NUCLEAR WASTE MANAGEMENT PROCEDURE
Sandia National Laboratories

Verification and Validation Plan Criteria

Form Number: NP 19-1-3

Page 1 of 1

1. **Software Name:** EQ3/6
2. **Software Version:** 8.0a
3. **Document Version:** 8.10
4. **ERMS #:** 550239

Prior to sign-off of the VVP, all items shall be appropriately addressed by the code sponsor so that "**Yes**" or "**N/A**" may be checked. Include this form as part of the VVP.

5. **Sufficient Test Cases** ☒ Yes
Does the VVP identify sufficient test cases and acceptance criteria to ensure the final software and end product satisfies the requirements of the RD? (Check Yes if peer review is identified to fulfill the validation requirements)

6. **Adequacy of Test Cases** ☒ Yes
Do the test cases demonstrate that the code adequately performs all intended functions and produces valid results for problems encompassing the range of permitted usage?

7. **Operational Control** ☒ Yes
If the software is used for operational control, do tests demonstrate required performance over the range of operation of the controlled function or process?

8. **Unintended Functions** ☒ Yes
Do the test cases show that the code does not perform any unintended function that either by itself or in combination with other functions can degrade the intended outcomes of the software?

9. **Test Result Validation.** (check one or more, where applicable as based on code functionality)
The test results will be compared to the following:

- hand calculations,	☐ Yes	☒ N/A
- manual inspection,	☐ Yes	☒ N/A
- calculations using comparable proven problems,	☒ Yes	☐ N/A
- empirical data and information from confirmed published data and correlation's and/or technical literature,	☒ Yes	☐ N/A
- other validated software of similar purpose,	☒ Yes	☐ N/A
- other independent software of similar purpose.	☐ Yes	☒ N/A
A documented peer review will be performed.	☐ Yes	☒ N/A
Do the test cases describe how the code results will be validated?	☒ Yes	

10. **Does the VVP specify the following, where applicable as based on code functionality?**

(a) required tests and test sequence	☒ Yes	☐ N/A
(b) required ranges of input parameters	☒ Yes	☐ N/A
(c) identification of the stages at which testing is required	☒ Yes	☐ N/A
(d) criteria for establishing test cases	☒ Yes	☐ N/A
(e) requirements for testing logic branches	☐ Yes	☒ N/A
(f) requirements for hardware integration	☐ Yes	☒ N/A
(g) anticipated output values	☒ Yes	☐ N/A
(h) acceptance criteria	☒ Yes	☐ N/A

11. **Installation and Regression Testing** ☒ Yes
Are test cases which are suitable for installation testing and regression testing identified in the set of verification and validation test cases?

12.	Yongliang Xiong **Code Team/Sponsor's Name** (*print*)	Signature	01/21/2010 Date
13.	Ahmed E. Ismail **Technical Reviewer's Name** (*print*)	Signature	1/21/2010 Date
14.	Christi D. Leigh **Responsible Manager's Name** (*print*)	Signature	1/21/2010 Date
15.	Jennifer Long **SCM Coordinator's Name** (*print*)	Signature	1/25/10 Date

Key for check boxes above:
Check **Yes** for each item reviewed and found acceptable
Check **N/A** for items not applicable, where applicable as based on code functionality

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NUCLEAR WASTE MANAGEMENT PROCEDURE Sandia National Laboratories	**Validation Document Criteria**	**Form Number: NP 19-1-7** **Page 1 of 1**

1. **Software Name:** EQ3/6
2. **Software Version:** 8.0a
3. **Document Version:** 8.10
4. **ERMS #:** 550239

Prior to sign-off of the VD, all items shall be appropriately addressed by the code sponsor so that "**Yes**" or "**N/A**" may be checked. Include this form as part of the VD.

5. **Is the following information included, where applicable?**
   - (a) computer program and version tested ☒ Yes ☐ N/A
   - (b) computer hardware and operating system used ☒ Yes ☐ N/A
   - (c) test equipment and calibrations ☐ Yes ☒ N/A
   - (d) date of test ☒ Yes ☐ N/A
   - (e) tester or data recorder ☒ Yes ☐ N/A
   - (f) simulation models used, ☒ Yes ☐ N/A
   - (g) test problem input and output files ☒ Yes ☐ N/A
   - (h) results and acceptability ☒ Yes ☐ N/A
   - (I) action taken in connection with any deviations noted ☒ Yes ☐ N/A
6. **Test Result Validation**
   The test results were compared to the following (check one or more, where applicable as based on code functionality):
   - hand calculations, ☐ Yes ☒ N/A
   - manual inspection, ☐ Yes ☒ N/A
   - calculations using comparable proven problems, ☒ Yes ☐ N/A
   - empirical data & information from confirmed published data and correlations and/or technical literature, ☒ Yes ☐ N/A
   - other validated software of similar purpose, ☒ Yes ☐ N/A
   - other independent software of similar purpose. ☐ Yes ☒ N/A
7. **Test Documentation Acceptability** ☒ Yes
   Do the tests meet the acceptance criteria identified in the approved VVP?
8. **Test Documentation Repeatability** ☒ Yes
   Are the tests documented in sufficient detail such that they can be repeated?
9. **Computer File Documentation** ☒ Yes
   Are the test case input and output files included in the Validation Document?
10. **Understandability of Documentation** ☒ Yes
    Are the validation methods, test data, results, and conclusions documented in a form that can be understood by an independent, technically competent individual?

11. Yongliang Xiong **Code Team/Sponsor** (*print*)	Yongliang Xiong Signature	01/21/2010 Date
12. Ahmed E. Ismail **Technical Reviewer** (*print*)	Signature	1/21/2010 Date
13. Christi Leigh **Responsible Manager** (*print*)	Signature	1/21/10 Date
14. Jennifer Long **SCM Coordinator** (*print*)	Jennifer Long Signature	1/25/10 Date

Key for check boxes above:

Check **Yes** for each item reviewed and found acceptable
Check **N/A** for items not applicable

Appendix A

NUCLEAR WASTE MANAGEMENT PROCEDURE Sandia National Laboratories	**Document Review and Comment (DRC)**	**Form Number: NP 6-1-1** **Page 1 of** 2

Entries must be complete, legible, and in reproducible ink or completed electronically.

Reviewers who have no comments must record "No Comments" in the comment block.

1. Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~d~~ AEI 1-22-10

2. Revision #: (if applicable) ~~N/A~~ 8.10 AEI 1-22-10

3. Document Description: (e.g. abstract, procedure, SAND report) NP 19-1 Document

4. Type of Review & Criteria. Shall be verified by the Reviewer:

☐ Technical (Technical adequacy, accuracy, completeness)
-Are objectives clearly stated and fulfilled?
-Is the technical activity clearly described?
-Are equations/calculations accurate?
-Does logic lead to reasonable conclusions?
-Are the results drawn from the data supported by data presented?
-*Data/tables/figures: Are they easily understood? Are legends complete?*
-Are the conclusions and assumptions adequately supported?

☐ QA (Compliance and completeness)
-Are applicable QA requirements adequately cited/ incorporated and met (content, reviews)?
- Has the technical review been performed by someone who is "independent"? (see NP 6-1, Section 2.2)

☒ Management(Completeness and correctness)
-Is report consistent with policy?
-Is there consensus with other program documents?
-Does the document meet applicable criteria?

☐ Other type of review (please specify or leave blank if not applicable)

5. Additional criteria: (if applicable)

6. Approval signatures:

Yongliang Xiong
Review Requester's/Delegate's Printed Name

Review Requester's/Delegate's Signature

1/21/2010
Date

Christi Leigh
Reviewer's Printed Name

Reviewer's Signature

1/21/10
Date

Document Review and Comment (DRC)

Form Number:
NP 6-1-1
Page 2 **of** 2

Type of Review: ☐ Technical ☐ QA ☒ Management ☐ Other CDL 1/22/10 CDL 1/22/10

Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ Rev. #: ~~N/A~~ 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
Comment#	Location	Comment	Accept	Reject		Accept	Reject
1	Global	I would like to make sure that the document tells the reader that all of the spreadsheets and so forth are stored in CMS and where they are stored. *If it is stated I missed this in my review.*	✓		The required text is in Page 23.	✓	
2	REVIEW SCOPE	I have reviewed the document for the criteria above. With the one enhancement that I mention above, the document meet all of the criteria.	✓		—	✓	
		---LAST COMMENT---				X	
						X	
						X	
						X	
						X	
						X	
						X	
						X	
						X	
						X	
						X	
						X	

Appendix A

NUCLEAR WASTE MANAGEMENT PROCEDURE Sandia National Laboratories	**Document Review and Comment (DRC)**	**Form Number: NP 6-1-1** **Page 1 of** 15

Entries must be complete, legible, and in reproducible ink or completed electronically.

Reviewers who have no comments must record "No Comments" in the comment block.

1. Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ AEI 1-22-10

2. Revision #: (if applicable) ~~N/A~~ 8.10 AEI 1-22-10

3. Document Description: (e.g. abstract, procedure, SAND report) NP 19-1 Document

4. Type of Review & Criteria. Shall be verified by the Reviewer:

☒ Technical (Technical adequacy, accuracy, completeness)
-Are objectives clearly stated and fulfilled?
-Is the technical activity clearly described?
-Are equations/calculations accurate?
-Does logic lead to reasonable conclusions?
-Are the results drawn from the data supported by data presented?
-Data/tables/figures: Are they easily understood? Are legends complete?
-Are the conclusions and assumptions adequately supported?

☐ QA (Compliance and completeness)
-Are applicable QA requirements adequately cited/ incorporated and met (content, reviews)?
- Has the technical review been performed by someone who is "independent"? (see NP 6-1, Section 2.2)

☐ Management(Completeness and correctness)
-Is report consistent with policy?
-Is there consensus with other program documents?
-Does the document meet applicable criteria?

☐ Other type of review (please specify or leave blank if not applicable)

5. Additional criteria: (if applicable)

6. Approval signatures:

Yongliang Xiong *Review Requester's/Delegate's Printed Name*	Yongliang Xiong *Review Requester's/Delegate's Signature*	12/10/2009 *Date*
Ahmed E. Ismail *Reviewer's Printed Name*	*Reviewer's Signature*	1/11/2010 *Date*

Document Review and Comment (DRC)

Form Number:
NP 6-1-1
Page 2 **of** 15

Type of Review: ☒ Technical ☐ QA ☐ Management ☐ Other

Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ ACI 1-28-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
Comment#	Location	Comment	Accept	Reject		Accept	Reject
	REVIEW SCOPE	I have reviewed the document for the criteria above. This review also included an examination of the spreadsheets, and EQ3/6 and FMT input and output files.	√		---	X	
1	p. 11, 4th par	"The objective of the task . . . to EQ3/6. This has been accomplished by translating the CHEMDAT file to EQ3/6." I believe there are several problems with this pair of sentences: (1) The goal of this task is the qualification of EQ3/6 for use in actinide chemistry. (2) If the goal of the task were to migrate the model from FMT to EQ3/6, and this was accomplished with the database conversion process, there would be no need for the software qualification. (3) The memo by Ismail et al. (2008) should be cited when discussing the conversion of the database from FMT to EQ3/6 format.	√		The objective of the task is the same as that stated in AP-140. However, the following changes were made: A clause was added noting the particular significance of applying EQ3/6 to actinide chemistry. The database conversion is now noted as "the first step in meeting this objective." Further clarification is made in the following paragraph on p. 12. Ismail et al. (2008) is now cited.	X	
2	p. 12, 2nd par.	"The FMT data file requires that a value be explicitly assigned to every parameter within the scope of the software that is potentially relevant to the chemical system represented on the file.": This statement is needlessly complicated. Every possible combination of binary and ternary parameters for every combination of species in the database must be specified, even if the parameter is zero.	√		Simplified as "The FMT data file requires that a value be explicitly assigned to every parameter within the scope of the software."	X	
3	p. 12, 3rd par.	"and is then writes on the data1 file to be used as a dimensioning parameter to be used by EQ3NR or EQ6": This fragment does not make sense as written. I suggest writing: "and then writes this value to the data1 file as an array dimension parameter to be used by EQ3NR or EQ6."		X	The suggestion was incorporated, except that we prefer "on the data1 file" to "to the data1 file."	X	

Document Review and Comment (DRC)

Form Number:
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Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ hu 1-22-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
4	p. 15, 1st par.	1 ion per kg water = $1.66 \cdot 10^{-24}$ m. Consequently, any value lower than this effectively implies a probabilistic result. If the concentration of, a species was, for example, 10^{-26} m, you would need 166 kg of water to have a concentration of one ion. Thus, if your system has only 1 kg of water, there's no guarantee that your system actually contains the ion in question at a concentration that low. Thus, a reporting cutoff makes some sense.		X	We note that FMT has this reporting cutoff, as it affects a very small number of results (which can then not be compared with EQ3/6 results). Whether this means anything more than that is not relevant to the code comparison. FMT does report activity coefficients for species with concentrations below this cutoff (this is now explicitly noted). As to the technical point raised, the FMT documentation itself offers no justification for the cutoff, though that is doubtless what someone was thinking. The significance of "very small concentrations" of species involved in various types of equilibria has been addressed elsewhere (cf. Bauer, 1990, "Physical Interpretation of Very Small Concentrations," Journal of Scientific Exploration, v. 4, p. 49-53, and references cited therein. The bottom line is that thermodynamics doesn't seem to care, likely because equilibrium encompasses the probabilistic. Thus, there is nothing overly substantial to support the cutoff.	X	
5	p. 14, par. Cont. from p. 13	"If a species would have a mass less than 1×10^{-24} mole": masses are not measured in moles. Please make units and names consistent.	√		In this instance, we have re-worded to use "mole number" instead of "mass." However, we have also added a paragraph noting that "mass" may be used in a broader sense than the Système International calls for, such that it may also refer to mole number. This is necessary to avoid stilted and awkward language. Context is sufficient to guide the reader.	X	

Document Review and Comment (DRC)

Form Number:
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Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ pd 1-12-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
6	p. 14, 2nd par.	"Fundamentally, changing the number of moles of O achieves charge balance principally by changing the masses of species . . . However, the masses of other species are also affected, and one of these is H_2O.": This is open to misinterpretation; I suggest changing "masses" to "the number of moles"		X	It is correct as moles and masses are interchangeable when the molecular weight of the species is considered. Therefore, it is not open to misinterpretation. See reply to comment 5.	X	
7	p. 16, 2nd par.	"These results valid the reincorporation": "valid" should be "validate."	√		In the version submitted for review, this had been corrected. When the reviewer printed, he probably did not select "Final". The correction has been re-verified.	X	
8	p. 16, 2nd par.	"Appendix C of this document . . . qualified version 8.0": These sentences deal with Appendices C and D, which are not found in this document. Delete.	√		They are deleted in the revised version.	X	
9	p. 17, Sec. 1.2	Testers: Replace "for the EQ3/6 side" and "for the FMT side" with "(EQ3/6)" and "(FMT)." Also, should Jennifer Long be listed as a tester for FMT as well?	√		Corrected as suggested. Jennifer Long is included as an FMT tester.	X	
10	p. 17, Sec. 1.3	"and" required after "preprocessor EQPT."	√		Added.	X	
11	p. 18, above R.17	"The present verification and validation plan adds a new one": too colloquial. Change "one" to "requirement"	√		Changed	X	
12	p. 18, Sec. 3.0	According to Table 5.2, six of the requirements (R.2, R.3, R.4, R.6, R.7, and R.15) are not tested in the present suite. An explanation of why this is so should be provided.	√		An explanation has been added.	X	
13	p. 19, 1st par. of Sec 5.0	"from the FMT side": As above, this *expression is too colloquial* for a formal document of this type. Please use "in EQ3/6" and "in FMT" instead of "on the EQ3/6 side" and "on the FMT side."	√		Changed.	X	
14	p. 19, 1st par. of Sec. 5.0	"(Np, Pu, and Th)" should be "(Np, Am, and Th)," since Am is In the model, and Pu technically is not.	√		In the version submitted for review, this had been changed. When the reviewer printed, he probably did not select "Final".	X	
15	p. 19, 2nd par of Sec 5.0	Because "Type 1," "Type 2," and "Type 3" are continually referred to throughout the remainder of the text, I would recommend making it easier to find these definitions by using either a numbered or bullet list to highlight each definition separately.	√		We included a bulleted list (with "Type *n*" strings) in the defining discussion to further clarify and aid in searching (e.g., "Type 1" for example had been defined simply as "the first type.").	X	
16	p. 19, 2nd par of Sec 5.0	"or at least a very small charge balance adjustment": I believe "least" should be "most" given the context.	√		Reworded.	X	

Document Review and Comment (DRC)

Form Number:
NP 6-1-1

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Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ ASI 1-22-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
17	p. 19, 2nd par of Sec 5.0	"not charged-balanced": "charged" should be "charge"	√		Changed as suggested.	X	
18	p. 20, 1st par	"All comparison calculations and plots": I do not see any plots in this document. Consider eliminating "and plots"	√		The reference to plots has been deleted.	X	
19	p. 20, 1st par	"there is a minimum of one": Change to "There is at least one"	√		Changed as suggested. However, we note that the original wording is equivalent to the suggested change..	X	
20	p. 20, 1st par.	"The relative difference calculation used for comparing values as a percent is defined as follows": This is confusing. I recommend rewriting as: "The relative difference (in percent) between EQ3/6 and FMT values is calculated as"	√		Changed as suggested.	X	
21	p. 20, first and second eqns	Please change "D" to "Δ" in both equations, as that is what is used throughout the rest of the document.	√		Changed as suggested.	X	
22	p. 20, after first eqn	"where *EQ3/6* is the value from EQ3/6 . . . corresponding FMT calculation": You have not defined what will happen if the FMT value is reported to be zero, which occurs in several places.	√		It is now noted that if the FMT value is zero, no relative comparison is made. It is noted that the FMT value is generally zero only if the reporting cutoff on mole number (1×10^{-24} mole) comes into play.	X	
23	p. 21, 1st par	"All of the EQ3/6 and FMT files are archived in CMS under the library of libAP-140.": This library cannot be correct; please identify the appropriate library.	√		LIBAP140 *is being created by* Jennifer Long.	X	
24	p. 20 Table 5-2	There is an additional row in this table; please delete.	√		Deleted.	X	
25	p. 23, 1st par. after Table 5.1-2	"However, such a result is generally not available, and using such a thing is not the usual way FMT inputs have": This is a sentence fragment. Please revise.	√		Rephrased.	X	

Document Review and Comment (DRC)

Form Number:
NP 6-1-1
Page 6 **of** 15

Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ AKI 1-22-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
26	p. 24, 1st par.	"Concentrations and other "linear" quantities agreeing within 1% and logarithmic quantities within 0.004 (roughly equivalent to 1%) and pH values agreeing within 0.01 unit will be deemed satisfactory without further explanation.": There is a major issue here that needs to be addressed. Because some quantities—such as the saturation indices in FMT—are only reported to three significant figures, it is often not possible to achieve agreement within 0.004 log units. This can lead to misleading comparisons and "false positives." The criterion of 0.004 log units needs to be discussed more carefully.	√		This issue is now addressed back where "acceptance criteria" are first discussed, around p. 15 (of the track-changes version).	X	
27	p. 24, 2nd par of Sec 5.1.3 (and elsewhere)	Please use the times symbol (×) rather than the letter "x" to represent multiplication.	√		Changed. We note that historically, outside the realm of typesetting, there was no difference between the symbol and the letter, other than the intent. However, this does look better.	X	
28	p. 24, Table 5.1-3 (and elsewhere)	The symbol λ should be a γ; this needs to be corrected in every table of this type.		X	There is no absolute convention regarding this, but λ is most often used to represent a mole fraction activity coefficient, which is what the activity coefficient of water is, while γ most often represents a molal activity coefficient, which is analogous but different. See for example T. Wolery, 1990, "On the thermodynamic framework of solutions," American Journal of Science, v. 290, p. 296-320. Thus for water in aqueous solutions we have λ(w), not γ(w), although some people do use "γ(w)" (unfortunately).	X	

Document Review and Comment (DRC)

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Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ AU 1-21-'10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
29	p. 24, Table 5.1-3 (and elsewhere)	Do not put the definitions of a_w, x_w, and γ_w as footnotes; instead, put them in the same cells as the symbols. This will improve clarity and readability of the report.	√		Dealt with, but in a different way. The "general parameter outputs" are now presented and discussed in a paragraph introducing Table 5.1-3. The reader is thereafter expected to know what they all are. We considered adding more words to the tables, but that now seems unnecessary The footnoting has been removed.	X	
30	p. 24, Table 5.1-3 (and elsewhere)	As discussed above, comparing results of different precisions is difficult. I don't believe you can say that there's a difference between the FMT and EQ3/6 results for anything other than the fugacity of CO_2 and pcH.	√		It is somewhat problematic. But the numbers in the tables do speak for themselves (apart from some instances where Excel muddied the waters, and we think we have corrected those). We do not need to be concerned about precision differences unless the calculated differences exceed the acceptance tolerances. In Table 5.1-3 there are no instances of that occurring. In general, reported precision is not an issue, with the exception of the situation regarding the saturation indices.	X	
31	p. 27, Table 5. 1-6	The saturation index tables are similarly compromised by the different levels of precision. As an example, the authors suggest that the difference between the EQ3/6 and FMT saturation indices for dolomite is 0.00284. However, the reason for this difference is that the EQ3/6 result is reported as 2.35284, while the FMT result is reported as 2.35. Thus, the entire difference is apparently the result of rounding issues. However, we do not know if the value FMT calculated is 2.3549 or 2.3451, and thus the absolute difference could be anywhere from 0 to 0.0077. All of the saturation index tables need to be reconsidered keeping this potential imbalance in mind.	√		See response to comment 26.	X	
32	p. 29	"The is the last test case": "The" should be "This"	√		Fixed.	X	

