANL-EBS-MD-000045 REV 03 by itself, the labels in the figures are not necessary.

SAR section 2.3.5 replicates these figures but includes the data point labels. The SAR cites Figures 7-68 and 7-72 of ANL-EBS-MD-000045 REV 03 as the source. In turn, the figures in ANL-EBS-MD-000045 REV 03 cite the source DTN and spreadsheets that provide the figures with the data point labels. Thus, while there may be a minor traceability issue from SAR 2.3.5 to ANL-EBS-MD-000045 REV 03, there is no traceability issue to the primary source."

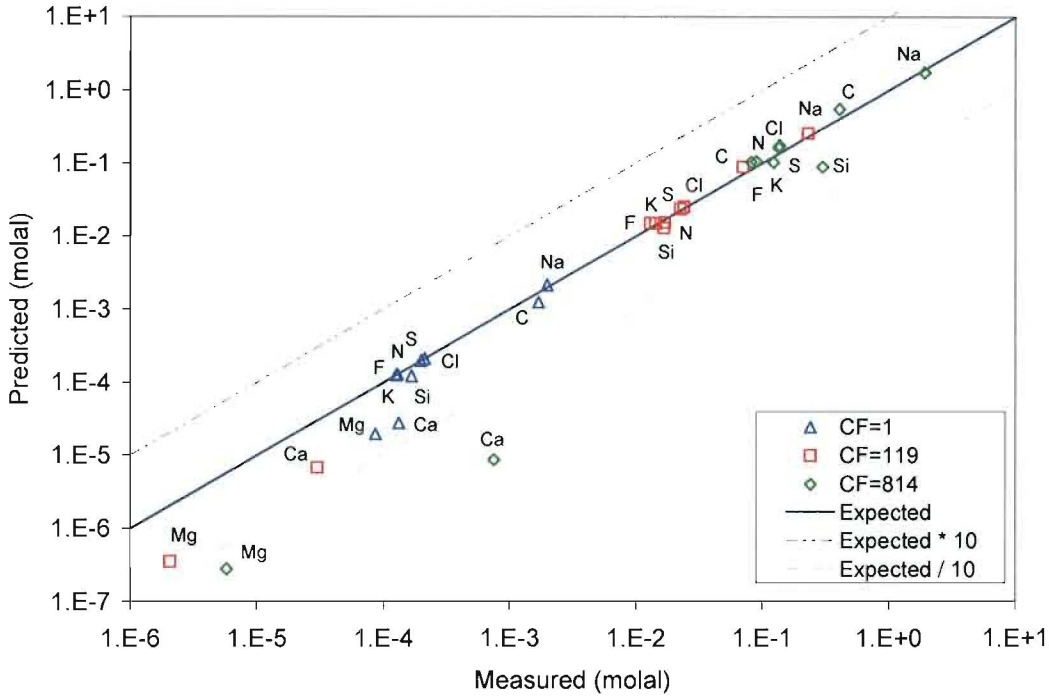
II Inputs and/or Software

No software or any types of calculations are used to evaluate the extent of conditions in this CR. No assumptions were used in this analysis.

III Analysis and Results

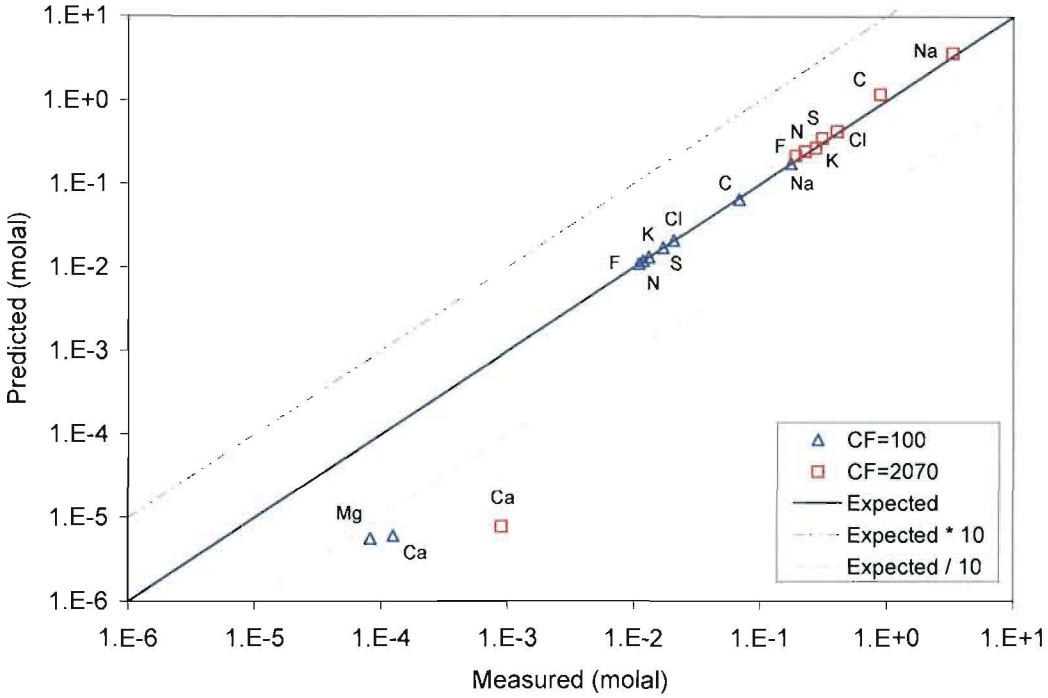
Issue #1: *Missing labels for data points in figures 7-68 and 7-72 in ANL-EBS-MD-000045 (REV 03).*

Evaluation: Per the CR description, traceability is sufficient given the relevant text explanation related to the significance of these figures in the report ANL-EBS-MD-000045 (REV 03). Also, the original figures are in DTN: SN0702T0509206.008, files 'j13n1pitpH.xls' and 'j13b1 v3.xls', and include the missing labels for the data points. Moreover, the figures with labeled data points that are used in SAR section 2.3.5 were obtained directly from the DTN source because they are correct. Therefore, the corrected figures 7-68 and 7-72 are given below to replace those with missing labels in the report ANL-EBS-MD-000045 (REV 03).



Output DTN: SN0702T0509206.008, file: *j13n1pitpH.xls*.

Figure 7-68. Predicted vs. Measured Concentrations for Synthetic J-13 Water Evaporation Experiments of Rosenberg et al. (1999 [DIRS 125338])



Output DTN: SN0702T0509206.008, file: *j13b1 v3.xls*.

Figure 7-72. Predicted vs. Measured Concentrations for 100x Synthetic J-13 Water Evaporation Experiments (DTN: LL000202905924.117 [DIRS 144913])

IV Impact Evaluation

Because the DTN contains the figures with the correct labels as shown above and the SAR used the correct figures already there is no impact to downstream documents. Because the information was already contained within the output files of the report and the correction of the figures is shown above, there is no impact to the conclusions of the In-Drift Precipitates/Salts Model (ANL-EBS-MD-000045 Rev 03).