Document Review and Comment (DRC)

Form Number:
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Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ ASL 1-22-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
33	p. 30, Table 5.2-3	Why is density reported to two decimal places, while solution mass and TDS are reported to six decimal places? Is it an Excel issue (whereby trailing zeros are not recorded on-screen)? If not, please explain the discrepancy; if it is due to dropping of trailing zeros, please fix this in the table.	√		In general, the precision of the numbers in the tables matches that of the actual code output (we did a sweep through all the tables in the report and corrected a fair number of precision display problems including the dropping of trailing zeros by Excel's "general" format). There is not necessarily a high degree of consistency in reported precision from one parameter to another within a code. Both codes generally provide enough (sometimes more than enough) precision than is always necessary (an exception is FMT's low precision for saturation indices). The density is reported as g/L by both codes. One or two decimal places is sufficient, because density is never much less than 1000 g/L. The solution mass and TDS, on the other hand, can be much smaller than 1000 g/L..	X	
34	p. 30, Table 5.2-3	I believe the deltas for pmH and pcH should be "-0.0006" and "-0.0007" respectively.	√		Fixed.	X	
35	p. 31, Table 5.2-6	The descriptor "swmajm" in the table header should be "deadseaw."	√		Changed.	X	

Document Review and Comment (DRC)

Form Number:
NP 6-1-1
Page 9 **of** 15

Document Title: Verification and Validation Plan and Verification Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10~~a~~ pa 1-22-10 Rev. #: 8.10

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
36	p. 37	Looking at the results of this table, I believe that in copying from Microsoft Excel, the authors have allowed trailing zeros to be suppressed. The correct number of significant digits should be reported, in order to make the comparisons cleaner. (See also comment 33 above.)	√		Yes, Excel was problematic in that regard. We have made a sweep through the tables to correct that. The Table in question is 5.3-4. The two "0" values for FMT were adjusted, the one for gypsum to "0.00000" to be consistent with the precision shown for the corresponding EQ3/6 and Δ values. We note that for an exactly saturated mineral, FMT actually gives empty space in the "Descriptor" column where the saturation index is otherwise given (this is a quirk of FMT). For halite, the FMT value was actually reported as "4.06E-10", which equates to zero at any reasonable precision of interest. We added discussion of this to the report.	X	
37	p. 38 (and elsewhere)	The terms "one-off" and "two-off" are not standard, and need to be either defined or replaced. (If I understand the authors' usage, "one-off" refers to a system with one deviation from an "apples-to-apples" comparison, while a "two-off" calculation has two such deviations.)	√		We have added discussion of how these terms are used.	X	
38	p. 38, last paragraph	The "3" in "HCO3^{-}" should be a subscript.	√		Changed.	X	
39	p. 40, paragraph before 5.4.2	This paragraph ("Although this may appear . . . on the EQ3/6 side.") is very confusing, Please revise the sentence to make the intent clearer. (If it's type 2 in FMT, just say so.)	√		Deleted this paragraph.	X	
40	p. 40, 2nd par of 5.4.3	"Perhaps surprisingly": Explain why the result is surprising, or delete this phrase.	√		Changed.	X	
41	p. 51, Table 5.5-7	The values reported appear to be molalities, not activity coefficients.	√		Fixed. Thermodynamic activities (which are generally of the same magnitude as molalities) had been erroneously entered in the table in place of the intended activity coefficients..	X	

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Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
42	p. 58, Table 5.7-2	In other tables to this point, the molalities for EQ3/6 have been reported to 5 significant figures, but now they are given to only three. Please be consistent in the reporting of molallities throughout the document.	√		Fixed by a general sweep through all the tables..	X	
43	p. 70, Table 5.11-1 (and following)	The tables in this section should correspond to test case 10, not test case 8 as listed. Please change captions accordingly.	√		Changed.	X	
44	p. 76, last paragraph	Delete ". However" between "several ways" and "most of the effect."	√		Changed.	X	
45	p. 78, 1st paragraph	Since you are referring to the chemical species rather than the EQ3/6 identity, please change Hydromagnesite5424 to hydromagnesite(5424).	√		Now use "hydromagnesite(5424)" and note that "Hydromagnesite5424" (the name used on the EQ3/6 data file and which appears in some of the tables) is equivalent..	X	
46	p. 81, Table 5.12-5	Please use comparable notation for numbers with similar exponents (for instance, Ox-- is written in scientific notation for FMT but in standard notation for EQ3/6.	√		Fixed during a general sweep through the tables..	X	
47	p. 86, last paragraph	"The only rub": This is too colloquial. Please revise.	√		Changed.	X	
48	p. 101	"truly excellent agreement": It is difficult to quantify "truly excellent." Recommend removing "truly" as a descriptor here.	√		Changed.	X	
49	p. 102, 1st par.	Same as comment 45 above.	√		Now use "hydromagnesite(5424)".	X	
50	p. 102, last par.	Please explain why the run was not repeated using the correct value for the molarity/molality facftor of ERDA-6 brine.		X	It is not necessary. This is more explicitly noted.	X	
51	p. 109, 1st par.	"Glauberiite" should be "glauberite."	√		Changed.	X	
52	p. 112, 1st par.	Same as comment 45 above.	√		Now use "hydromagnesite(5424)".	X	
53	p. 115, Table 5.14-5	Where do the values for this table come from? I can't find a match in the provided EQ3/6 and FMT files.		X	See Excel file "C4PGWBX"	X	

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Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
54	p. 127, last par.	Please be consistent in the use of "molality/molarity" or "molarity/molality."	√		Changed.	X	
55	p. 137, 3rd par.	"In practice, the 0.004 criterion . . . Put succinctly, this criterion was of limited usefulness." If the criterion is useless, it should not be used as a criterion, and a more appropriate and applicable criterion should be defined and used in its place.	√		See response to comment 26.	X	
56	p. 138, 3rd. par.	Delete "one or more of" after "analyses only with"	√		Changed.	X	
57	p. 139, References	Please provide complete references for Brush (2005) and Brush et al (2008).	√		Added.	X	
58	p. 143	It would be helpful to have an explicit definition of the forms of J(x) and J'(x) that are used in the present comparisons.		X	We prefer to refer the reader to the original references so as not to add a collection of complicated equations to this discussion. If we included the equations, we would then have to explain all the variables and parameters contained therein. That would overwhelm the discussion and detract from the main points we are trying to make here.	X	
59	p. 144, Footnote to Table A-1	The values for J(24) and J'(24) are clearly erroneous, as the functions are defined such that they must be monotonically increasing, and neither value listed is consistent with that definition.	√		We added to the footnote that the J'(24) value is inconsistent with a monotonically increasing function. The value given for J(24), however, is not at variance with a monotonically increasing function.	X	
60	p. 152, last par.	"some small discontinuity": This phrase is unclear. Please explain what is meant more explicitly.	√		Rephrased to clarify.	X	
61	p. 154	"agaom" should be "again"	√		Fixed	X	

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Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
62	Table B-5	"Here there is nothing remarkable.": This is a surprising comment, given that a number of discrepancies are well outside the 0.004 limit, and cannot be due to simple rounding and truncation errors. Such a statement needs more justification.	√		We added some discussion. We note that the differences for saturation indices are about the same magnitude of those seen in the body of the report, which are largely ascribed to the limited reporting precision used by FMT. However, we note that we expect some additional difference due to the model corrections (change in J(x) approximation and different values for A^{φ} and $\beta^{(1)}_{NaCl}$). The acceptance criteria do not apply to the comparisons given in Appendix B, owing to the model corrections. We are simply showing the effect of those corrections. This is now explicitly called out at the beginning of the appendix.	X	
63	General	There are an excessive number of typographical errors that need to be corrected. These include misspelled words, extraneous spaces and periods, and other minor errors that should be fixed.	√		Fixed. Several sweeps were made.	X	
	Review Scope	During the review process, a decision was made to incorporate additional tests into the EQ3/6 v8.0a validation process. These new tests handle the verification of the remaining EQ3/6 technical requirements, and act as a regression test for the migration from version 8.0 to version 8.0a. The comments below represent the updated document, as all previous comments were reconciled as indicated above.	√		---	X	
64	Page 18 (End of Section 1.0)	A brief paragraph should be added to the introduction indicating that regression testing from version 8.0 to version 8.0a was also included in the testing process	√		Added.	X	
65	Page 18 (Sec 1.1)	Delete spurious red left bracket.	√		Corrected.	X	
66	Page 20 (Sec 4.0)	The testing environment should be changed to reflect the fact that the machine to be qualified is Yongliang Xiong's desktop machine, not Tom Wolery's desktop machine.	√		Changed.	X	

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Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
67	Page 21 (Sec 5.0)	The bullet list has become misformatted. Please correct the formatting so that it is a numbered or bulleted list with proper indentation.	√		Corrected.	X	
68	Page 21 (and later)	The use of the "V8.0—Test #X" notation is useful for referring to the old cases as they were performed in the V8.0 validation, but not as ID's for the cases in the present document. Please call these cases 15-19, so that they can be more easily referred to in future documentation. This notation should be used in the remainder of the document as well.	√		Changed.	X	
69	Pages 21-22 (Table 5-1)	Add the version 8.0 to version 8.0a test cases (#15-#19) to the existing list of cases.	√		Added.	X	
70	Page 22	Remove highlighting on "in library LIBAP140."	√		Removed.	X	
71	Pages 24-25 (Tables 5-2 and 5-3)	Combine Tables 5-2 and 5-3 into a single table by adding columns for test cases 15-19 to the table. (There is enough space to do so. If needed, add a row which indicates that Test Cases 1-14 are for the EQ3/6-FMT comparison, while 15-19 are for the EQ3/6 v8.0 to v8.0a comparison.)	√		Changed.	X	
72	Page 25	It will be necessary to add a paragraph indicating which tests will be needed for regression testing of the baseline. Obviously test cases 15-19 will need to be included; I also recommend including one or two from Cases 10-14.	√		Added.	X	
73	Sections 5.3.2 through 5.15.2 ("Acceptance Criteria")	Since different criteria are being used for the EQ3/6-to-FMT and v8.0-to-v8.0a comparisons, you need to update the text here. The correct statement should read "The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see section 5.1.2).	√		Changed.	X	
74	Page 134, Table 5-15.4	"Test Case #13" should be "Test Case #14"	√		Corrected.	X	
75	Page 141, Section 5.16.1	Change text to "This test case verifies functional requirement R.3 for comparison of Version 8.0 with Version 8.0a."	√		Changed.	X	

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Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
76	Page 142, Section 5.16.2	I understand what you're trying to say here, but I don't think you can say it in the way written here. The fundamental problem is that EQ3/6 version 8.0 and version 8.0a report to different precisions. As a consequence of this, the same internal floating-point variable can be reported as two different numbers that, when the higher-precision of Version 8.0 is rounded, are not "equal." However, this is a reporting artefact, and not an actual discrepancy in the data. For instance, the number 1.00145; Version 8.0a would call this 1.0015, while rounding rules applied to Version 8.0 would give you 1.0014. These are not in conflict with one another, and should not be reported as such. Moreover "0.00%" implies that rounding is required to reach this value; however, "0.00%" also implies zero change, such that "0.001%" might be construed as a failing value, when this is not what is intended. I would instead recommend that you rewrite this paragraph, making the criteria that the results should agree, except within rounding errors. This would suggest limits of 0.005% and 0.001 for linear- and logarithmic-scale quantities.	√		The paragraph has been rewritten.	X	
77	Page 142, Section 5.16.3	"The results are within the usual 0.00% acceptance criterion.": Delete "usual" from this sentence, and change the threshold amount of 0.00% to an actual nonzero value, as suggested in comment 76 above.	√		Changed.	X	
78	Page 149, Section 5.17.1	Change text to "This test case verifies functional requirement R.2 for comparison of Version 8.0 with Version 8.0a."	√		Changed.	X	
79	Page 150, before Table 5.17-4	"for all phases": change to "for both phases"	√		Changed.	X	
80	Page 151, Section 5.18-1	Change text to "This test case verifies functional requirements R.1, R.3, and R.4 for comparison of Version 8.0 with Version 8.0a."	√		Changed.	X	

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Reviewer's Comments (Enter “LAST COMMENT” in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
81	Page 151, before Table 5.18-2	See comment 77.	√		Changed.	X	
82	Page 163, Section 5.19.1	Change text to “This test case verifies functional requirements R.1, R.3, and R.7 for comparison of Version 8.0 with Version 8.0a.”	√		Changed.	X	
83	Page 164, before Table 5.19-2	See comment 77.	√		Changed.	X	
84	Page 166, Section 5.20.1	Change text to “This test case verifies functional requirements R.1 and R.6 for comparison of Version 8.0 with Version 8.0a.”	√		Changed.	X	
85	Page 167, before Table 5.20-2	See comment 77.	√		Changed.	X	
86	Page 168, before Table 5.20-5	“The acceptance crietian of 0.000 is met for all points of reaction progress.”: Again, this is the same issue as addressed in comment 77. Please revise text accordingly.	√		Changed.	X	
87	Page 171, Section 6.0	Add a short paragraph to the conclusions stating that comparisons between version 8.0 and version 8.0a were performed, and that all results were within the established acceptance criteria.	√		Added.	X	
88	General	Please do a global search and replace for “ . “ (a period with a space on both sides) in the table headers, changing them to “. “ (a period followed by a space). They are very distracting.	√		Changed.	X	
		LAST COMMENT					

Appendix A

NUCLEAR WASTE MANAGEMENT PROCEDURE
Sandia National Laboratories

Document Review and Comment (DRC)

Form Number: NP 6-1-1
Page 1 of 2

Entries must be complete, legible, and in reproducible ink or completed electronically.

Reviewers who have no comments must record "No Comments" in the comment block.

1. Document Title: EQ3/6 Version 8.0a Verification and Validation Plan / Validation Document (document version 8.10)

2. Revision #: (if applicable) 8.0a

3. Document Description: (e.g. abstract, procedure, SAND report) NP 19-1 VVP/VD

4. Type of Review & Criteria. Shall be verified by the Reviewer:

☐ Technical (Technical adequacy, accuracy, completeness)
-Are objectives clearly stated and fulfilled?
-Is the technical activity clearly described?
-Are equations/calculations accurate?
-Does logic lead to reasonable conclusions?
-Are the results drawn from the data supported by data presented?
-Data/tables/figures: Are they easily understood? Are legends complete?
-Are the conclusions and assumptions adequately supported?

☒ QA (Compliance and completeness)
-Are applicable QA requirements adequately cited/ incorporated and met (content, reviews)?
<u>- Has the technical review been performed by someone who is "independent"? (see NP 6-1, Section 2.2)</u>

☐ Management(Completeness and correctness)
-Is report consistent with policy?
-Is there consensus with other program documents?
-Does the document meet applicable criteria?

☐ Other type of review (please specify or leave blank if not applicable)

5. Additional criteria: (if applicable)

6. Approval signatures:

Yongliang Xiong	Yongliang Xiong	01/25/2010
Review Requester's/Delegate's Printed Name	*Review Requester's/Delegate's Signature*	*Date*
Mario Chavez	Mario Chavez	1/25/10
Reviewer's Printed Name	*Reviewer's Signature*	*Date*

Document Review and Comment (DRC)

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Type of Review: ☐ Technical ☐ QA ☐ Management ☐ Other

Document Title: EQ3/6 Version 8.0a Verification and Validation Plan / Validation Document (document version 8.10) Rev. #: 8.0a

Reviewer's Comments (Enter "LAST COMMENT" in row below last entry)			Review Requester's/Delegate's Response			Reviewer's Response	
Comment#	Location	Comment	Accept	Reject		Accept	Reject
	p. 12 1st paragraph	We need to cite Analysis Plan AP-140 (Wolery 2008, Analysis Plan for EQ3/6 Analytical Studies (ERMS#548930)" and change control form (Wolery, 2009, Change Control for EQ3/6, Version 8.0 [Proposed 8.0A] ERMS 551823. governing this report .	X		Reference added	X	
	p. 14 3rd paragraph	Please add this sentence or a similar one explaining why 8.0a was chosen rather then 9.0 as the EQ 3/6 version number "The changes described below were implemented for SNL-WIPP by Tom Wolery as part of the SNL-WIPP Software Agreement TS03197 with Lawrence Livermore National Laboratory (LLNL). As acquired software SNL does not have access to the source code or design for EQ 3/6 and therefore does not control the version numbers of any of the EQ 3/6 releases from LLNL."	X		Clarification added.	X	
	p. 14 last paragraph	Please cite the software problem report documented by WIPP for these issues. i.e., Brush, 2009 SOFTWARE PROBLEM REPORT (SPR) 2009-03 FOR EQ3/6, VERSION 8.0. ERMS 551949	X		Citation added.	X	
	p. 21	The version 8.00 VVP/VD has 3 additional interface functions that were tested and should be mentioned here even if you are not going to retest them now.	X		These requirements has been listed as not to be tested.	X	
	p. 24 Table 5-1	As we are only extending the version EQ 3/6 8.00 validation the test case numbers should also be extended past the 8.00 test cases starting at Test Case #19. So Table 5-1 would show the previous cases for TC # 3, 4, 9, 12, & 15 then add your new 14 cases. If we are not extending 8.00 then please state so.	X		It is now stated in the requirements listing that the present document replaces the previous VVP/VD.	X	
	p. 26 Table 5-2	To avoid confusion this RTM should mimic the version 8.00 matrix with then new 14 cases appended or define these as replacements to the 8.0 VD.	X		It is repeated before Table 5-1 and 5-2 that the new tests replace the previous version 8.0 test suite.	X	
		Last Comment					

WIPP

VERIFICATION AND VALIDATION PLAN

/ VALIDATION DOCUMENT

for

EQ3/6 Version 8.0a for Actinide Chemistry

Document Version 8.10

ERMS #550239

January 25, 2010

TABLE OF CONTENTS

LIST OF TABLES

1.0 INTRODUCTION

This document describes how the EQ3/6 version 8.0a software package was tested, and the results of the testing. Version 8.0a is a minor modification of version 8.0. Version 8.0 is qualified software under WIPP (Gilkey, 2006), but the scope of qualification excludes calculations involving actinide chemistry. FMT (e.g., Babb and Novak, 1995, 1997; Novak, 1996; Wang, 1998) has been the principal geochemistry modeling tool used on WIPP for many years, especially for calculations involving actinide chemistry. Version 2.4 (Wang, 1998) has been stable for over ten years, although the supporting thermodynamic database continued to be improved (Xiong, 2005). The present report extends the qualification of EQ3/6 so that it can be used in place of FMT in future WIPP applications. This is needed because FMT has certain limitations, which will be discussed below. These limitations have been worked around in the past, but pose greater problems for anticipated future applications. This work was performed as part of Analysis Plan AP-140 (Wolery, 2008) and the corresponding change control form (Wolery, 2009).

Both EQ3/6 and FMT contain options to use the equations of Pitzer (1973, 1991) to describe the thermodynamic activity coefficients of aqueous species. Both codes also offer alternative equations (notably the B-dot equation of Helgeson, 1969), but only the Pitzer equations are pertinent here. Each code has a supporting thermodynamic data file that includes at its core the classic model of Harvie et al. (1984), which is a Pitzer-based model for the system Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O to high ionic strengths at 25°C. EQ3/6 offers a suite of supporting data files, only one of which can be used in a given run. Some support the use of Pitzer's equations, and others support the use of other equations. The "data0.hmw" data file is intended to be a pure representation of the Harvie et al. (1984) model (the complete model, with no additions). This data file and extensions thereof (e.g., Xiong, 2004) have supported previous applications of EQ3/6 on WIPP. In contrast, FMT appears to have a single supporting thermodynamic data file (CHEMDAT), which has been developed by adding more species and data to the Harvie et al. (1984) model. The FMT source code contains provision for using the B-dot equation, but there appears to be no data file to support its usage. The B-dot equation should only be used in cases of dilute aqueous solutions (where Pitzer's equations can also be used). Since WIPP must address concentrated brines, usage of the B-dot equation is not generally appropriate and the lack of an FMT data file supporting its usage is not important.

As noted above, the driving force for fully qualifying EQ3/6 is related to FMT limitations. There are two principal functional limitations and one practical limitation. The first functional limitation, which is obvious when FMT problems are set up, is that the code lacks a proper front end for initiating calculations. Instead of entering the initial solution composition in terms of concentrations, pH, and so forth, the user must provide the number of moles of each chemical element. These mole numbers are typically normalized to either 1 kg of solvent water (if one has the concentrations as molalities) or 1 L of solution (if one has molarities instead). In processing analyzed solution compositions, approximations affecting the output pH must necessarily be made (e.g., how much "HCO_3" is actually $CO_{2(aq)}$ or CO_3^{2-}). Previous WIPP application has worked around the fact that pH should be an input when dealing with natural brine compositions.

If the starting brine is expected to be near-neutral, interpreting aqueous carbonate as HCO_3 almost guarantees such a result, as some HCO_3 goes to $CO_{2(aq)}$ and some to CO_3^{2-}, with most remaining as HCO_3^-. Otherwise, the brine of interest is usually that occurring after reaction of an initial brine with basic solids (such as MgO) to equilibrium with the same or other basic minerals such as brucite [$Mg(OH)_2$]. The mineral equilibrium then essentially determines the final pH. EQ3/6 has a proper front end in the EQ3NR code. This code allows pH to be used as an input in defining an aqueous solution, although other inputs (such as assumption of specified mineral equilibria) can also be used to calculate it as an output. EQ3NR calculates mole totals for a set of aqueous basis species for subsequent use by EQ6, the reaction path code. These are analogous (and relatable to) mole totals for the chemical elements. Using mole totals for basis species allows for greater versatility than using mole totals for chemical elements. It permits, for example, modeling of redox disequilibrium without needing to treat, say, acetate as a pseudo-element.

The second functional limitation of FMT is that it has a phase selection algorithm that is prone to failure. The core equilibrium solver is a Gibbs energy minimization routine that operates for a specified phase assemblage (aqueous solution plus minerals). The phase selection algorithm operates at a higher level. Examination of the source code reveals that the algorithm used is overly simplistic, and that it lacks means to recover from a choice that turns out to be wrong. For flash (instant equilibration) calculations, it is possible to modify the input to specify *a priori* a phase assemblage, which if correct (or sufficiently nearly so), will allow FMT to complete the calculation. Usually EQ3/6 calculations have been used to find the assemblages to be specified (cf. AP-143, p. 14, first full paragraph). A "reaction path" calculation is effectively a series of flash calculations for small increments of change in mass balance totals (e.g., for the chemical elements in FMT). FMT is thus not useful for reaction path calculations, given that it has difficulty adjusting to changes in the phase assemblage along the path and that the user can specify only one assemblage per run.

The major practical limitation of FMT concerns the supporting data file. It is inordinately complex and difficult to safely modify in its present state. It contains blocks of data which should be calculated in software from other data on the file. At present, it is incumbent upon the user to make sure that there are no inconsistencies. There is no software to check for inconsistencies. Adding more species and data to the data file at this point would be very difficult. In contrast, the EQ3/6 data file structures are more transparent and manageable. Potential inconsistencies are minimized by design. The EQPT preprocessor computes secondary data (molecular weights from molecular formulas and atomic weights, computing polynomial fit coefficients, etc.) and checks for various types of potential errors.

The objective of the task to which this document is a part is the migration of the WIPP geochemistry model as represented by FMT and its most recent supporting thermodynamic data file FMT_050405.CHEMDAT (Xiong, 2005) to EQ3/6, in particular to support the use of EQ3/6 in calculations involving actinide chemistry (previous qualification of EQ3/6 excluded such calculations). The first step in meeting this objective has been accomplished by translating the CHEMDAT file to EQ3/6 format (Ismail et al., 2008). The resulting file is data0.fmt. This file does not follow the format of data0.hmw. Instead, it is modeled after data0.ypf, a more recent

EQ3/6 Pitzer-based data file that was created by the Yucca Mountain Project. The newer format uses a more logical scheme for grouping Pitzer interaction coefficients. It also has a better formulation for describing their temperature dependence. This aspect is not relevant to the present task, as the WIPP geochemistry model as presently constituted is restricted to 25°C. It is important to note that data0.fmt is a faithful translation in that no data from the WIPP geochemistry model were lost, no "extra" data were included, and no corrections were made.

The work described in the present document represents the second step in the model migration. It shows that the model is not sensibly affected by unknown software issues, such as differences in model equations, use of embedded data, or use of different numerical methods and tolerance parameters. This is accomplished by making a comparison of results obtained from EQ3/6 v. 8.0a (using data0.fmt) and FMT v. 2.4 (using FMT_050405.CHEMDAT) on a suite of "WIPP relevant" problems, including problems with actinide elements. Some of these problems were taken from the EQ3/6 test case library. Most were taken from previous FMT test cases or applications. Several of the problems taken from previous FMT usage include actinide chemistry. The intent is this comparison was to thoroughly test the codes against each other in ways that would reflect usage on WIPP.

The changes described below were implemented for SNL-WIPP by Tom Wolery as part of the SNL-WIPP Software Agreement TS03197 with Lawrence Livermore National Laboratory (LLNL). As EQ3/6 is considered to be acquired software, SNL does not have access to the source code or design for EQ3/6 and therefore does not control the version numbers of any of the EQ3/6 releases from LLNL.

Initial testing using EQ3/6 version 8.0 revealed some issues with both EQ3/6 and FMT. EQ3/6 is designed so that if a Pitzer coefficient is zero (usually because a value is unavailable), that coefficient need not explicitly appear on the data file. The FMT data file requires that a value be explicitly assigned to every parameter within the scope of the software. In creating data0.fmt, most of the zero-valued Pitzer coefficients were omitted, allowing for a smaller data file. It was discovered that EQ3/6 version 8.0 was not treating the omitted Pitzer ψ coefficients in the expected way. EQ3/6 has traditionally evaluated the Pitzer equations in terms of the primitive λ and μ coefficients (cf. Pitzer, 1991). The EQ3/6 database preprocessor breaks down the usual reported Pitzer coefficients ($\beta^{(0)}$, $\beta^{(1)}$, C^{φ}, θ, ψ, and ζ; λ and μ are reported for a few combinations of species) into a set of conventionally defined λ and μ equivalents (see Wolery, 1992, Section 3). The problem here was that if a ψ was omitted, the corresponding μ was also omitted. Unfortunately, the relation between a ψ and its corresponding μ involves other Pitzer parameters (e.g., $\mu_{cc'a}$ is a function of $\psi_{cc'a}$, C^{φ}_{ca} and $C^{\varphi}_{c'a}$, where c denotes a cation, c' a different cation, and a an anion). This problem was fixed in EQ3/6 version 8.0a by changing how the Pitzer C^{φ}, ψ, and ζ coefficients are handled and how the equations are evaluated. These coefficients are all "third order." There was no issue with the C^{φ} and ζ coefficients, but the treatment of them was changed for consistency. There was also no issue with the "second order" coefficients (for which all mappings are simple one-to-one relationships).

Some lesser issues were also addressed in EQ3/6 version 8.0a. Two problems documented in Yucca Mountain Project Software Problem Reports (for which YMP used workarounds) were fixed to avoid potential future problems in WIPP work. These were SPR001420060309 (possible error in treating multi-term TST rate law input) and SPR001520060309 (output of erroneous NBS pH value when activity coefficients are not normalized to the NBS scale). In addition, a small problem in the EQPT database preprocessor was fixed. EQPT counts the number of distinct Pitzer alpha coefficient sets on a data0 file and then writes this value on the data1 file to be used as a dimensioning parameter by EQ3NR or EQ6. The problem is that in version 8.0, the default value of two is written, regardless of the actual value. In EQ3NR or EQ6, this leads to a memory access violation when the actual required dimension is greater than two. The data0.fmt data file has more than two distinct sets of Pitzer alpha coefficients (Brush, 2009). Some changes were made to accommodate a new compiler (Lahey/Fujitsu Fortran 95 5.70d). The original compiler (Lahey Fortran 90 4.50h) is no longer available. The new compiler is actually a completely new compiler (Fujitsu).

It should be noted that the changes made to create EQ3/6 version 8.0a were needed to handle behavior involving the highly-charged cations and anions found in actinide-bearing species. As a result, previous applications of EQ3/6 version 8.0 to non-actinide solutions should be unaffected by these changes.

Some additional functional changes were made in EQ3/6 version 8.0a. The WIPP brine density model was added to the software (version 8.0 has no density model) and the code output was expanded to include the density (g/L) and various density-dependent parameters: TDS (total dissolved salts, g/L), the pcH, and volumetric concentrations (molarities, mg/L) of the basis species (these are all typical outputs of FMT). This change affected both the normal output file and the .csv (comma-separated-variable) output file. Having EQ3/6 calculate these data facilitates both comparisons with FMT and future WIPP work with EQ3/6. Because it is expected that pmH will be the usual type of pH input in future WIPP applications, a more straightforward option for inputting this was added. An option was added to turn off the pre-Newton-Raphson optimizer in EQ6 (it was thought that this was causing a problem with a test case, although the problem was eventually traced to the input data). Lastly, an option to use the Pitzer (1975, eq. 47) approximation for the J(x) function used in evaluating higher-order electrostatic terms was put back in EQ3/6. This option had at one time been deleted in favor of exclusive use of the later Harvie (1981, Appendix B) approximation. It was put back in to allow certain comparisons with FMT, the need for which will be explained below.

Some issues were also identified early on with the FMT code and the CHEMDAT data file. Pitzer's equations were extended by Pitzer (1975) to include higher-order electrostatic terms. In his 1975 paper, Pitzer presented various results including the "eq. 47" approximation. Harvie (1981, Appendix B) later produced another approximation thought to be more accurate. This was incorporated into the Harvie et al. (1984) model for the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system. Since the WIPP geochemistry model is built upon the Harvie et al. (1984) model, FMT should be using the Harvie (1981) approximation for consistency. However, it was discovered (by examination of the source code) that FMT actually uses the older Pitzer (1975, eq. 47) approximation.

Two additional issues were discovered. FMT uses a value of 0.39 for the A^{φ} Debye-Hückel parameter and 0.2644 for the Pitzer coefficient $\beta^{(1)}_{NaCl}$. These are the values given in the Harvie et al. (1984) paper. However, they are believed to be typographical errors. The actual values consistent with the Harvie et al. (1984) model are 0.392 and 0.2664, respectively. Plummer et al. (1988, the manual for the PHRQPTZ code) documented the value of A^{φ} actually used in the Harvie et al. (1984) model. They further point out that this is the value previously used by Harvie and Weare (1980, p. 984). Plummer et al. (1988) do not address in words the correct value for $\beta^{(1)}_{NaCl}$. However, they cite the value of 0.2664 in a listing of the PHRQPTZ data base (see p. 150 of their report). Harvie and Weare (1980, Table 1, p. 987) also gave this value. This value is also given by Pitzer (1991, Table 2, p. 100). Other supporting evidence comes from the NONLIN code written by Andy Felmy (another student of John Weare, who was Harvie's supervising professor and co-author). The WIPP NONLIN manual (WIPP, 1996) refers to an A^{φ} value of 0.39 at the top of p. 12. However, the source code contains the 0.392 value. The same report (p. 53) gives 0.2664 for $\beta^{(1)}_{NaCl}$ in the listing of the binary.dat data file. In the case of FMT, the value of A^{φ} is set in the source code, while the $\beta^{(1)}_{NaCl}$ value is taken from the CHEMDAT thermodynamic data file. In the case of EQ3/6, both parameters are taken from the supporting thermodynamic data file (data0).

Because the approximation for higher-order electrical interactions and the A^{φ} parameter value are built into the FMT source code, no consideration was given to making corrections on the FMT side. After all, the point of this exercise is to replace FMT with EQ3/6. It would have been more feasible to correct the value of $\beta^{(1)}_{NaCl}$. However, since most of the test cases are taken from historical FMT runs, it was decided to leave this as a correction to be done after the code comparison exercise was complete. Thus, the 0.2644 value was left on the translated WIPP geochemistry model data file (data0.fmt). Furthermore, the value of A^{φ} on that data file was set to 0.39 for consistency with FMT, also with the understanding that once the code comparison exercise was complete, this would be corrected to the correct value of 0.392. For most of the comparisons, it was decided to run EQ3/6 with the normal (and now the default) approximation of Harvie (1981) for the higher-order electrostatic terms, and to make only limited runs using the alternative approximation of Pitzer (1975, eq. 47). It should be noted that the higher-order electrostatic terms depend on A^{φ} in addition to the choice of approximation of the J(x) function. This is because x here depends on A^{φ}.

In past related code comparison validation studies (e.g., EQ3/6 vs. FMT, one EQ3/6 version vs. another, one FMT version vs. another), the acceptance criterion has generally been an agreement within 5% for quantities that are not intrinsically logarithmic, such as pH and saturation indices. In the present study, since the codes would be using the same database, a higher level of agreement was expected. AP-140 specifies an acceptance criterion of 1% for "linear" quantities and 0.004 for logarithmic quantities (1% corresponds to 0.00432), with 0.01 specifically for pH. However, it was recognized due to the lack of a proper front end that it would be difficult to ensure that EQ3/6 and FMT are solving exactly the same problems. There is therefore an exception to the acceptance criteria if deviations can be explained. Because a specific criterion of 0.01 was assigned to pH, the 0.004 criterion for logarithmic quantities only applies to saturation indices (log Q/K, where Q is the ion activity product and K is the equilibrium constant). It was later determined that FMT reports saturation indices to only three significant figures. Thus if a saturation index value is, for example, -3.15, the precision only supports comparison to the nearest 0.01 unit. If the saturation index is, for example, -31.5, the precision would drop to the nearest 0.1 unit (this is not common). This precision issue creates many "false positives." In dealing with differences in saturation index values, the 0.004 value is not useful and attention focuses instead on whether precision issues explain the differences. It is noted that the comparisons for saturation indices are largely redundant to the comparisons for other parameters, notably molalities and activity coefficients of solute species and the activity of water, as these parameters essentially determine the Q part.

One possible source of discrepancy is in the translation of the WIPP geochemistry model from CHEMDAT to data0.fmt. CHEMDAT contains standard state thermodynamic data in the form of dimensionless chemical potentials for chemical species. For data0.fmt, these must be translated into log K (equilibrium constant) values for a set of chemical reactions. The log K values on EQ3/6 data files are only given to four decimal places. If EQ3/6 used ln K instead of base-ten log K, this translation would happen to be exact in all cases. That is because ln K is a linear combination of the dimensionless chemical potentials. These potentials are given to at most four decimal places, and the reactions used for the EQ3/6 data file involve integer multipliers. Thus, no precision is lost to this point. Because log K is used instead of ln K, a division by ln(10) (approximately 2.302585) is required. This extends the number of decimal places beyond those for the original dimensionless chemical potentials. There is therefore a potential loss of precision of 0.00005 log K unit in the overall translation. This is thought to be not significant. There is no loss of precision in the Pitzer coefficients. As noted above, the comparison exercise will be using the uncorrected FMT values for A^{φ} and $\beta^{(1)}_{NaCl}$, so these cannot cause a difference.

An obvious source of possible discrepancy concerns the choice of approximation for the higher-order electrostatic interactions function J(x). This will be addressed in some test cases by making additional EQ3/6 runs using the Pitzer (1975, eq. 47) formulation, complementing ones made using the formulation of Harvie (1981).

EQ3/6 and FMT are different codes. They use different means of setting up and handling problems. They employ fundamentally different numerical solvers. They have different convergence tests and tolerances, cutoffs, and such. All of these things can potentially lead to differences in code outputs.

In chemical thermodynamics, the mole number or number of moles is often the relevant measure of quantity of a species or substance, not the "mass" in the sense of the Système International (SI) of units (in which the mole is also a recognized unit). In order to avoid stilted and awkward phraseology, we will follow the common practice in the computational chemical modeling literature (e.g., Wolery and Daveler, 1992) of using the word "mass" in a broader sense, meaning that in many instances this will refer to what is actually the mole number. Thus, a "mass balance total" may refer to what is actually a "mole number balance total," and the "mass" of a species, or adjustments thereto, may be given in units of moles. In some instances, mass may refer to mass in the SI sense, in which case units of grams or kilograms may be given. Regardless of the usage of the word "mass," the intent should be clear from the context.

For basic equilibrium solving, EQ3/6 uses a Newton-Raphson procedure in which the concentrations or masses of basis species (all aqueous) and mineral or gas species are adjusted to satisfy specified mass balance totals. Equilibria involving non-basis aqueous species are implicitly satisfied (the concentrations and masses of these species are implicitly adjusted). FMT uses a Gibbs energy minimization algorithm in which mass balance is implicitly satisfied and the concentrations and masses of all species are adjusted to satisfy all the relevant equilibria. The basic equilibrium solvers for both codes are designed to run with an externally specified phase assemblage, and operate within a phase selection algorithm that adjusts the assemblage as needed. It has been noted previously that FMT's phase selection algorithm is not robust. That is not an issue here, where results are to be compared for runs that successfully completed. A close examination of both codes suggests that the only significant likely differences in results (e.g., 1% in a "linear" parameter) will not be due to differences in equilibrium solvers or tolerances. The basic equilibrium solvers are both robust. The default convergence tolerances are comparably tight. It is necessary to note that FMT has a lower-bound cut-off for the mole numbers of chemical species. If a species has a calculated mole number less than 1×10^{-24}, zero values are reported for its molality and activity (but a calculated value is reported for its activity coefficient).

A difference in problem setup has already been noted, namely the lack of a proper "front end" in FMT. The problem setup is closely associated with how the codes handle the problem of charge balance. In EQ3/6, the user can deal with charge balance in a variety of ways. One is to ignore it. In an EQ3NR run, which defines the initial aqueous solution, this is the default condition. In a subsequent EQ6 run (where for example the initial solution is reacted with minerals), the charge imbalance in the original solution is maintained constant. Alternatively, the user may specify a basis species (usually Cl^- or Na^+) whose concentration is to be adjusted to satisfy charge balance in the EQ3NR run. The concentration of H^+ may also be adjusted, although this is generally appropriate in only a limited range of circumstances, such as calculating the pH of a pH buffer solution.

FMT treats charge balance differently. It does not allow an unbalanced system. The usual procedure is to adjust the number of moles of O (elemental oxygen) to achieve balance. A different chemical element can be specified on the CHEMDAT file. However, there is almost no experience in doing this. Historically, virtually all if not all WIPP applications of FMT have involved balancing on O. Fundamentally, changing the number of moles of O achieves charge balance principally by changing the masses of species such as HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$. These are all C species with different amounts of oxygen and charge. However, the masses of other species are also affected, and one of these is H_2O. Usually the resulting change in mass of H_2O is less than 1% (perhaps on the order of 0.1%), due to the relatively high abundance of this species. In EQ3NR calculations, however, the mass of H_2O is fixed at 1 kg. So if one starts FMT with input assuming 1 kg of H_2O (used in calculating the elemental mole numbers), the result is something slightly different. The resulting concentration of say Na^+ may be slightly altered because the mole number is the same but the amount of solvent water has changed slightly.

Although FMT requires a charge-balanced system, there are some twists on this. It is possible to specify an input pH (on the "Pitzer" scale) using equilibrium with a fictive solid (there are two to choose from for this purpose "H^+(solid)" and "OH-/H2O(solid)"). The intent of providing these species was not so much to specify a starting pH as to fix the pH as during a reaction progress run. They can, however, be used to specify a starting pH as long as it is understood that their continued presence will fix the pH. These two fictive solids have electrical charge. Because the system of aqueous solution plus solids must be charge-balanced, any excess of one of these implies a charge-imbalanced solution. These species appear on the CHEMDAT data file and were not included in the translation of the WIPP geochemistry model as represented by the data0.fmt data file because EQ3/6 is not set up to deal with such species. The option to use such species in FMT appears to have been rarely used. Another FMT option is to specify a mass of a fictive charged aqueous species. There are two of these to choose from, NegIon (which has a -1 charge) and PosIon (which has a +1 charge). These were included in the translation to data0.fmt. Each was assigned to a fictive chemical element ("Null-" and "Null+", respectively). NegIon has been used in FMT applications, and will appear in a couple of the test cases discussed later in this document.

Appendix A presents results pertaining to approximations (Pitzer, 1975, eq. 47; Harvie, 1981, Appendix B) for the J(x) function and its derivative J'(x). These results validate the reincorporation of the Pitzer (1975, eq. 47) approximation into EQ3/6. However, it is to be emphasized that this reincorporation has only been made for use in making test case comparisons in the present document. Only the Harvie (1981) approximation should be used in future applications. Appendix B of this document presents some results in how the WIPP geochemistry model results have changed once EQ3/6 is used in conjunction with the Harvie (1981) approximation and the corrected values of A^φ and $\beta^{(1)}_{NaCl}$.

Finally, regression testing from Version 8.0 to Version 8.0a has also been included in the testing process.

1.1 Software Identifier

Code Name:	EQ3/6
Version:	8.0a
CMS Library:	LIBEQ36 Class QA080A
Execution Platform:	PC-compatible with Microsoft Windows 95, 98, 2000, NT4, or XP. This software may operate on other Windows systems, such as Vista and Windows 7.

1.2 Points of Contact

Code Author:	Thomas J. Wolery Lawrence Livermore National Laboratories Livermore, CA 94550 Telephone: (925) 422-5789 Fax: (925) 423-0153
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Testers:	Thomas J. Wolery, Yongliang Xiong, and Jennifer Long

1.3 Code Overview

EQ3/6 was developed by Thomas J. Wolery at the Lawrence Livermore National Laboratory (LLNL) (Wolery and Jarek, 2003). EQ3/6 is a software package for modeling geochemical problems involving fluid-mineral interactions and/or solution-mineral-equilibria in aqueous systems. The software package has a speciation-solubility code, EQ3NR, and a reaction path modeling code, EQ6. Supporting software includes the data file preprocessor EQPT, and the conversion programs XCON3 and XCON6. Supporting databases include a number of thermodynamic data files with either the Davies and B-dot equations or Pitzer equations for activity coefficient models.

2.0 REQUIREMENTS

The requirements for EQ3/6 Version 8.0 (which version 8.0a succeeds) are listed in the Requirements Document (WIPP, 2006). The requirements also apply to version 8.0a. They are reproduced here for the reader's convenience.

2.1 Functional Requirements

EQ3/6 is required to perform the following functions:

R.1 Perform aqueous speciation calculations, given total concentrations of dissolved components and other parameters such as pH, pHCl, Eh, pe, oxygen fugacity, and CO_2 fugacity.

R.2 Perform aqueous speciation calculations with charge balancing on a specified ion.

R.3 Perform aqueous speciation calculations with mineral equilibrium constraints.

R.4 Perform "single point" thermodynamic equilibrium calculations.

R.5 Perform reaction-path calculations without inclusion of chemical kinetics.

R.6 Perform reaction-path calculations with inclusion of chemical kinetics.

R.7 Perform reaction-path calculations for fluid-center flow-through open system.

R.8 Determine activity coefficients using Pitzer's equations, assuming an appropriate Pitzer thermodynamic data file is provided.

2.2 External Interface Requirements

R.9 EQ3NR and EQ6 require a binary thermodynamic data file.

R.10 EQ3NR requires a text input file (.3i) describing the speciation-solubility problem.

R.11 EQ3NR generates a text output file (.3o) describing the results of the calculation.

R.12 EQ3NR generates a text "pickup" file (.3p) that contains a compact description of the aqueous solution. It may be used as the bottom part of an EQ6 input file.

R.13 EQ6 requires a text input file (.6i) describing the reaction-path problem.

R.14 EQ6 generates a text output file (.6o) describing the results of the calculation.

R.15 EQ6 generates a text "tab" file (.6t) that contains certain data in tabular form suitable for supporting local graphics post-processing.

R.16 EQ6 generates a text "pickup" file (.6p) that may be used as an input file to restart a reaction path calculation where a previous run segment ended.

The ability of the software to meet requirements R.1 through R.16 has already been established (Gilkey, 2006). The present verification and validation plan adds a new requirement for version 8.0a.

R.17 EQ3/6, using an appropriate translation of the FMT database used in the WIPP geochemistry model, must produce results for WIPP-relevant and near-relevant problems which are substantially the same as those produced by FMT. The WIPP-relevant problems must include examples involving actinides, and some must include both actinides and organic complexing agents.

The present document tests all of these functionalities, and replaces the validation and verification performed for version 8.0 of EQ3/6. R.2-4, R.6-7, and R.15 are being tested for the migration from EQ3/6 version 8.0 to version 8.0a, while the remaining requirements are tested as part of the EQ3/6-to-FMT comparison.

3.0 FUNCTIONALITY NOT TESTED

The following additional EQ3/6 functionality will not be tested.

- EQ6 generates a text "scrambled tab" file. It provides a capability for continuing a tab file across successive EQ6 runs.

In addition, the following added functionality, previously tested as part of the version 8.0 qualification, will not be tested here:

A.1 EQPT translates a text file containing the thermodynamic data into a binary thermodynamic data file readable by EQ3NR and EQ6.

A.2 XCON3 translates an EQ3NR text input file from a previous version of EQ3/6 into an input file readable by EQ3NR Version 8.0.

A.3 XCON6 translates an EQ6 text input file from a previous version of EQ3/6 into an input file readable by EQ6 Version 8.0.

4.0 TESTING ENVIRONMENT

EQ3/6 Version 8.0a for actinide chemistry was tested in the following environment:

Hardware Platform:	Yongliang Xiong's desktop Dell Precision (T5400) PC at Sandia National Laboratories Carlsbad Programs Group (S906503)
Operating System:	Microsoft Windows XP Professional
Target PC Tester:	Yongliang Xiong
Test Date:	January 5, 2010

5.0 FUNCTIONAL TESTING

Nineteen test cases were chosen for this study. These are summarized in Table 5-1. All of the problems have some degree of WIPP relevance. Three of the test cases (swmajm, deadseaw, and gypnaclx) are modified EQ3/6 test problems. The others are taken from previous FMT runs, and include examples of both historical test cases and actual applications. Some but not all of the members of this set include actinides (Np, Am, and Th).

For purposes of code comparison, we define three types of test cases:

- Type 1: The initial solution is pure water. It is by definition charge-balanced.
- Type 2: The initial aqueous solution composition is defined in a manner that guarantees charge balance, or the composition is pre-adjusted for charge balance, so that no subsequent adjustment is necessary in the code runs for which output will be compared. This may be because the composition is simple (e.g., 4.0 m NaCl) or because of a previous adjustment made using one of the codes.
- Type 3: The initial aqueous solution composition is not charge balanced. A potential discrepancy between the codes may result from how this is dealt with.

The Type 1 examples include the test cases gypnaclx, f24vc7b3, f24vc7m, f24vc7k4, and f24vc7x. The initial solution in each case is pure water, which is then reacted with a set of minerals. Thus one likely cause of discrepancy (different means of addressing charge imbalance) is absent. We note that one would expect ~1 × 10^{-7} moles each of H^+ and OH^- for 1 kg of "pure" H_2O. This is small enough that it will not matter whether or not these species are included in the elemental mole totals input to FMT. The Type 2 test cases include swmajm and deadseaw. In each of these, the initial aqueous solution composition has been adjusted for charge balance using a preliminary calculation (here using EQ3NR). The modified composition (the Cl^- was adjusted in these examples) then defines the actual test problem input to both codes. Again, there should be no charge balance adjustment (or a negligible one) when the modified problem is run using either code. The Type 3 test cases include all of the remaining test cases. Each involves a starting aqueous solution that is not charge balanced (to which minerals may or may not be added). This type of problem may show differences in code results due to the different means of addressing the charge imbalance.

In addition, in order to test the code migration from Version 8.0 to Version 8.0a, the following test cases from Version 8.0 are tested against Version 8.0a: Test Case #15, taken from Test 3 of Version 8.0; Test Case #16, taken from Test 4 of Version 8.0; Test Case #17, taken from Test 9 of Version 8.0; Test Case #18, taken from Test 12 of Version 8.0; and Test Case #19, taken from Test 15 of Version 8.0. The functional requirements covered by these test cases are listed in Table 5-2. Functional requirement R.8 is covered by Test Cases 1-3 of Version 8.0a. Version 8.0 Test Cases 2, 7, and 13 have been incorporated into the test suite for Version 8.0a. Version 8.0 test cases 5, 6, 8, and 10 through 18 are not tested against Version 8.0a, as the functionalities for these test cases are already covered by the EQ3/6-to-FMT comparison test cases. The present test cases replace the test cases defined for version 8.0 of EQ3/6.

Table 5-1. Summary of Test Cases for Unit Tests (#1 through #14) and for Verification Tests (#15 through #19) for Migration from Version 8.0 to Version 8.0a

Test	Code	EQ3/6 file	FMT File	Description
1	EQ3NR	swmajm	swmajm_08-27-09	Sea water test case, major cations and anions with Br and B
2	EQ3NR	deadseaw	deadsea_08-27-09	Dead sea brine test case with Br
3	EQ6	gypnaclx	gypnacl_01-14-09	Solubility of gypsum in a saturated NaCl solution
4	EQ6	f24vc1	fmt_test1	Speciation in WIPP SPC (Salado Primary Constituent) brine
5A	EQ3	f24vc3s1	fmt_test3	ThO_2 (am) solubility in NaCl solutions up to 6 m at pmH 3.8
5B	EQ3	f24vc3s2	fmt_test3	ThO_2 (am) solubility in NaCl solutions up to 6 m at pmH 5.5
6	EQ6	f24vc7m	fmt_test7a	Invariant point of aphthitate/glaserite–picromerite/schoenite–halite–sylvite in Na-K-Mg-Cl-SO_4 system
7	EQ6	f24vc7b3	fmt_test7b	Invariant point of borax–teepleite–halite in Na-Cl-B_4O_7 system
8	EQ6	f24vc7k4	fmt_test7c	Invariant point of K-carbonate–K-Na-carbonate–sylvite in Na-K-Cl-CO_3 system
9	EQ6	f24vc7x	fmt_test7d	Invariant point of halite–sylvite in Na-K-Cl system
10	EQ6	f24vc8	fmt_test8	Speciation of Am(III), Th(IV), and Np(V) in WIPP SPC brine
11	EQ6	c4pgwb	fmt_cra1bc_gwb_hmg_orgs_007	Solubility of Am(III), Th(IV), and Np(V) in WIPP GWB brine
12	EQ6	c4per6	fmt_cra1bc_er6_hmg_orgs_011	Solubility of Am(III), Th(IV), and Np(V) in WIPP ERDA-6 brine
13	EQ6	c4pgwbx	fmt_edta_gwb_hmg_orgs_x_007	Solubility of Am(III), Th(IV), and Np(V) in WIPP GWB brine, assuming that the inventory of EDTA increases by a factor of 10 in comparison with the 2004 PABC inventory
14	EQ6	c4per6x	fmt_edta_er6_hmg_orgs_x_011	Solubility of Am(III), Th(IV), and Np(V) in WIPP ERDA-6 brine, assuming that the inventory of EDTA increases by a factor of 10 in comparison with the 2004 PABC inventory
15	EQ3	oxcalhem	N/A	Using mineral solubility constraints
16	EQ3	custbuf	N/A	Calculating the composition of a custom pH buffer

17	EQ6	pptmins	N/A	Finding precipitates from multiply-saturated sea water
18	EQ6	microft	N/A	Microcline dissolution in a fluid-centered flow-through open system
19	EQ6	pptqtz	N/A	Kinetics of quartz precipitation

All comparison calculations were performed with Microsoft Excel. There is at least one comparison spreadsheet per test case. In instances in which variations were introduced in the EQ3/6 calculations, such as using the Pitzer (1975) approximation for higher-order electrostatic terms, additional spreadsheets are included. The spreadsheets, along with all other files used in this analysis, are archived in class QA080A of library LIBEQ36 in the WIPP CMS. The relative difference (in percent) between the EQ3/6 and FMT output values is calculated as:

$$\Delta = 100 * \left| \frac{EQ3/6 - FMT}{FMT} \right|$$

where *EQ3/6* is the value from EQ3/6 Version 8.0a, and *FMT* is the value from a corresponding FMT calculation. If the reported FMT value is zero, the percent difference is not calculated and the affected values are not compared. Generally this only happens when the previously noted FMT reporting cutoff of 1×10^{-24} mole on the abundance of a species is triggered. For intrinsically logarithmic quantities (pH, saturation indices), the absolute difference is used instead:

$$\Delta = \left| EQ3/6 - FMT \right|$$

All of the EQ3/6 and FMT files are archived in CMS in the libraries of LIBEQ36 Class QA080A and LIBFMT, respectively.

Table 5-2 presents the relationship between the requirements and the test cases.

In addition, it is suggested that test cases #15 through #19, original Version 8.0 seawater test case without Br and B, and original Version 8.0 Dead Sea brine test case without Br, be used for regression testing of the baseline.

Table 5-2. Requirements Coverage by Test Case for Unit Tests (#1 through #14) and Verification Tests (#15 through #19) for Migration from Version 8.0 to Version 8.0a

Requirement Type and Number	**Test Number**																		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Functional R.1	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X	X	X
Functional R.2																X			
Functional R.3															X		X	X	
Functional R.4																	X		
Functional R.5			X	X	X	X	X	X	X	X	X	X	X	X					
Functional R.6																			X
Functional R.7																		X	
Functional R.8	X	X	X	X	X	X	X	X	X	X	X	X	X	X					
External Int. R.9	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
External Int. R.10	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
External Int. R.11	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
External Int. R.12	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X				
External Int. R.13			X	X	X	X	X	X	X	X	X	X	X	X			X	X	X
External Int. R.14			X	X	X	X	X	X	X	X	X	X	X	X			X		X
External Int. R.15																		X	
External Int. R.16			X	X	X	X	X	X	X	X	X	X	X	X					
Functional R.17	X	X	X	X	X	X	X	X	X	X	X	X	X	X					

5.1 Test Case #1 – swmajm: Sea Water Major Components with Br and B

5.1.1 Test Overview

This is a modified version of the EQ3NR seawater test case described in Section 7.3 (p. 103–110) of Wolery (1992). Seawater is the classic brine, although it has an ionic strength of only 0.72 molal. Many more concentrated brines are derived from seawater, directly (by evaporation) or indirectly (by dissolution of salt minerals laid down by evaporation).

Test Files:

Thermodynamic data file:	data1.fmt
EQ3NR input file:	swmajm.3i
EQ3NR output files:	swmajm.3o, swmajm.3p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	SWMAJM_08-27-09.IN; SWMAJM_08-27-09.INGUESS
FMT output files:	SWMAJM_08-27-09.OUT; SWMAJM_08-27-09.FOR088

This test case is a modified version of the test case "swmaj" from Version 8.0, EQ3/6, which does not have Br or B species. In the modified version, the Br (bromide) and B (borate) were included, as data0.fmt contains Br and B species and including them reduces the charge imbalance. The input concentration data for Br and B were taken from swtst, a more inclusive EQ3/6 seawater test case (cf. Wolery, 1992). This test case requires a pH input. The problem was otherwise modified by making a preliminary EQ3NR run (swmajt) which used the original NBS pH as input and adjusted Cl^- for charge balance. The output "Pitzer scale" pH and adjusted Cl^- concentration were then used to redefine the inputs for the modified problem. The modified problem is then "type 2," meaning that no subsequent charge balancing should be necessary, at least when running the problem with EQ3/6. It was originally intended to use pmH as the pH input for the modified problem, but it was discovered that the mechanism planned for inputting this to FMT (using the fictive solid "H^+(solid)") would not accommodate this.

The primary inputs for this test case are given in Table 5.1-1. These are the direct inputs to EQ3NR (input file: swmajm.3i).

Table 5.1-1. Test Case #1 (swmajm) Primary Inputs.

Basis Species	Molality
Na^+	0.4854435
K^+	0.0105794
Ca^{2+}	0.0106617
Mg^{2+}	0.05508565
Cl^-	0.5658134
SO_4^{2-}	0.0292615
HCO_3^-	0.002022
Br^-	0.00087294
$B(OH)_4^-$	0.00042665

Pitzer pH	8.2526

The corresponding FMT inputs (mole totals for the chemical elements) are shown in Table 5.1-2. These were calculated from the data given in Table 5.1-1 (see worksheet "FMT input" of spreadsheet swmajm.xls).

Table 5.1-2. Calculated Test Case #1 (swmajm) Inputs for FMT.

Element	Moles
H	111.02059872
O	55.63325366
Na	0.4854435
K	0.0105794
Mg	0.05508565
Ca	0.0106617
Cl	0.5658134
S	0.0292615
C	0.002022
B	0.00042665
Br	0.00087294
Pitzer pH	8.2526

*Normalized to 1 kg H_2O
(55.50843506 mole, using atomic
weights from data0.fmt).

Calculation of the charge imbalance using the elemental mole totals in Table 5.1-2 gives a value of -0.00014039 equivalents. This small imbalance results because the pH input in Table 5.1-1 could not be used in the calculation of the elemental mole totals. Note that the molality of the individual species H^+ would not be the appropriate quantity to use in such a calculation. Rather, the correct quantity would be the total molality of H^+ as a basis species. Such a quantity has numerical significance, but no physical significance. This quantity is actually calculated by EQ3/6, and the value from the EQ3NR calculation for the swmajm problem could have been used in the calculation of the elemental mole totals to get a result with tighter charge balance. However, without using EQ3/6 or some similar code, such a quantity is generally unavailable. In any case, consideration of such a quantity has not been part of the usual procedure used to construct FMT input files. We have elected to follow the usual procedure, recognizing that this will be a source of some finite difference in the code outputs.

In FMT the run, the code reads the input data (Table 5.1-2) from the input file SWMAJM_08-27-09.IN. The file SWMAJM_08-27-09.INGUESS is required to be present by the code, but its contents are ignored.

This problem is somewhat unusual for FMT in that a pH input is made. As will be noted below, this will result in the creation of a small mass of the fictive solid "H+(solid)". The input data associated with this pH option only specifies the desired pH value. It does not include a mass for the fictive solid.

5.1.2 Acceptance Criteria

Compare the key outputs including aqueous species concentrations calculated by EQ3/6 with those calculated by FMT. Concentrations and other "linear" quantities agreeing within 1% and logarithmic quantities within 0.004 (roughly equivalent to 1%) and pH values agreeing within 0.01 unit will be deemed satisfactory without further explanation. With reasonable explanation, larger differences may be acceptable. It is noted that a 5% criterion (for linear quantities, at least) was adopted in the EQ3/6 validation test for Version 8.0 in comparison with a wide range of independent codes including EQUIL, GEOCHEM, MINEQL2, and SOLMNEQ. This looser criterion is more appropriate when different supporting databases are used, other non-identical model factors may be present, and convergence tests and tolerances may vary.

5.1.3 Evaluation

Code outputs were assembled into the spreadsheet swmajm.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.1-3 compares the results for a set of general parameter outputs. These parameters are important ones that do not fit into any of the similar comparison tables given below. They include the solution mass, the H_2O (solvent) mass, the ionic strength, the density, the TDS (total dissolved solutes), the activity of water (a_w), the mole fraction of water (x_w), the activity coefficient of water (λ_w), the CO_2 fugacity, the Pitzer pH, the pmH, and the pcH. It is noted that a_w and λ_w are defined on a mole fraction basis ($a_w = x_w\lambda_w$); the symbol λ is used here instead of the γ used for the molal activity coefficients of solute species in order to emphasize the different nature (cf. Wolery, 1990, 1992). The Pitzer pH, the pmH, and the pcH are all forms of pH. The Pitzer pH is the "pH" reported by FMT, equivalent to -log $a(H^+)$ where $\gamma(H^+)$ is calculated using the single-ion formulation of the Pitzer equations without subsequent rescaling (cf. Wolery, 1992, Section 3). The pmH is -log $m(H^+)$ and the pcH is -log $c(H^+)$, where *m* and c are molality and molarity, respectively.

The results shown in the table are all well within the general acceptance criteria. In some instances, the differences appear mainly due to the use of different output precisions (e.g., TDS, density). There is a very small but definite difference in the H_2O mass, because regardless of the precision shown below, the value of this quantity for EQ3NR output is exactly 1000 g. Not shown in this table is that the FMT calculation produced 1.96066×10^{-6} mole of the fictive "H+(solid)", which has no place in the EQ3NR calculation. This appears to be small enough not to matter, given the general agreement of other outputs (as shown in Table 5.1-3 and following comparison tables for this test case). Not shown is whatever adjustment FMT made to the O mole total to achieve system charge balance. FMT does not provide detailed output describing this. Unless it is fairly substantial, it is difficult to infer from the output that is provided (e.g., mole numbers for chemical species) owing to precision issues. However, it appears to have been small enough not to matter.

Table 5.1-3. Test Case #1 (swmajm) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1036.431819	1036.4	-0.003%
H_2O mass, g	1000.000407	1000.0	0.000%
Ionic strength, m	0.722227	0.72223	0.000%
density, g/L	1023.99	1024.0	0.001%
TDS, g/L	35.99424791	35.994	-0.001%
a_w	0.981278	0.98128	0.000%
x_w	0.97953	0.97953	0.000%
λ_w	1.002	1.0018	-0.020%
fCO_2	0.0004117	0.000411767	0.016%
pH (Pitzer)	8.2526	8.2526	0.0000
pmH	8.1200	8.1200	0.0000
pcH	8.1253	8.1252	-0.0001

Table 5.1-4 compares the calculated molalities of the individual chemical solute species. The differences are all well under 1%.

Table 5.1-4. Test Case #1 (swmajm) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	0.565813	0.56581	-0.001%
Na+	0.485443	0.48544	-0.001%
Mg++	0.054979	0.054979	0.000%
SO4--	0.0292615	0.029261	-0.002%
Ca++	0.0106307	0.010631	0.003%
K+	0.0105794	0.010579	-0.004%
HCO3-	0.00180903	0.0018090	-0.002%
Br-	0.00087294	0.00087294	0.000%
B(OH)3(aq)	0.000333862	0.00033388	0.005%
CO3--	8.80828E-05	0.000088172	0.101%
MgCO3(aq)	0.000087130	0.000087051	-0.091%
B(OH)4-	7.15433E-05	0.000071546	0.004%
CaCO3(aq)	2.57419E-05	0.000025719	-0.089%
MgB(OH)4+	1.59734E-05	0.000015961	-0.078%
CO2(aq)	1.20158E-05	0.000012014	-0.015%
CaB(OH)4+	5.26937E-06	5.2651E-06	-0.081%
MgOH+	3.53746E-06	3.5351E-06	-0.067%
OH-	3.06767E-06	3.0676E-06	-0.002%
H+	7.58499E-09	7.5859E-09	0.012%
HSO4-	2.36693E-09	2.3646E-09	-0.098%
B3O3(OH)4-	5.12263E-10	5.1228E-10	0.003%
B4O5(OH)4--	6.00844E-13	6.0127E-13	0.071%

Table 5.1-5 compares the calculated thermodynamic activity coefficients of the individual chemical species. These differences are also all well under 1%.

Table 5.1-5. Test Case #1 (swmajm) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	0.6913	0.69119	-0.015%
Na+	0.6393	0.63929	-0.001%
Mg++	0.2082	0.20797	-0.111%
SO4--	0.1076	0.10750	-0.095%
Ca++	0.1904	0.19024	-0.084%
K+	0.5904	0.59034	-0.011%
HCO3-	0.6058	0.60576	-0.007%
Br-	0.5169	0.51689	-0.002%
B(OH)3(aq)	1.008	1.00763	-0.037%
CO3--	0.1019	0.10181	-0.086%
MgCO3(aq)	1.000	1.00000	0.000%
B(OH)4-	0.4761	0.47610	0.000%
CaCO3(aq)	1.000	1.00000	0.000%
MgB(OH)4+	0.6120	0.61193	-0.012%
CO2(aq)	1.130	1.13006	0.005%
CaB(OH)4+	0.5849	0.58492	0.004%
MgOH+	0.8814	0.88125	-0.017%
OH-	0.5767	0.57663	-0.012%
H+	0.7370	0.73689	-0.016%
HSO4-	0.7079	0.70795	0.006%
B3O3(OH)4-	0.4097	0.40964	-0.015%
B4O5(OH)4--	0.053042	0.05299	-0.097%

The thermodynamic activity of a solute species is the product of its molality and activity coefficient. Because the activity coefficient is of more direct interest than the activity, tables comparing activity results will not be presented for test cases discussed in this document. Such comparisons are available, however, in the comparison spreadsheets (swmajm.xls for the present test case).

Table 5.1-6 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. In a few cases (e.g., Nahcolite, Gaylussite, Arcanite) the acceptance criterion of 0.004 for a logarithmic quantity is slightly exceeded. However, it is obvious that this is a consequence of FMT only reporting values to three significant figures. Considering precision, the results are basically identical.

Table 5.1-6. Test Case #1 (swmajm) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ	abs(Δ)

Dolomite	2.35	2.35284	0.00284	0.00284
Magnesite	0.846	0.84518	-0.00082	0.00082
Calcite	0.666	0.66526	-0.00074	0.00074
Aragonite	0.479	0.47846	-0.00054	0.00054
Gypsum	-0.632	-0.63230	-0.00030	0.00030
Anhydrite	-0.834	-0.83428	-0.00028	0.00028
Nesquehonite	-1.85	-1.84624	0.00376	0.00376
Mirabilite	-2.37	-2.37297	-0.00297	0.00297
Halite	-2.49	-2.48633	0.00367	0.00367
Brucite	-2.56	-2.56197	-0.00197	0.00197
Epsomite	-2.62	-2.62041	-0.00041	0.00041
Hexahydrite	-2.86	-2.85820	0.00180	0.00180
Nahcolite	-3.07	-3.06546	0.00454	0.00454
Thenardite	-3.23	-3.23120	-0.00120	0.00120
B(OH)3	-3.44	-3.44274	-0.00274	0.00274
Glauberite	-3.47	-3.47058	-0.00058	0.00058
Sylvite	-3.51	-3.51204	-0.00204	0.00204
Hydromagnesite4323	-4.23	-4.23625	-0.00625	0.00625
Kieserite	-4.33	-4.32957	0.00043	0.00043
Hydromagnesite5424	-4.33	-4.33637	-0.00637	0.00637
Gaylussite	-4.42	-4.42443	-0.00443	0.00443
Pirssonite	-4.58	-4.57761	0.00239	0.00239
Syngenite	-4.67	-4.66731	0.00269	0.00269
Arcanite	-5.13	-5.13482	-0.00482	0.00482
Natron	-5.32	-5.32063	-0.00063	0.00063
Na_Metaborate	-5.32	-5.32156	-0.00156	0.00156
Kalicinite	-5.45	-5.44607	0.00393	0.00393
Mg2Cl(OH)3.4H2O	-5.62	-5.62059	-0.00059	0.00059
Bloedite	-5.65	-5.64869	0.00131	0.00131
Na2CO3.7H2O	-5.66	-5.66061	-0.00061	0.00061
Thermonatrite	-6.55	-6.55337	-0.00337	0.00337
Labile_Salt	-6.58	-6.57790	0.00210	0.00210
Kainite	-6.89	-6.88822	0.00178	0.00178
Picromerite/Schoenite	-7.08	-7.07673	0.00327	0.00327
Bischofite	-7.26	-7.26186	-0.00186	0.00186

The two codes are in excellent agreement for the seawater test case. This is the case despite the facts that there is a small inconsistency in the code inputs (which was deliberately minimized) and that different approximations were used for the J(x) higher-order electrostatic term function.

5.2 Test Case #2 – deadseaw: Dead Sea Brine Test Case with Br

5.2.1 Test Overview

This is a modified version of the EQ3NR deadsea (Dead Sea brine) test case described in Section 7.8 (p. 138–146) of Wolery (1992). This test case is relevant to WIPP, as Dead Sea brine has a high ionic strength (7.87 molal) similar to that of the WIPP GWB (8.26 molal) (Xiong and Lord, 2008), and the magnesium concentration of Dead Sea brine (1.56 molal) is comparable to that of WIPP GWB (1.16 molal). In terms of design, this test case is much like that presented for seawater (ionic strength 0.72 molal). It just involves a much more concentrated brine.

Test Files:

Thermodynamic data file:	data1.fmt
EQ3NR input file:	deadseaw.3i
EQ3NR output files:	deadseaw.3o, deadseaw.3p
Thermodynamic data file:	FMT_050405.CHEMDAT
FMT input files:	deadsea_08-27-09.in; deadsea_08-27-09.inguess
FMT output files:	deadsea_08-27-09.out; deadsea_08-27-09.for088

This test case originated from the test case "deadsea" of Version 8.0, EQ3/6, which did not include bromide because bromide is not included on the data0.hmw data file used in earlier testing. Bromide was included in the present test case as data0.fmt contains bromide species and including bromide helps reduce charge imbalance. Otherwise, the test case was modified by making a preliminary EQ3NR run to determine the Pitzer pH and to adjust the Cl- to achieve electrical neutrality (as was done for the swmajm test case). In the original deadsea test case and the preliminary EQ3NR run here, pH was assumed to be controlled by the heterogeneous equilibrium of the brine with the atmospheric partial pressure of CO_2 (taken as $10^{-3.5}$ bar, which is now low due to rising CO_2 levels). The preliminary run gave a Pitzer pH of 8.0303 and adjusted the concentration of chloride from 5.80980 molal to 5.81024 molal. The modified problem is then "type 2," meaning that no subsequent charge balancing should be necessary, at least when running the problem with EQ3/6.

The primary inputs for this test case are given in Table 5.2-1. These are the direct inputs to EQ3NR (input file: deadseaw.3i).

Table 5.2-1. Test Case #2 (deadseaw) Primary Inputs.

Basis Species	Molality
Na^+	1.7519
K^+	0.1739
Mg^{2+}	1.5552
Ca^{2+}	0.4274
Cl^-	5.81028
SO_4^{2-}	0.0063
HCO_3^-	0.0039

Br^-	0.0602
Pitzer pH	8.0303

The corresponding FMT inputs (mole totals for the chemical elements) are shown in Table 5.2-2. These were calculated from the data given in Table 5.2-1 (see worksheet "FMT input" of spreadsheet deadseaw.xls).

Table 5.2-2. Calculated Test Case #2 (deadseaw) Inputs for FMT.

Element	Moles
H	111.02077012
O	55.54533506
Na	1.7519
K	0.1739
Mg	1.5552
Ca	0.4274
Cl	5.81028
S	0.0063
C	0.0039
Br	0.0602
Pitzer pH	8.0303

*Normalized to 1 kg H_2O (55.50843506 mole, using atomic weights from data0.fmt).

Calculation of the charge imbalance using the elemental mole totals in Table 5.2-2 gives a value of 0.00402 equivalents. This small imbalance (larger than that in the seawater test case) results for the reason presented in discussing Test Case #1 (swmajm), namely the lack of a total molality for H^+ as a basis species.

In FMT the run, the code reads the input data (Table 5.2-2) from the input file DEADSEAW_08-27-09.IN. The file DEADSEAW_08-27-09.INGUESS is required to be present by the code, but its contents are ignored.

This problem is again unusual for FMT in that a pH input is made. As in the swmajm test case, this will result in the creation of a small mass of the fictive solid "H+(solid)". This is the last test case in this EQ3/6-FMT comparison study that will involve specifying a pH input.

5.2.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.2.3 Evaluation

Code outputs were assembled into the spreadsheet deadseaw.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.2-3 compares the results for the set of general parameter outputs. These outputs are the same as those defined for Test Case #1 (swmajm). The results in the present instance are all well within the general acceptance criteria. Again, in some instances, the calculated differences appear mainly due to the use of different output precisions (e.g., TDS, density). There is again a very small but definite difference in the H_2O mass, because the value of this quantity for EQ3NR output is exactly 1000 g (regardless of the precision shown). Not shown in this table is that the FMT calculation produced 3.87703 x 10^{-6} mole of the fictive "H+(solid)", which has no place in the EQ3NR calculation. This is small enough not to matter, given the general agreement of other outputs (as shown in Table 5.2-3 and following comparison tables for this test case). Not shown is whatever adjustment FMT made to the O mole total to achieve system charge balance. FMT does not provide detailed output describing this. However, it appears to have been small enough not to matter.

Table 5.2-3. Test Case #2 (deadseaw) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1313.677222	1313.7	0.002%
H2O mass, g	1000.020379	1000.0	-0.002%
Ionic strength, m	7.870338	7.8705	0.002%
density, g/L	1181.49	1181.5	0.001%
TDS, g/L	282.0956838	282.1	0.002%
a_w	0.752615	0.75262	0.001%
x_w	0.850126	0.85012	-0.001%
λ_w	0.8853	0.88531	0.001%
fCO2	0.0003162	0.000316277	0.024%
pH (Pitzer)	8.0303	8.0303	0.0000
pmH	8.5035	8.5029	-0.0006
pcH	8.5496	8.5489	-0.0007

Table 5.2-4 compares the calculated molalities of the individual chemical solute species. The differences are all well under 1%, as they were in the swmajm test case.

Table 5.2-4. Test Case #2 (deadseaw) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.81016	5.8103	0.002%
Na+	1.75186	1.7519	0.002%
Mg++	1.55223	1.5523	0.005%
Ca++	0.426816	0.42683	0.003%
K+	0.173896	0.17390	0.002%
Br-	0.0601988	0.060200	0.002%

SO4--	0.00629987	0.0063000	0.002%
MgCO3(aq)	0.00230784	0.0023060	-0.080%
MgOH+	0.000631254	0.00063163	0.060%
CaCO3(aq)	0.000575202	0.00057473	-0.082%
CO3--	0.000508476	0.00051087	0.471%
HCO3-	0.000504698	0.00050474	0.008%
OH-	4.72506E-06	4.7242E-06	-0.018%
CO2(aq)	3.70165E-06	3.7019E-06	0.007%
H+	3.13663E-09	3.1413E-09	0.149%
HSO4-	8.20467E-11	8.1669E-11	-0.460%

Table 5.2-5 compares the calculated activity coefficients of the individual chemical solute species. These differences are also well under 1%, as they were in the swmajm test case.

Table 5.2-5. Test Case #2 (deadseaw) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	2.164	2.16421	0.010%
Na+	0.7608	0.75963	-0.154%
Mg++	0.9230	0.92193	-0.115%
Ca++	0.5009	0.50038	-0.104%
K+	0.3168	0.31637	-0.135%
Br-	0.2622	0.26224	0.016%
SO4--	0.036162	0.036000	-0.449%
MgCO3(aq)	1.000	1.00000	0.000%
MgOH+	0.2842	0.28379	-0.144%
CaCO3(aq)	1.000	1.00000	0.000%
CO3--	0.0037355	0.0037200	-0.448%
HCO3-	0.7665	0.76666	0.020%
OH-	0.1721	0.17215	0.027%
CO2(aq)	2.817	2.81644	-0.020%
H+	2.973	2.96893	-0.137%
HSO4-	2.465	2.46547	0.019%

Table 5.2-6 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. Again a few cases (e.g., Dolomite, Calcite) the acceptance criterion of 0.004 for a logarithmic quantity is slightly exceeded. However, considering the rather low precision FMT uses in reporting saturation indices, the results are basically identical.

Table 5.2-6. Test Case #2 (deadseaw) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	5.13	5.12512	-0.00488
Hydromagnesite5424	2.32	2.31748	-0.00252

Magnesite	2.27	2.26825	-0.00175
Calcite	2.01	2.01447	0.00447
Aragonite	1.83	1.82767	-0.00233
Hydromagnesite4323	1.11	1.10975	-0.00025
Anhydrite	0.0496	0.04731	-0.00229
Gypsum	0.0212	0.01886	-0.00234
Halite	-0.346	-0.34673	-0.00073
Nesquehonite	-0.769	-0.76882	0.00018
Sylvite	-1.06	-1.05991	0.00009
Brucite	-1.14	-1.13954	0.00046
Mg2Cl(OH)3.4H2O	-1.39	-1.39183	-0.00183
Glauberite	-2.46	-2.46630	-0.00630
Epsomite	-2.47	-2.47146	-0.00146
Hexahydrite	-2.59	-2.59404	-0.00404
Bischofite	-2.84	-2.84120	-0.00120
Pirssonite	-2.87	-2.86853	0.00147
Carnalite	-2.88	-2.87620	0.00380
Nahcolite	-2.88	-2.88520	-0.00520
Gaylussite	-3.06	-3.06100	-0.00100
Thenardite	-3.11	-3.10851	0.00149
Syngenite	-3.15	-3.15317	-0.00317
Mirabilite	-3.40	-3.40243	-0.00243
Kieserite	-3.49	-3.48933	0.00067
Kainite	-3.82	-3.82628	-0.00628
Arcanite	-4.38	-4.38706	-0.00706
CaCl2.4H2O	-4.68	-4.68224	-0.00224
Polyhalite	-4.77	-4.78429	-0.01429
Kalicinite	-4.95	-4.95328	-0.00328
Bloedite	-5.03	-5.03141	-0.00141
Labile_Salt	-5.67	-5.68136	-0.01136
Na2CO3.7H2O	-5.88	-5.87681	0.00319
Natron	-5.88	-5.88248	-0.00248
Picromerite/Schoenite	-6.06	-6.0648	-0.00480
Thermonatrite	-6.08	-6.07828	0.00172
Leonite	-6.16	-6.16666	-0.00666
Aphthitalite/Glaserite	-7.13	-7.14035	-0.01035

The two codes are once again in excellent agreement despite the facts that there is a small inconsistency in the code inputs (which was deliberately minimized) and that different approximations were used for the J(x) higher-order electrostatic term function. It is notable that the difference in J(x) approximation is no more problematic for Dead Sea brine than seawater, despite the former brine being approximately tenfold more concentrated.

5.3 Test Case #3 – gypnaclx: Solubility of Gypsum in a Saturated NaCl Solution

5.3.1 Test Overview

This is a modified version of the EQ3/6 deadsea (Dead Sea brine) test case described in Section 6.6 (p. 144–156) of Wolery and Daveler (1992). In that test case, excess gypsum ($CaSO_4 \cdot 2H_2O$) was reacted with pure water. Then halite (NaCl) was added to the system until the final system was saturated with both gypsum and halite. The modified problem simply adds an excess of both minerals to pure water to achieve the same end point. This problem is "type 1" since it starts with pure water. It is analogous to test cases #6-10 (in the f24vc7) series, which will be discussed later in this document. Those problems also involve the addition of minerals to pure water (but the mineral sets are different). For this type of problem, the codes can effectively calculate the pH of the pure water (or of the saturated solution) from charge balance. Thus, an initial pH input is not required, and the fictive "H+(solid)" does not appear in the FMT runs. This test case is relevant to WIPP, as WIPP ERDA-6 is an NaCl-rich brine similar to the concentrated solution produced here.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	gynaclx.6i
EQ6 output files:	gynaclx.6o, gynaclx.6p
Thermodynamic dada file:	FMT_050405.CHEMDAT
FMT input files:	gypnacl_01-14-09.in; gypnacl_01-14-09.inguess
FMT output files:	gypnacl_01-14-09.out; gypnacl_01-14-09.for088

This test case specifies that sufficient halite and gypsum be reacted with "pure" water to produce a solution that is saturated with both salts. Here 8-10 moles of halite and 1 mole of gypsum are sufficient to saturate 1 kg of water. The initial pure water may contain trace amounts of Na^+, Ca^{2+}, Cl^-, and SO_4^{2-} to allow the codes to set up the necessary bookkeeping. For this purpose, a concentration less than 1×10^{-10} molal would be considered sufficiently low. For both codes, this calculation is a two-step process. First, the pure water must be set up, using EQ3NR on the EQ3/6 side and an FMT run with a .IN file on the FMT side. Then the minerals must be added, using EQ6 on the EQ3/6 side (the pure water information from the EQ3NR pickup file is added to the EQ6 input file) and using FMT run with a .INGUESS file (which contains the pure water information from the .FOR88 file from the previous run). When the second FMT run is done, the code reads all the inputs from the gypnacl_01-14-09.INGUESS only, but the presence of gypnacl_01-14-09.IN is still required by the code.

5.3.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.3.3 Evaluation

Code outputs were assembled into the spreadsheet gypnaclx.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.3-1 compares the results for the set of general parameter outputs. These outputs are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria. The largest differences are for the solution mass and the H_2O mass. The EQ3/6 H_2O mass is not the 1000 g produced by a normal EQ3NR run because EQ6 started with 1000 g of H_2O. As gypsum ($CaSO_4.2H_2O$) dissolves in water, it produces more H_2O. The FMT results appear to differ because of an intent to scale the final system to 1000 g H_2O (see listing of the gypnacl_01-14-09.INGUESS below). Thus, the absolute masses of the final systems produced by the two codes are slightly different. For our purposes, this does not matter as long as the systems are otherwise identical (the extensive parameters such as absolute mass may differ, but the intensive parameters such as concentrations, TDS, density, and pH are essentially the same). Here the only extensive parameters that will be discussed are the solution mass and the H_2O mass. The dissolved and remaining amounts of the minerals are also extensive, but will not be addressed here (or much in subsequent test cases) because the aqueous solution composition comprises a sufficient basis for comparing the codes. The remaining amount of a mineral is often not relevant, and the dissolved amount is often readily apparent from the aqueous solution data and the mass of the final solution.

Table 5.3-1. Test Case #3 (gypnaclx) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1359.931043	1362.1103	0.160%
H2O mass, g	1000.000003	1001.5837	0.158%
Ionic strength, m	6.231571	6.2325	0.015%
density, g/L	1205.07	1205.1	0.002%
TDS, g/L	318.9449746	318.96	0.005%
a_w	0.753941	0.75393	-0.001%
x_w	0.819799	0.8198	0.000%
λ_w	0.9197	0.91966	-0.004%
pH (Pitzer)	6.6968	6.6967	-0.0001
pmH	7.3563	7.3562	-0.0001
pcH	7.4088	7.4087	-0.0001

The gypnacl_01-14-09.INGUESS is listed as follows. The code reads and uses the first column (moles of species) only. The data in the last column are the number of moles of the initial solution without rescaling. Usually the numbers in the first column of a .INGUESS file are scaled to 1000 g (~55.508 moles) of H2O. Here that is not the case.

```
5.542143210000000E+01 H2O                                      WATER 5.555999989948464E+01
```

```
9.990763436344562E-19 Na+                             Na+ 9.999999998939304E-19
0.000000000000000E+00 K+                               K+ 0.000000000000000E+00
9.990763437404276E-19 Ca++                           Ca++ 1.000000000000000E-18
0.000000000000000E+00 Mg++                           Mg++ 0.000000000000000E+00
0.000000000000000E+00 MgOH+                         MgOH+ 0.000000000000000E+00
1.004225223677234E-07 H+                               H+ 1.005153640128771E-07
9.990761010863508E-19 Cl-                             Cl- 9.999997571215870E-19
9.990668053212081E-19 SO4=                           SO4= 9.999904527624145E-19
9.537319391746201E-24 HSO4-                         HSO4- 9.546136740701484E-24
1.004225223677234E-07 OH-                             OH- 1.005153640128771E-07
1.000000000000000E+00 CaSO4.2H2O___________________Gypsum 0.000000000000000E+00
8.000000000000000E+00 NaCl_________________________Halite 0.000000000000000E+00
```

Table 5.3-2 compares results for solute species molalities. These are all within the 1% acceptance criterion. The differences for Ca++ and SO4--, however, are notably greater than for the other species.

Table 5.3-2. Test Case #3 (gypnalcx) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.05707	6.0569	-0.003%
Na+	6.05707	6.0569	-0.003%
Ca++	0.0436248	0.043884	0.594%
SO4--	0.0436248	0.043884	0.594%
OH-	7.22453E-08	7.2253E-08	0.011%
H+	4.40284E-08	4.4036E-08	0.017%
HSO4-	2.82170E-08	2.8217E-08	0.000%

Table 5.3-3 compares results for solute species activity coefficients. These are also all within the 1% acceptance criterion. Again, however, the differences for Ca++ and SO4--, however, are notably greater than for the other species. This might be due to the different J(x) approximations. This possibility will be addressed later in this section.

Table 5.3-3. Test Case #3 (gypnalcx) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.019	1.01906	0.006%
Na+	0.9948	0.99472	-0.008%
Ca++	1.282	1.27438	-0.594%
SO4--	0.018945	0.018840	-0.573%
OH-	0.5231	0.52300	-0.020%
H+	4.566	4.56562	-0.008%
HSO4-	0.5605	0.56053	0.006%

Table 5.3-4 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant minerals. In one case (thenardite) the acceptance criterion of 0.004 for a logarithmic quantity is slightly exceeded. This is explained by the fact that FMT reports saturation indices to only three significant figures. Here we note that when a mineral is exactly saturated (the calculated saturation index is exactly zero), FMT does not

explicitly report the saturation index value. Rather, the place where the value would be given (in the "Descriptor" column of the .OUT file) is left blank. In this table (and in similar tables given later in this report), such a blank value will be represented as zero to the precision used for saturation indices by EQ3/6. In this case, there is the curious exception that for halite (which is saturated), a saturation index of 4.06E-10 was reported. This non-zero result is for our purposes equivalent to zero. It probably reflects convergence tolerances.

Table 5.3-4. Test Case #3 (gypnaclx) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Anhydrite	0.0269	0.02693	0.00003
Gypsum	0.00000	0.00000	0.00000
Halite	4.06E-10	0.00000	0.00000
Glauberite	-0.613	-0.61346	-0.00046
Thenardite	-1.24	-1.23529	0.00471
Mirabilite	-1.52	-1.52165	-0.00165
Labile_Salt	-1.95	-1.95378	-0.00378
CaCl2.4H2O	-5.88	-5.87934	0.00066

The results of the two codes are in excellent agreement. However, the EQ3/6 run was repeated in a modified test case gypnaclx_P75 in which EQ3/6 was directed to use the same J(x) approximation (Pitzer, 1975) as FMT. Test cases so modified in this report will be referred to as "one-off." The results of this were compared with FMT using the spreadsheet gypnaclx_P75. Table 5.3-5 shows the results for solute species molalities, while Table 5.3-6 shows those for solute species activity coefficients. The results are again within the acceptance criterion of 1%. However, the differences for Ca++ and SO4-- no longer stand out, and the differences overall are notably smaller. Although a better comparison is obtained here, it is reiterated that both codes should be using the Harvie (1981) approximation for actual applications (but this approximation is not in any present version of FMT)

Table 5.3-5. Test Case #3 One-Off (gypnalcx_P75) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.05707	6.0570	-0.001%
Na+	6.05707	6.0570	-0.001%
Ca++	0.0436248	0.043625	0.000%
SO4--	0.0436248	0.043625	0.000%
OH-	7.22453E-08	7.2241E-08	-0.006%
H+	4.40284E-08	4.4028E-08	-0.001%
HSO4-	2.82170E-08	2.8213E-08	-0.014%

Table 5.3-6. Test Case #3 One-Off (gypnalcx_P75) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.019	1.01883	-0.017%
Na+	0.9948	0.99472	-0.008%
Ca++	1.282	1.28204	0.003%
SO4--	0.018945	0.018950	0.001%
OH-	0.5231	0.52312	0.004%
H+	4.566	4.56562	-0.008%
HSO4-	0.5605	0.56053	0.006%

5.4 Test Case #4 – Speciation of WIPP SPC Brine

5.4.1 Test Overview

This test case is to compare the speciation for WIPP SPC brine predicted by two codes. The WIPP SPC brine is similar to the currently used WIPP GWB. This test case is Test Case # 1 of FMT validation tests (Wang, 1998). This is a "type 3" problem in that the lack of a proper front-end in FMT may affect the results, including the calculated pH.

This is not a simple speciation problem. The input brine composition is expected to be supersaturated with magnesite ($MgCO_3$). This mineral is then expected to be precipitated to achieve saturation, modifying the solution composition.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	f24vc1.6i
EQ6 output files:	f24vc1.6o, f24vc1.6p
Thermodynamic data file:	FMT_050405.CHEMDAT
FMT input files:	fmt_test1.in; fmt_test1.inguess
FMT output files:	fmt_test1.out; fmt_test1.for088

Table 5.4-1 gives the input data described by Wang (1998). These are the element totals from the FMT_SPC_BM.IN file.

Table 5.4-1. Test Case #4 (f24vc1) FMT inputs.

Element	Moles
H	111.084063
O	55.7650233
Na	2.0
K	0.84
Mg	1.55999951
Ca	0.0164
Cl	5.83
C	0.00507101504
S	0.0436
Br	0.0109
B	0.0218
NegIon	0.0532

This elemental composition is closely charge-balanced (-5.1984×10^{-7} equivalents) assuming the expected oxidation states of the elements (see worksheet "input table" of spreadsheet f24vc1.xls). Wang (1998) provides no information regarding the source of the numbers in this table. In particular there is no documentation of the chemical formulas associated with the original data, so it is impossible to tell if the B value was calculated from $B(OH)_3$ or $B(OH)_4^-$, or some combination of these, or whether the C value was calculated from HCO_3^- or CO_3^{2-} or $CO_{2(aq)}$, or some combination of these.

Table 5.4-2 shows the corresponding input data prepared for EQ3/6. Because the number of moles of H in Table 5.4-1 is nearly equal to what one would expect from 1 kg of H_2O, the original concentrations used to calculate the elemental mole totals in that table were almost certainly molalities. The elements other than H and O were then mapped to the corresponding data0.fmt basis species.

Table 5.4-2. Test Case #4 (f24vc1) EQ3/6 inputs.

Basis species	Molality
Na+	2.0
K+	0.84
Mg++	1.55999951
Ca++	0.0164
Cl-	5.83
HCO3-	0.00507101504
SO4--	0.0436
Br-	0.0109
B(OH)4-	0.0218
NegIon	0.0532

This is nominally consistent (note the absence of a pH value) with a charge imbalance of -0.015371995 eq/kg.H_2O (see worksheet "input table" of spreadsheet f24vc1.xls), notably greater than the implied -5.1984×10^{-7} eq/kg.H_2O for the element total data. If one were to use $B(OH)_{3(aq)}$ as the basis species for B, the calculated charge imbalance becomes +0.006428005 (smaller magnitude, changed sign). If in addition one were to use CO_3^{2-} as the basis species for C, the imbalance becomes +0.00135699, still smaller in magnitude. There is not much possibility for further reduction by appealing to a different combination of basis species. One would not expect HSO_4^- to be more appropriate than SO_4^{2-} (and this would only make the calculated imbalance more positive) and an input for OH^- appears unlikely to have been available. In theory, if one were to assign a single basis species to each chemical element, one could invert the element total data in Table 5.4-1 and look for a set of basis species that would yield a near-zero charge balance. This would have to include H^+ or OH^- for H. Total molalities or mole totals for these are generally unobtainable by chemical analysis of complex solutions. From that and the preceding analysis, it seems fairly clear that the element mole total data in Table 5.4-1 were not obtained in the expected manner (e.g., how such data were obtained for the swmajm and deadseaw test cases) from the usual compositional data.

It appears most probably that the element totals in Table 5.4-1 were derived instead from a full speciation model, possibly an EQ3/6 run, using a presently unknown set of inputs. A potential way to obtain EQ3/6 input that is more consistent with the FMT input would be to construct the data (pH plus molalities of basis species) from the speciation model calculated by FMT. The necessary data could be taken from the FMT output file. Although that approach could be taken to show consistency between EQ3/6 and FMT, it would require using output from one code as input to another, which is generally not what one is aspiring to accomplish in comparing the results of two codes. Also, we are trying to compare the codes using the ways that each would normally be used. Therefore, the data in Tables 5.4-1 and 5.4-2 will be used in the present comparison. It will be understood that there is an unavoidable degree of inconsistency in the code inputs.

5.4.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2). However, as it has been noted above that there is an unavoidable degree of inconsistency in the code inputs, it will be understood that the usual numerical criteria may be exceeded even in the absence of other factors that may contribute to differences in the results from the two codes.

5.4.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc1.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.3-4 compares the results for the set of general parameter outputs. These outputs are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria (1% for "linear" quantities and 0.01 for pH), even the pH results. The most notable difference is for the ionic strength (0.345%). In absolute terms, the ionic strength difference is 0.026131 molal. This nearly matches what the NegIon component would be expected to contribute (0.0266 molal). An examination of the FMT source code revealed that FMT does not include a contribution from NegIon when calculating the ionic strength (see subroutine apitzer.for). When doing this calculation, FMT uses special lists of cations, anions, and neutral species taken from the chemdat data file. These lists are separate from the main list of species on that data file. There is a potential for inconsistency with the main species list on the data file, but examination of the data file revealed no actual inconsistencies. The omission of NegIon from the list of anions appears to have been a deliberate choice. On the EQ3/6 side, NegIon was created on the data0.fmt data file as a negatively charged species with no other specific qualities. EQ3/6 does include it in calculating the ionic strength. Whether to include such a fictive species in the ionic strength calculation (or any other calculation apart from that for charge balance) is largely a matter of taste. Although EQ3/6 would include NegIon and PosIon in such calculations, it (unlike FMT) does treat charged-imbalanced systems. It does not consider the charge imbalance in calculating the ionic strength (to do so would require assigning a charge number). Therefore, it is merely noted here that the two codes treat NegIon and PosIon differently in some regards, and this will necessarily add to differences in some of the code outputs. The difference in the ionic strength values will necessarily lead to differences in calculated activity coefficients, and hence to differences in other parameters.

Table 5.4-3. Test Case #4 (f24vcl) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1330.407384	1330.4703	0.005%
H2O mass, g	999.9972674	1000.0616	0.006%
Ionic strength, m	7.569169	7.5953	0.345%
density, g/L	1190.11	1190.1	-0.001%
TDS, g/L	295.5674535	295.55	-0.006%
a_w	0.758695	0.7582	-0.065%
x_w	0.842589	0.8426	0.001%
λ_w	0.9004	0.89983	-0.063%
fCO2, bars	0.00182	0.00181584	-0.229%
pH (Pitzer)	6.5051	6.5069	0.0018
pmH	6.9898	6.9910	0.0012
pcH	7.0382	7.0394	0.0012

Note that the H_2O mass in the EQ3/6 calculation is not precisely 1000 g. This is because the precipitation of magnesite ($MgCO_3$) creates a small amount of water. This can be understood by examining the precipitation reaction, which can be written as: $Mg^{2+} + 2\ HCO_3^- \square\ MgCO_3(s) + H_2O + CO_{2(aq)}$.

Table 5.3-4 compares results for solute species molalities. Most differences are within the usual 1% acceptance criterion. Exceptions are for CO_3^{2-}, $B_4O_5(OH)_4^{2-}$, and HSO_4^- All differences are within 2%. Given the factors discussed above (inconsistencies in inputs, treatment of NegIon), not to mention the usage of J(x) approximations, these results are considered acceptable.

Table 5.4-4. Test Case #4 (f24vcl) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.83002	5.8296	-0.007%
Na+	2.00001	1.9999	-0.005%
Mg++	1.55395	1.5539	-0.003%
K+	0.840002	0.83995	-0.006%
SO4--	0.0436001	0.043597	-0.007%
B(OH)3(aq)	0.0202511	0.020250	-0.005%
Ca++	0.0163816	0.016381	-0.004%
Br-	0.0109	0.010899	-0.009%
MgB(OH)4+	0.00112935	0.00112830	-0.093%
B(OH)4-	0.000362398	0.00036338	0.271%
HCO3-	0.000140358	0.00014057	0.151%
CO2(aq)	2.18481E-05	2.1793E-05	-0.252%
CaB(OH)4+	1.83288E-05	1.8303E-05	-0.141%
MgOH+	1.78189E-05	1.7876E-05	0.320%
B3O3(OH)4-	1.24753E-05	1.2528E-05	0.422%
MgCO3(aq)	1.24349E-05	1.2434E-05	-0.007%
CO3--	1.58972E-06	1.6152E-06	1.603%

B4O5(OH)4--	3.54373E-07	3.6091E-07	1.845%
CaCO3(aq)	1.18621E-07	1.1857E-07	-0.043%
H+	1.02365E-07	1.0210E-07	-0.259%
OH-	8.80709E-08	8.8365E-08	0.334%
HSO4-	2.20433E-08	2.1708E-08	-1.521%

Table 5.3-5 compares results for solute species activity coefficients. Most are within the 1% acceptance criterion. The exceptions are for SO_4^{2-} and CO_3^{2-}. All results are within 2%. Given the factors discussed above (inconsistencies in inputs, treatment of NegIon, use of different J(x) approximations), these results are quite acceptable.

Table 5.4-5. Test Case #4 (f24vc1) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.789	1.78649	-0.140%
Na+	0.7683	0.76718	-0.145%
Mg++	0.9613	0.95631	-0.519%
K+	0.3463	0.34578	-0.150%
SO4--	0.033103	0.03269	-1.251%
B(OH)3(aq)	1.558	1.55812	0.007%
Ca++	0.5208	0.51785	-0.567%
Br-	0.2666	0.26656	-0.014%
MgB(OH)4+	1.466	1.46420	-0.123%
B(OH)4-	0.1219	0.12198	0.068%
HCO3-	0.4773	0.47709	-0.044%
CO2(aq)	2.747	2.74726	0.010%
CaB(OH)4+	0.9193	0.91833	-0.105%
MgOH+	0.3158	0.31427	-0.485%
B3O3(OH)4-	0.4153	0.41572	0.101%
MgCO3(aq)	1.000	1.00000	0.000%
CO3--	0.0061740	0.0061094	-1.046%
B4O5(OH)4--	0.0048178	0.0047764	-0.859%
CaCO3(aq)	1.000	1.00000	0.000%
H+	3.053	3.04789	-0.167%
OH-	0.2778	0.27778	-0.007%
HSO4-	1.948	1.94491	-0.159%

Table 5.4-6 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. The usual acceptance criterion of 0.004 for a logarithmic quantity is exceeded in a number of cases. Some instances would be expected due to FMT reporting saturation indices with very limited precision. However, several instances here clearly exceed the limits of FMT's limited output precision. All results are within 0.04 unit, however, so overall agreement is acceptable considering the factors that have been discussed above.

Table 5.4-6. Test Case #4 (f24vc1) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Magnesite	0.00000	0.00000	0.00000
Halite	-0.366	-0.36691	-0.00091
Sylvite	-0.418	-0.41921	-0.00121
Anhydrite	-0.548	-0.55547	-0.00747
Gypsum	-0.569	-0.57750	-0.00850
Dolomite	-0.828	-0.82864	-0.00064
B(OH)3	-1.47	-1.47061	-0.00061
Syngenite	-1.49	-1.50934	-0.01934
Epsomite	-1.62	-1.63455	-0.01455
Calcite	-1.67	-1.67104	-0.00104
Hexahydrite	-1.75	-1.76034	-0.01034
Aragonite	-1.86	-1.85784	0.00216
Arcanite	-2.13	-2.14366	-0.01366
Glauberite	-2.14	-2.14742	-0.00742
Thenardite	-2.18	-2.18685	-0.00685
Kainite	-2.35	-2.36149	-0.01149
Carnallite	-2.36	-2.36380	-0.00380
Mirabilite	-2.44	-2.44874	-0.00874
Kieserite	-2.66	-2.67164	-0.01164
Polyhalite	-2.89	-2.92555	-0.03555
Bischofite	-2.96	-2.96950	-0.00950
Picromerite/Schoenite	-2.97	-2.98769	-0.01769
Nesquehonite	-3.03	-3.02746	0.00254
Leonite	-3.08	-3.09595	-0.01595
Bloedite	-3.27	-3.28245	-0.01245
Aphthitalite/Glaserite	-3.30	-3.31441	-0.01441
Nahcolite	-3.58	-3.58464	-0.00464
Brucite	-4.16	-4.16360	-0.00360
Labile_Salt	-4.41	-4.43441	-0.02441
Teepleite(20C)	-4.56	-4.56513	-0.00513
Na_Metaborate	-4.74	-4.73706	0.00294
Kalicinite	-4.99	-4.99184	-0.00184
Borax	-5.68	-5.68373	-0.00373
K-Pentaborate(30C)	-5.85	-5.84610	0.00390
Mg2Cl(OH)3.4H2O	-5.99	-5.98886	0.00114
CaCl2.4H2O	-6.23	-6.23420	-0.00420
Na_Pentaborate	-6.47	-6.46712	0.00288

In Table 5.4-6, the saturation index for magnesite ($MgCO_3$) is precisely zero because magnesite was actually precipitated to achieve equilibrium with the aqueous solution. Table 5.4-7 compares how much magnesite was precipitated according to the two codes. The magnitude of the calculated difference is well under 1%.

Table 5.4-7. Test Case #4 (f24vc1) Calculated Moles of Magnesite Precipitated, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Magnesite	0.00489467	0.0048945	-0.003%

The results of the two codes are in fair agreement. Some are outside the usual numerical limits, but these are not too bad and are explainable as arising from a combination of factors including an inconsistency in the code inputs, the different treatment of NegIon, and the use of different J(x) approximations. Overall, the results are acceptable.

The EQ3/6 run was repeated in a one-off test case f24vc1_P75 in which EQ3/6 used the same J(x) approximation (Pitzer, 1975) as FMT. The results of this were compared with FMT using the spreadsheet f24vc1_P75.xls, which is the direct source of the following tables. Table 5.4-8 compares the general parameter outputs. These results are not much different from those given in Table 5.4-3. The difference is ionic strength is about the same, reflecting the difference in the way the two codes treat NegIon. The difference in CO_2 fugacity is slightly larger, but the differences in pH are slightly smaller. As before, all of these results satisfy the usual acceptance criteria.

Table 5.4-8. Test Case #4 One-Off (f24vc1_P75) General Parameter Outputs, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1330.407384	1330.4702	0.005%
H2O mass, g	999.9972674	1000.0616	0.006%
Ionic strength, m	7.569169	7.5953	0.345%
density, g/L	1190.11	1190.1	-0.001%
TDS, g/L	295.5674535	295.55	-0.006%
a_w	0.758695	0.75817	-0.069%
x_w	0.842589	0.8426	0.001%
λ_w	0.9004	0.89981	-0.066%
fCO2, bars	0.00182	0.00181476	-0.288%
pH (Pitzer)	6.5051	6.5067	0.0016
pmH	6.9898	6.9912	0.0014
pcH	7.0382	7.0396	0.0014

Table 5.4-9 shows the results for solute species molalities. The usual 1% acceptance criterion is now satisfied for all but two species ($B_4O_5(OH)_4^{2-}$ and HSO_4^-). This is down from three in Table 5.4-4, in which the difference for CO_3^{2-} also exceeded 1%. The differences for the two remaining species are now smaller.

Table 5.4-9. Test Case #4 One-Off (f24vc1_P75) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.83002	5.8296	-0.007%
Na+	2.00001	1.9999	-0.005%
Mg++	1.55395	1.5539	-0.003%
K+	0.840002	0.83995	-0.006%
SO4--	0.0436001	0.043597	-0.007%
B(OH)3(aq)	0.0202511	0.020250	-0.005%
Ca++	0.0163816	0.016381	-0.004%
Br-	0.0109	0.010899	-0.009%
MgB(OH)4+	0.00112935	0.0011283	-0.093%
B(OH)4-	0.000362398	0.00036322	0.227%
HCO3-	0.000140358	0.00014042	0.044%
CO2(aq)	2.18481E-05	2.1780E-05	-0.312%
CaB(OH)4+	1.83288E-05	1.8303E-05	-0.141%
MgOH+	1.78189E-05	1.7876E-05	0.320%
B3O3(OH)4-	1.24753E-05	1.2523E-05	0.382%
MgCO3(aq)	1.24349E-05	1.2434E-05	-0.007%
CO3--	1.58972E-06	1.6054E-06	0.986%
B4O5(OH)4--	3.54373E-07	3.5897E-07	1.297%
CaCO3(aq)	1.18621E-07	1.1857E-07	-0.043%
H+	1.02365E-07	1.0204E-07	-0.317%
OH-	8.80709E-08	8.8323E-08	0.286%
HSO4-	2.20433E-08	2.1818E-08	-1.022%

Table 5.4-10 shows the results for solute species activity coefficients. All of these results satisfy the usual 1% acceptance criterion. Previously, the differences for SO_4^{2-} and CO_3^{2-} (see Table 5.4-5) exceeded 1%.

Table 5.4-10. Test Case #4 One-Off (f24vc1_P75) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.789	1.78608	-0.163%
Na+	0.7683	0.76807	-0.030%
Mg++	0.9613	0.95786	-0.358%
K+	0.3463	0.34618	-0.035%
SO4--	0.033103	0.03283	-0.818%
B(OH)3(aq)	1.558	1.55812	0.007%
Ca++	0.5208	0.51880	-0.384%
Br-	0.2666	0.26656	-0.014%
MgB(OH)4+	1.466	1.46589	-0.008%
B(OH)4-	0.1219	0.12198	0.068%
HCO3-	0.4773	0.47698	-0.067%
CO2(aq)	2.747	2.74726	0.010%

CaB(OH)4+	0.9193	0.91939	0.010%
MgOH+	0.3158	0.31463	-0.371%
B3O3(OH)4-	0.4153	0.41562	0.078%
MgCO3(aq)	1.000	1.00000	0.000%
CO3--	0.0061740	0.0061362	-0.612%
B4O5(OH)4--	0.0048178	0.0047973	-0.425%
CaCO3(aq)	1.000	1.00000	0.000%
H+	3.053	3.05141	-0.052%
OH-	0.2778	0.27778	-0.007%
HSO4-	1.948	1.94491	-0.159%

Table 5.4-11 shows the results for mineral saturation indices. All differences are less than 0.025 in magnitude, somewhat better than before (see Table 5.4-6), but some still exceed the limit imposed by FMT's limited reporting precision.

Table 5.4-11. Test Case #4 One-Off (f24vc1_P75) Calculated Mineral Saturation Indices, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Mineral	FMT	EQ3/6	Δ
Magnesite	0.00000	0.00000	0.00000
Halite	-0.366	-0.36645	-0.00045
Sylvite	-0.418	-0.41875	-0.00075
Anhydrite	-0.548	-0.5528	-0.00480
Gypsum	-0.569	-0.57487	-0.00587
Dolomite	-0.828	-0.82864	-0.00064
B(OH)3	-1.47	-1.47061	-0.00061
Syngenite	-1.49	-1.50378	-0.01378
Epsomite	-1.62	-1.63198	-0.01198
Calcite	-1.67	-1.67104	-0.00104
Hexahydrite	-1.75	-1.75774	-0.00774
Aragonite	-1.86	-1.85784	0.00216
Arcanite	-2.13	-2.14074	-0.01074
Glauberite	-2.14	-2.14184	-0.00184
Thenardite	-2.18	-2.18394	-0.00394
Kainite	-2.35	-2.35841	-0.00841
Carnallite	-2.36	-2.36277	-0.00277
Mirabilite	-2.44	-2.44594	-0.00594
Kieserite	-2.66	-2.66899	-0.00899
Polyhalite	-2.89	-2.91467	-0.02467
Bischofite	-2.96	-2.96891	-0.00891
Picromerite/Schoenite	-2.97	-2.98219	-0.01219
Nesquehonite	-3.03	-3.02749	0.00251
Leonite	-3.08	-3.09042	-0.01042
Bloedite	-3.27	-3.27692	-0.00692
Aphthitalite/Glaserite	-3.30	-3.30858	-0.00858
Nahcolite	-3.58	-3.58464	-0.00464
Brucite	-4.16	-4.16335	-0.00335

Labile_Salt	-4.41	-4.42594	-0.01594
Teepleite(20C)	-4.56	-4.56442	-0.00442
Na_Metaborate	-4.74	-4.73683	0.00317
Kalicinite	-4.99	-4.99184	-0.00184
Borax	-5.68	-5.68325	-0.00325
K-Pentaborate(30C)	-5.85	-5.84579	0.00421
Mg2Cl(OH)3.4H2O	-5.99	-5.98821	0.00179
CaCl2.4H2O	-6.23	-6.23359	-0.00359
Na_Pentaborate	-6.47	-6.46681	0.00319

Table 5.4-12 compares how much magnesite was precipitated according to the two codes. The magnitude of the calculated difference is well under 1%, as was the case before (Table 5.4-7).

Table 5.4-12. Test Case #4 One-Off (f24vc1_P75) Calculated Moles of Magnesite Precipitated, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Mineral	FMT	EQ3/6	Δ
Magnesite	0.00489467	0.0048946	-0.001%

Some things could have been done to further run these differences to ground, but it did not seem worthwhile to do so. For example, the problem inputs could have been redefined to eliminate inconsistency. In the process, extra chlorine/chloride could have been included to take the place of NegIon.

5.5 Test Case #5A – Solubility of ThO_2(am) in NaCl solution at pmH 3.8

5.5.1 Test Overview

The purpose of this test case is to compare thorium concentrations in NaCl solution predicted by EQ3/6 and FMT. ThO_2(am) is currently used as a source-term solubility-controlling phase for +IV actinides in WIPP Performance Assessment (WIPP PA). This is a part of Test Case #3 from the validation of FMT v. 2.4 (Wang, 1998). The original test case models a titration that is intended to model the solubility of ThO_2(am) as a function of pcH in 6 molal NaCl solution in comparison with experimental data. Although both EQ3/6 and FMT have modes for modeling titration processes, they do not operate in quite the same manner. Therefore, only the ends of the titration will be compared in the present document. Test Case #5A models the more acidic end (pmH 3.8). Test Case #5B will address the less-acidic one (pmH 5.5).

In theory, this is a "type 2" problem. The initial "medium" solution (5.9 molal NaCl plus 0.1 molal HCl) composition is simple and there should be no issues with charge balancing that might adversely affect the computed pH. Neither code actually computes this solution. On the EQ3/6 side, the desired system was directly calculated using EQ3NR by including a specification of ThO_2(am) solubility to constrain the concentration of Th^{4+}. On the FMT side, the original titration mode input files were re-run with the current chemdat database. Owing to the simplicity of this case, the formal inputs will not be listed in tables here. The FMT inputs will be looked at in detail at the end of the evaluation of this test case.

Test Files:

Thermodynamic data file:	data1.fmt
EQ3 input file:	f24vc3s1.3i
EQ3 output files:	f24vc3s1.3o, f24vc3s1.3p
Thermodynamic data file:	FMT_050405.CHEMDAT
FMT input files:	fmt_test3.in; fmt_test3.inguess
FMT output files:	fmt_test3.out; fmt_test3.for088

5.5.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.5.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc3s1.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.5-1 compares the results for the set of general parameter outputs. These outputs are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria. However, FMT has somewhat higher values for the solution mass and the H_2O mass. This suggests that despite the simplicity of the problem input, there is nonetheless a minor "front end" problem, as additional water seems to have been created in the FMT run. The slightly lower ionic strength appears to correlate with this.

Table 5.5-1. Test Case #5A (f24vc3s1) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1355.052388	1354.1	-0.070%
H2O mass, g	1000.902916	1000.0	-0.090%
Ionic strength, m	6.144212	6.1498	0.091%
density, g/L	1202.00	1202.00	0.000%
TDS, g/L	314.1495638	314.4	0.080%
a_w	0.755084	0.75481	-0.036%
x_w	0.823289	0.82316	-0.016%
λ_w	0.9172	0.91697	-0.025%
pH (Pitzer)	3.1371	3.1420	0.0049
pmH	3.7953	3.8021	0.0068
pcH	3.8470	3.8528	0.0058

Table 5.5-2 compares results for solute species molalities. These are mostly within the usual 1% acceptance criterion. The differences for H^+ and OH^- are slightly above 1%. This could be due to the difference in J(x) approximations, especially given that a quadrivalent ion (Th^{4+}) is present at a non-trace concentration. It could also be due to the "front end" problem noted above.

Table 5.5-2. Test Case #5A (f24vc3s1) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.99459	6.0000	0.090%
Na+	5.89468	5.9000	0.090%
Th++++	0.0249374	0.024960	0.091%
H+	0.000160202	0.00015810	-1.312%
Th(OH)4(aq)	5.52414E-08	5.5205E-08	-0.066%
OH-	1.97257E-11	1.9938E-11	1.076%
Total Th	0.024937	0.024961	0.092%

Table 5.5-3 compares results for solute species activity coefficients. These are all within the 1% acceptance criterion, with the notable exception of the case for Th^{4+}. This is almost certainly due in part to the use of different J(x) approximations, but it might also be due in part to the "front end" problem.

Table 5.5-3. Test Case #5A (f24vc3s1) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.073	1.07349	0.046%
Na+	0.9777	0.97836	0.068%
Th++++	0.6098	0.58264	-4.454%
H+	4.552	4.56037	0.184%
Th(OH)4(aq)	1.000	1.00000	0.000%
OH-	0.529	0.52905	0.010%

Table 5.5-6 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. The usual acceptance criterion of 0.004 for a logarithmic quantity is satisfied. There are only two minerals listed, one of which is required to be saturated.

Table 5.5-4. Test Case #5A (f24vc3s1) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
ThO2(am)	0.00000	0.00000	0.00000
Halite	-0.00155	-0.00012	0.00143

The results of the two codes are in fair agreement. However, the EQ3/6 run was repeated in a one-off test case f24vc3s1_P75 in which EQ3/6 used the same J(x) approximation (Pitzer, 1975) as FMT. The results of this were compared with FMT using the spreadsheet f24vc3s1_P75.xls, which is the direct source of the following tables. Table 5.5-5 compares the general parameter outputs. Some of the differences (e.g., the pH results) are now smaller. However, it is clear that extra water was created in the FMT run. The ionic strength is therefore still smaller in the FMT result.

Table 5.5-5. Test Case #5A One-Off (f24vc3s1_P75) General Parameter Outputs, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1355.052388	1354.1	-0.070%
H2O mass, g	1000.902916	1000.0	-0.090%
Ionic strength, m	6.144212	6.1498	0.091%
density, g/L	1202.00	1202.2	0.017%
TDS, g/L	314.1495638	314.4	0.080%
a_w	0.755084	0.75481	-0.036%
x_w	0.823289	0.82316	-0.016%
λ_w	0.9172	0.91697	-0.025%
pH (Pitzer)	3.1371	3.1352	-0.0019
pmH	3.7953	3.7943	-0.0010
pcH	3.8470	3.8460	-0.0010

Table 5.5-6 shows the results for solute species molalities. In all instances, the 1% acceptance criterion is now satisfied.

Table 5.5-6. Test Case #5A One-Off (f24vc3s1_P75) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.99459	6.0000	0.090%
Na+	5.89468	5.9000	0.090%
Th++++	0.0249374	0.024960	0.091%
H+	0.000160202	0.00016058	0.236%
Th(OH)4(aq)	5.52414E-08	5.5204E-08	-0.068%
OH-	1.97257E-11	1.9630E-11	-0.485%
Total Th	0.024937	0.024960	0.090%

Table 5.5-7 shows the results for solute species activity coefficients. In this case, the results for Th^{4+} are now notably better (+1.745% versus the previous -4.454%). This still exceeds the usual 1% acceptance criterion. However, given that it is close and that the "front end" problem is likely responsible (any change in the ionic strength would strongly affect the activity coefficient of a highly charged species), this is acceptable.

Table 5.5-7. Test Case #5A One-Off (f24vc3s1_P75) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.073	1.07349	0.046%
Na+	0.9777	0.97836	0.068%
Th++++	0.6098	0.62044	1.745%
H+	4.552	4.56142	0.207%
Th(OH)4(aq)	1.000	1.00000	0.000%
OH-	0.529	0.52893	-0.013%

Other results obtained from the comparison using this "one-off" case are less germane to the discussion and will not be presented here. They can be found in the spreadsheet f24vc3s1_P75.xls.

It is unclear why there should be a noticeable front-end problem. Table 5.5-8 gives the actual FMT inputs from the FMT input file, FMT_TEST3.IN. Note that the problem here is set up to already include (hopefully) excess ThO_2(am). It is not set up, as in some other test cases, to first generate an initial water composition, then react it with one or more solids. This should be an acceptable approach.

Table 5.5-8. Test Case #5A Actual FMT Inputs from FMT_TEST3.IN.

Element	Moles
H	1.11117763E+02
O	5.57090817E+01
Na	5.90000000E+00

Cl	6.00000000E+00
Th	1.00100000E-01

Table 5.5-9 shows conceptually the composition of the system for 1 kg of H_2O. This represents, in theory, the data from which the data in Table 5.5-8 would have been derived.

Table 5.5-9. Test Case #5 Inferred Data from Which the Element Totals in Table 5.5-8 Would Have Been Derived (1 kg of H_2O also present).

Component	Moles
H (as H^+)	0.1
Na	5.9
Cl	6.0
ThO2	0.1001

Table 5.5-10 shows the elemental mole totals calculated from the data in Table 5.5-9, assuming the EQ3/6 atomic weights from data0.fmt that give 55.50843506 moles of H_2O per kg. Note that the difference for H is precisely double that for O. This implies that the original FMT input simply assumed more moles of water. Back-calculating, a value of 55.5088817 moles of H_2O per kg must have been used. Using the FMT atomic weights from the chemdat file, one would have 55.50868156 moles per kg, which lies in between. Using this value, the mass of extra water in the FMT input would be 0.0080463 g. However, the FMT run itself had an extra 0.902916 g. So the source of the extra water in the FMT run is not explained by this.

Table 5.5-10. Test Case #5 Recalculated Elemental Mole Totals and Calculated Differences from the Values in Table 5.5-8.

Element	Moles	Δ(Relative to the Values in Table 5.5-8)
H	1.11116870E+02	-8.92880000E-04
O	5.57086351E+01	-4.46640000E-04
Na	5.90000000E+00	0.00000000E+00
Cl	6.00000000E+00	0.00000000E+00
Th	1.00100000E-01	0.00000000E+00

It is clear that the FMT output does seem to have extra water that cannot be accounted for, given an examination of the FMT inputs (which are well charge-balanced). It is possible that a more direct FMT calculation (avoiding the titration mode, which seems to be not very straightforward) would give closer results, although this was not attempted. It is noted that the .IN file contains a composition for a component described as "Plain old pure H2O". This does have the composition of pure water. The purpose of this is unknown, but it could potentially be a source of the extra water.

When both codes use the same J(x) approximation, the results are in fairly good agreement. Given that there is a definite issue with the FMT result, the performance of EQ3/6 is considered acceptable.

5.6 Test Case #5B – Solubility of ThO_2(am) in NaCl solution at pmH 5.5

5.6.1 Test Overview

The purpose of this test case is to compare thorium concentrations in NaCl solution predicted by EQ3/6 and FMT. ThO_2(am) is currently used as a source-term solubility-controlling phase for +IV actinides in WIPP Performance Assessment (WIPP PA). This is a part of Test Case #3 from the validation of FMT v. 2.4 (Wang, 1998). The original test case models a titration that is intended to model the solubility of ThO_2(am) as a function of pcH in 6 molal NaCl solution in comparison with experimental data. Although both EQ3/6 and FMT have modes for modeling titration processes, they do not operate in quite the same manner. Therefore, only the ends of the titration will be compared in the present document. Test Case #5B addresses the less-acidic one (pmH 5.5). Test Case #5A (discussed previously) models the more acidic end (pmH 3.8).

In theory, this is a "type 2" problem. The modeled system for this test case is supposed to be a 6.0 molal NaCl solution at pmH close to 5.5, saturated with ThO_2(am). The pmH is formulated as an output, essentially calculated from charge balance as in Test Case #5A. The actual FMT inputs for the "medium" components were 5.2707224 molar Na^+ and 5.27072516 molar Cl^- (Wang, 1998). The source gives no information as to the derivation of these rather precise values. The difference between the Na^+ and Cl^- concentrations is important, however, to the pmH value that is obtained. Using the WIPP density model, the density and the TDS mg/L ratio could have been obtained by assuming a pure 6 molal NaCl solution, ignoring the dissolved thorium. The molarities could then have been input to EQ3/6. However, to keep things a bit more precise, we elected to simply use the corresponding molalities (5.99997625 for Na^+ and 5.99997940 for Cl^-) as the inputs to EQ3/6. This is reasonable because the outputs of major interest are the pmH and the dissolved thorium. On the EQ3/6 side, this test case was run using the EQ3NR code only, as was done for Test Case #5A. On the FMT side, the results were again taken from the original titration run, updated to run with the current chemdat database.

Test Files:

Thermodynamic data file:	data1.fmt
EQ3 input file:	f24v3s2.3i
EQ3 output files:	f24v3s2.3o, f24v3s2.3p
Thermodynamic data file:	FMT_050405.CHEMDAT
FMT input files:	fmt_test3.in; fmt_test3.inguess
FMT output files:	fmt_test3.out; fmt_test3.for088

5.6.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.6.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc2.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.6-1 compares the results for the set of general parameter outputs. These outputs are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria except those for the solution mass and the H_2O mass. This is because the FMT system is scaled to 1 L of solution, while the EQ3/6 system is scaled to 1 kg H_2O. This difference has no other practical significance and it may be ignored. Note that the ionic strength values match very closely. This signifies that there is no significant difference in the relative amounts of H_2O, unlike the situation found for Test Case #5A.

Table 5.6-1. Test Case #5B (f24vc3s2) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1186.492943	1350.7	13.840%
H2O mass, g	878.4572099	1000.0	13.836%
Ionic strength, m	5.999979	6.0000	0.000%
density, g/L	1200.40	1200.4	0.000%
TDS, g/L	311.6469119	311.65	0.001%
a_w	0.759249	0.75925	0.000%
x_w	0.822246	0.82224	-0.001%
λ_w	0.9234	0.92338	-0.002%
pH (Pitzer)	4.8517	4.8507	-0.0010
pmH	5.5044	5.5034	-0.0010
pcH	5.5556	5.5546	-0.0010

Table 5.6-2 compares results for solute species molalities. With one exception, these are within the 1% acceptance criterion. In the case of Th^{4+}, the difference is just under 8%. This is likely due to the difference in J(x) approximations, the effect of which will be directly examined later in this section. It should be noted that at the higher pmH associated with this test case, there is much less dissolved thorium than in the pmH 3.8 case (Test Case #5A). Also, the highly charged Th^{4+} species is now less abundant than the electrically neutral $Th(OH)_{4(aq)}$. The difference in total dissolved thorium is within the 1% acceptance criterion.

Table 5.6-2. Test Case #5B (f24vc3s2) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.99998	6.0000	0.000%
Na+	5.99998	6.0000	0.000%
H+	3.13043E-06	3.1376E-06	0.229%
Th(OH)4(aq)	5.58526E-08	5.5856E-08	0.006%
Th++++	3.10808E-09	3.3542E-09	7.919%

OH-	9.95011E-10	9.9265E-10	-0.237%
Total Th	5.89607E-08	5.92099E-08	0.423%

Table 5.6-3 compares results for solute species activity coefficients. Again with one exception, these are all within the 1% acceptance criterion. The problematic species is again the highly charged Th^{4+}. This again suggests the effect of the different J(x) approximations.

Table 5.6-3. Test Case #5B (f24vc3s2) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	0.9912	0.99106	-0.014%
Na+	0.9912	0.99106	-0.014%
H+	4.495	4.49469	-0.007%
Th(OH)4(aq)	1.000	1.00000	0.000%
Th++++	0.6708	0.62734	-6.479%
OH-	0.5465	0.54651	0.002%

Table 5.6-4 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. The usual acceptance criterion of 0.004 for a logarithmic quantity is satisfied for both minerals.

Table 5.6-4. Test Case #5B (f24vc3s2) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
ThO2(am)	0.00000	0.00000	0.00000
Halite	-0.0218	-0.02181	-0.00001

The results of the two codes are almost in fair agreement. However, the EQ3/6 run was repeated in a one-off test case f24vc3s2_P75 in which EQ3/6 used the same J(x) approximation (Pitzer, 1975) as FMT. The results of this were compared with FMT using the spreadsheet f24vc3s2_P75. Table 5.6-5 shows the results for solute species molalities. The differences are again within the usual acceptance criterion of 1% for all species except Th^{4+}. However, the difference for that species has been markedly reduced from 7.919% (Table 5.6-2) to just above the 1% level. The difference in total dissolved thorium is within the 1% criterion. Given that there is some minor degree of "front end" problem, these results are acceptable.

Table 5.6-5. Test Case #5B One-Off (f24vc3s2_P75) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.99998	6.0000	0.000%
Na+	5.99998	6.0000	0.000%
H+	3.13043E-06	3.1384E-06	0.255%
Th(OH)4(aq)	5.58526E-08	5.5856E-08	0.006%
Th++++	3.10808E-09	3.1402E-09	1.033%

OH-	9.95011E-10	9.9238E-10	-0.264%
Total Th	5.89607E-08	5.89959E-08	0.060%

Table 5.6-6 shows the results for solute species activity coefficients. These are now all within the usual 1% criterion.

Table 5.6-6. Test Case #5B One-Off (f24vc3s2_P75) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	0.9912	0.99106	-0.014%
Na+	0.9912	0.99106	-0.014%
H+	4.495	4.49469	-0.007%
Th(OH)4(aq)	1.000	1.00000	0.000%
Th++++	0.6708	0.67081	0.002%
OH-	0.5465	0.54651	0.002%

Other results obtained in this one-off comparison are less germane and will not be presented here, but are contained in the spreadsheet f24vc3s2_P75.xls. The results of the two codes are in notably better agreement, which is now acceptable given that some minor "front-end" problem cannot be eliminated. It is clear that for this problem, which J(x) approximation is used is of some importance. It is reiterated that for practical applications, any code should be using the Harvie (1981) approximation, not the Pitzer (1975, eq. 47) approximation.

5.7 Test Case #6 – Invariant point of aphthitate/glaserite–picromerite/schoenite–halite–sylvite in the Na-K-Mg-Cl-SO_4-H_2O system

5.7.1 Test Overview

This test case is to compare the composition of the invariant point of aphthitate/glaserite ($NaK_3(SO_4)_2$)–picromerite/schoenite ($K_2Mg(SO_4)_2.6H_2O$)–halite (NaCl)–sylvite (KCl) in the system Na-K-Mg-Cl-SO_4-H_2O. This is a part of Test Case #7 from the validation of FMT v. 2.4 (Wang, 1998). This problem adds an excess of the relevant minerals to pure water to achieve the desired end point. This is thus a "type 1" problem. It is analogous to test cases #4 (where the minerals were gypsum and halite). For this type of problem, the codes can effectively calculate the pH (of the pure water or the resulting saturated solution) from charge balance.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	f24vc7m.6i
EQ6 output files:	f24vc7m.6o, f24vc7m.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_test7a.in; fmt_test7a.inguess
FMT output files:	fmt_test7a.out; fmt_test7a.for088

5.7.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.7.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc7m.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.7-1 compares the results for the set of general parameter outputs. These are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria applicable to these quantities (1% for "linear" quantities and 0.01 unit for pH).

Table 5.7-1. Test Case #6 (f24v7m) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1909.875807	1911.1012	0.064%
H2O mass, g	1283.095434	1283.5106	0.032%

Ionic strength, m	11.168471	11.181	0.112%
density, g/L	1267.07	1267.3	0.018%
TDS, g/L	415.826417	416.17	0.083%
a_w	0.674306	0.67415	-0.023%
x_w	0.800789	0.80070	-0.011%
λ_w	0.8421	0.84195	-0.018%
pH (Pitzer)	5.4307	5.4306	-0.0001
pmH	6.2197	6.2201	0.0004
pcH	6.2896	6.2901	0.0005

Table 5.7-2 compares results for solute species molalities. These are all within the 1% acceptance criterion. The difference for SO4-- is the greatest.

Table 5.7-2. Test Case #6 (f24v7m) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.72269	6.7219	-0.012%
Na+	2.6298	2.6302	0.015%
Mg++	2.04119	2.0435	0.113%
K+	1.61358	1.6153	0.107%
SO4--	0.801529	0.80531	0.472%
MgOH+	4.60825E-06	4.6139E-06	0.123%
HSO4-	4.01186E-06	4.0181E-06	0.156%
H+	6.02997E-07	6.0241E-07	-0.097%
OH-	6.60712E-09	6.6073E-09	0.003%

Table 5.7-3 compares results for solute species activity coefficients. These are also all within the 1% acceptance criterion. Again, the difference for SO4-- is the greatest. One might expect tighter agreement if the EQ3/6 run were repeated using the Pitzer (1975, eq. 47) approximation for the J(x) function (as was found in the analogous Test Case #3). However, that will not be pursued in the present instance.

Table 5.7-3. Test Case #6 (f24v7m) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	2.439	2.44174	0.112%
Na+	0.8623	0.86139	-0.105%
Mg++	1.708	1.70569	-0.135%
K+	0.3001	0.29950	-0.199%
SO4--	0.030858	0.03077	-0.291%
MgOH+	0.2135	0.21306	-0.207%
HSO4-	2.177	2.17771	0.033%
H+	6.151	6.15886	0.128%
OH-	0.2773	0.27708	-0.081%

Table 5.7-4 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. The acceptance criterion of 0.004 for a logarithmic quantity is slightly exceeded in a small number of instances, as is generally the case due to the fact that FMT reports saturation indices to only three significant figures.

Table 5.7-4. Test Case #6 (f24v7m) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Halite	0.00000	0.00000	0.00000
Sylvite	0.00000	0.00000	0.00000
Aphthitalite/Glaserite	0.00000	0.00000	0.00000
Picromerite/Schoenite	0.00000	0.00000	0.00000
Leonite	-0.00645	-0.00622	0.00023
Bloedite	-0.297	-0.29732	-0.00032
Epsomite	-0.381	-0.38124	-0.00024
Hexahydrite	-0.456	-0.45600	0.00000
Arcanite	-0.460	-0.46030	-0.00030
Kainite	-0.485	-0.48488	0.00012
Thenardite	-0.608	-0.60810	-0.00010
Kieserite	-1.11	-1.11219	-0.00219
Mirabilite	-1.38	-1.38021	-0.00021
Carnallite	-1.49	-1.48520	0.00480
Bischofite	-2.51	-2.51010	-0.00010
Mercallite	-5.95	-5.95038	-0.00038
K3H(SO4)2	-6.05	-6.04598	0.00402
Brucite	-6.05	-6.04797	0.00203
Na3H(SO4)2	-6.76	-6.76268	-0.00268

The results of the two codes are in excellent agreement, despite the use of different approximations for J(x).

5.8 Test Case #7 – Invariant point of borax–teepleite–halite in the system Na-Cl-B_4O_7-H_2O

5.8.1 Test Overview

This test case is to compare the composition of the invariant point of borax–teepleite–halite in Na-Cl-B_4O_7 system. This is also a part of Test Case #7 from the validation of FMT v. 2.4 (Wang, 1998). This problem adds an excess of the relevant minerals to pure water to achieve the desired end point. It is thus a "type 1" problem, analogous to Test Cases #4 and #6. For this type of problem, the codes can effectively calculate the pH from charge balance.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	f24vc7b3.6i
EQ6 output files:	f24vc7b3.6o, f24vc7b3.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_test7b.in; fmt_test7b.inguess
FMT output files:	fmt_test7b.out; fmt_test7b.for088

5.8.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.8.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc7b3.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.8-1 compares the results for the set of general parameter outputs. These are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria applicable to these quantities (1% for "linear" quantities and 0.01 unit for pH).

Table 5.8-1. Test Case #7 (f24v7b3) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1498.156524	1498.1972	0.003%
H2O mass, g	1002.88799	1002.9062	0.002%
Ionic strength, m	7.334729	7.3349	0.002%

density, g/L	1269.55	1269.6	0.004%
TDS, g/L	419.6941569	419.7	0.001%
a_w	0.733123	0.73312	0.000%
x_w	0.79161	0.79161	0.000%
λ_w	0.9261	0.92612	0.002%
pH (Pitzer)	11.4228	11.4228	0.0000
pmH	12.0631	12.0631	0.0000
pcH	12.1338	12.1337	-0.0001

Table 5.8-2 compares results for solute species molalities. These are all within the 1% acceptance criterion.

Table 5.8-2. Test Case #7 (f24v7b3) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Na+	7.31508	7.3151	0.000%
Cl-	5.80166	5.8015	-0.003%
B(OH)4-	1.47092	1.4708	-0.008%
B4O5(OH)4--	0.0196498	0.019775	0.637%
OH-	0.00262592	0.0026253	-0.024%
B(OH)3(aq)	0.00210038	0.0021008	0.020%
B3O3(OH)4-	0.000572800	0.00057295	0.026%
H+	8.64686E-13	8.6486E-13	0.020%

Table 5.8-3 compares results for solute species activity coefficients. These are also all within the 1% acceptance criterion, despite the fact that the two codes are using different approximations for the J(x) function. Again, one might expect a tighter comparison if one were to re-run EQ3/6 using the Pitzer (1975, eq. 47) approximation, but that will not be pursued here.

Table 5.8-3. Test Case #7 (f24v7b3) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Na+	0.8977	0.89764	-0.007%
Cl-	0.9762	0.97611	-0.009%
B(OH)4-	0.1112	0.11115	-0.047%
B4O5(OH)4--	0.0030253	0.00301	-0.635%
OH-	0.7448	0.74490	0.014%
B(OH)3(aq)	0.6953	0.69518	-0.017%
B3O3(OH)4-	0.079471	0.07947	-0.002%
H+	4.368	4.36817	0.004%

Table 5.8-4 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. The acceptance criterion of 0.004 for a logarithmic quantity is slightly exceeded in one instance. Such instances are expected because FMT reports saturation indices to only three significant figures.

Table 5.8-4. Test Case #7 (f24v7b3) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Halite	0.00000	0.00000	0.00000
Borax	0.00000	0.00000	0.00000
Teepleite(20C)	0.00000	0.00000	0.00000
Na_Metaborate	-0.568	-0.56805	-0.00005
B(OH)3	-2.81	-2.80507	0.00493

The results of the two codes are in excellent agreement, despite the use of different approximations for the J(x) function.

5.9 Test Case #8 – Invariant point of K-carbonate–K-Na-carbonate–sylvite in the system Na-K-Cl-CO_3-H_2O

5.9.1 Test Overview

This test case is to compare the composition of the invariant point of K-carbonate–K-Na-carbonate–sylvite in the system Na-K-Cl-CO_3-H_2O. This test case involves a solution with very high ionic strength (~25 molal). This is yet another part of Test Case #7 from the validation of FMT v. 2.4 (Wang, 1998). This problem adds an excess of the relevant minerals to pure water to achieve the desired end point. It is thus a "type 1" problem, analogous to Test Cases #4, #6 and #7. For this type of problem, the codes can effectively calculate the pH from charge balance.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	f24vc7k4.6i
EQ6 output files:	f24vc7k4.6o, f24vc7k4.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_test7c.in; fmt_test7c.inguess
FMT output files:	fmt_test7c.out; fmt_test7c.for088

5.9.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.9.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc7k4.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.9-1 compares the results for the set of general parameter outputs. These are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria applicable to these quantities (1% for "linear" quantities and 0.01 unit for pH).

Table 5.9-1. Test Case #8 (f24vc7k4) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	3368.133151	3368.2914	0.005%
H2O mass, g	1576.223548	1576.2791	0.004%

Ionic strength, m	25.127572	25.128	0.002%
density, g/L	1517.69	1517.7	0.001%
TDS, g/L	807.4404251	807.45	0.001%
a_w	0.421080	0.42106	-0.005%
x_w	0.686204	0.68619	-0.002%
λ_w	0.6136	0.61362	0.003%
fCO2, bars	1.707E-09	1.70722E-09	0.013%
pH (Pitzer)	13.8027	13.8027	0.0000
pmH	13.1857	13.1858	0.0001
pcH	13.3343	13.3344	0.0001

Table 5.9-2 compares results for solute species molalities. These are all within the 1% acceptance criterion.

Table 5.9-2. Test Case #8 (f24vc7k4) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
K+	15.0921	15.092	-0.001%
CO3--	8.29047	8.2903	-0.002%
Na+	1.74502	1.7453	0.016%
Cl-	0.239619	0.24032	0.293%
HCO3-	0.00826824	0.0082919	0.286%
OH-	0.00826824	0.0082919	0.286%
CO2(aq)	8.53840E-12	8.5366E-12	-0.021%
H+	6.52048E-14	6.5193E-14	-0.018%

Table 5.9-3 compares results for solute species activity coefficients. These are also all within the 1% acceptance criterion. One might expect tighter results if EQ3/6 were run using the Pitzer (1975, eq. 47) approximation for the J(x) function, but that will not be pursued here.

Table 5.9-3. Test Case #8 (f24vc7k4) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
K+	2.935	2.93495	-0.002%
CO3--	0.2427	0.24266	-0.016%
Na+	0.8834	0.88349	0.010%
Cl-	0.7482	0.74611	-0.280%
HCO3-	0.083694	0.083445	-0.298%
OH-	32.59	32.48628	-0.318%
CO2(aq)	6.593	6.59326	0.004%
H+	0.2415	0.24160	0.042%

Table 5.9-4 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. In one instance (Kalicinite) the acceptance criterion of 0.004 for a logarithmic quantity is slightly exceeded. This is explained by the usual reason (FMT reports saturation indices to only three significant figures).

Table 5.9-4. Test Case #8 (f24vc7k4) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
K2CO3.3/2H2O	0.00000	0.00000	0.00000
KNaCO3.6H2O	0.00000	0.00000	0.00000
Sylvite	0.00000	0.00000	0.00000
Thermonatrite	-0.178	-0.17779	0.00021
K_Trona	-1.36	-1.36338	-0.00338
Na2CO3.7H2O	-1.49	-1.48971	0.00029
Kalicinite	-1.79	-1.79499	-0.00499
Trona	-2.00	-1.99900	0.00100
Halite	-2.13	-2.12876	0.00124
Natron	-2.25	-2.25207	-0.00207
Nahcolite	-2.57	-2.56885	0.00115
K8H4(CO3)6.3H2O	-7.00	-6.99777	0.00223

The results of the two codes are in excellent agreement, despite the two codes using different approximations for the J(x) function.

5.10 Test Case #9 – Invariant point of halite (NaCl)–sylvite (KCl) in the system Na-K-Cl-H_2O

5.10.1 Test Overview

This test case is to compare the composition of the invariant point of halite–sylvite in the system Na-K-Cl-H_2O. This test case is not in the validation test cases for FMT Version 2.4. It was constructed for the present validation effort. It is analogous to Test Cases #4, #6, #7, and #8. This is again a “type 1” problem in which minerals are added to pure water to obtain a saturated system. This problem was created simply because of the importance of the two minerals in many brine-water systems. It is also interesting in that the resulting solution is electrically “symmetrical” owing to the presence of only monovalent ions. Thus, there are no higher-order electrostatic term contributions to the activity coefficients, and the fact that the two codes use different approximations for the J(x) function cannot contribute to any differences in the results.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	f24vc7x.6i
EQ6 output files:	f24vc7x.6o, f24vc7x.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_test7d.in; fmt_test7d.inguess
FMT output files:	fmt_test7d.out; fmt_test7d.for088

5.10.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.10.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc7x.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding “linear” quantities for comparison with the corresponding FMT outputs.

Table 5.10-1 compares the results for the set of general parameter outputs. These are the same as those defined for the previous test cases. The results in the present instance are all well within the general acceptance criteria applicable to these quantities (1% for “linear” quantities and 0.01 unit for pH). Note that the differences are much smaller than those seen in results for the analogous problems (Test Cases #4, #6, #7, and #8). This is presumably a result of the electrical symmetry of the solution precluding differences due to differences in the approximations used for the J(x) function.

Table 5.10-1. Test Case #9 (f24vc7x) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1454.170445	1454.1752	0.000%
H2O mass, g	1000.000001	1000.0000	0.000%
Ionic strength, m	7.186734	7.1868	0.001%
density, g/L	1251.00	1251.0	0.000%
TDS, g/L	390.7171037	390.72	0.001%
a_w	0.724098	0.72410	0.000%
x_w	0.794318	0.79432	0.000%
λ_w	0.9116	0.9116	0.000%
pH (Pitzer)	6.6197	6.6198	0.0001
pmH	7.3459	7.3459	0.0000
pcH	7.4112	7.4113	0.0001

Table 5.10-2 compares results for solute species molalities. These are all within the 1% acceptance criterion.

Table 5.10-2. Test Case #9 (f24vc7x) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	7.18673	7.1868	0.001%
Na+	5.06625	5.0661	-0.003%
K+	2.12048	2.1207	0.010%
H+	4.50953E-08	4.5093E-08	-0.005%
OH-	4.50953E-08	4.5093E-08	-0.005%

Table 5.10-3 compares results for solute species activity coefficients. These are also all within the 1% acceptance criterion. The results for both molalities and activity coefficients are generally better than in the analogous test cases previously presented (Test Cases #4, #6, #7, and #8). Again, this is probably because the electrically symmetrical aqueous solution precludes any differences due to the use of different J(x) approximations.

Table 5.10-3. Test Case #9 (f24vc7x) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	0.9578	0.95763	-0.017%
Na+	1.066	1.06635	0.033%
K+	0.5441	0.54400	-0.018%
H+	5.323	5.32231	-0.013%
OH-	0.6741	0.67406	-0.006%

Table 5.10-4 compares results for saturation indices (log Q/K, where Q is the activity product and K the equilibrium constant) for the relevant mineral species. Agreement is basically exact because there are only two minerals and both of these are required to be saturated.

Table 5.10-4. Test Case #9 (f24vc7x) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Halite	0.00000	0.00000	0.00000
Sylvite	0.00000	0.00000	0.00000

The results of the two codes are in excellent agreement.

5.11 Test Case #10 – Speciation of Am(III), Th(IV), and Np(V) in WIPP SPC brine

5.11.1 Test Overview

This test case is to compare the speciation of Am(III), Th(IV), and Np(V) in WIPP SPC brine predicted by two codes. This is Test Case #8 from the validation of FMT v. 2.4 (Wang, 1998). It is essentially the same as Test Case #3 from that study, which was used as Test Case #4 (see Section 5.4) in the present document. That test case models the composition of SPC brine from which magnesite ($MgCO_3$) precipitates until equilibrium is achieved. In the present test case, the original system is reacted with 1 x 10^{-5} mole each of $Am(OH)_{3(s)}$, $ThO_{2(am)}$, and NpO_2OH(aged) (magnesite still precipitates). This is a "type 3" problem in that the lack of a proper front-end in FMT may affect the results, including the calculated pH.

It will be recalled from the discussion of Test Case #4 that there was some inconsistency with the problem inputs and a further problem caused by the way that the two codes treat the fictive species Neglon (EQ3/6 includes it in calculating the ionic strength, FMT does not). Therefore, the quality of the comparison in the present test case is expected to be similarly adversely affected.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	f24vc8.6i
EQ6 output files:	f24vc8.6o, f24vc8.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_test8.in; fmt_test8.inguess
FMT output files:	fmt_test8.out; fmt_test8.for088

5.11.2 *Acceptance Criteria*

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.11.3 Evaluation

Code outputs were assembled into the spreadsheet f24vc8.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.11-1 compares the results for the set of general parameter outputs. These outputs are the same as those defined for the previous test cases. The results in the present instance are all well within the usual acceptance criteria (1% for "linear" quantities and 0.01 for pH). They are very similar to those obtained for Test Case #4 (Table 5.4-3). As before, the ionic strength is greater in the EQ3/6 results because EQ3/6 includes a contribution from NegIon.

Table 5.11-1. Test Case #10 (f24vc8) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1330.413991	1330.4735	0.004%
H2O mass, g	1000.000053	1000.0617	0.006%
Ionic strength, m	7.569175	7.5953	0.345%
density, g/L	1190.11	1190.1	-0.001%
TDS, g/L	295.5697723	295.55	-0.007%
a_w	0.758695	0.75622	-0.326%
x_w	0.842589	0.8426	0.001%
λ_w	0.9004	0.89749	-0.323%
fCO2, bars	0.001748	0.00174032	-0.439%
pH (Pitzer)	6.5139	6.5171	0.0032
pmH	6.9987	7.0012	0.0025
pcH	7.0471	7.0496	0.0025

Table 5.11-2 compares results for solute species molalities. In many instances, these are within the usual 1% acceptance criterion. However, there are some very prominent exceptions. The difference for the most abundant Th species ($Th(CO_3)_5^{6-}$) is +66.953%. The next two most prominent exceptions are $NpO_2(CO_3)_3^{5-}$ (+40.087%) and $Am(CO_3)_4^{5-}$ (+36.913%). These two do not much affect the total concentrations of the corresponding actinides because other species are more important in determining them. Because these three very highly charged species are the most drastically impacted, it would be expected that the difference in J(x) approximations would be a notable contributor. The effect of NegIon on ionic strength and other "front end" effects are also likely factors.

Table 5.11-2. Test Case #10 (f24vc8) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.83002	5.8296	-0.007%
Na+	2.00001	1.9999	-0.005%
Mg++	1.55394	1.5538	-0.009%
K+	0.839998	0.83994	-0.007%
SO4--	0.0435994	0.043597	-0.006%
B(OH)3(aq)	0.0202218	0.020219	-0.014%
Ca++	0.0163812	0.016380	-0.007%
Br-	0.0109	0.010899	-0.009%
MgB(OH)4+	0.00115083	0.0011508	-0.003%
B(OH)4-	0.000369294	0.00037062	0.359%
HCO3-	0.000137539	0.00013762	0.059%
CO2(aq)	2.09793E-05	2.0887E-05	-0.440%
CaB(OH)4+	1.86770E-05	1.8667E-05	-0.054%
MgOH+	1.81841E-05	1.8260E-05	0.417%
B3O3(OH)4-	1.26756E-05	1.2738E-05	0.492%

MgCO3(aq)	1.24349E-05	1.2434E-05	-0.007%
NpO2+	5.97904E-06	5.9677E-06	-0.190%
CO3--	1.58974E-06	1.6153E-06	1.608%
Th(CO3)5(6-)	5.98665E-07	9.9949E-07	66.953%
AmSO4+	6.72412E-07	6.5268E-07	-2.935%
Am+++	6.21005E-07	6.2999E-07	1.447%
B4O5(OH)4--	3.66918E-07	3.7430E-07	2.012%
AmOH++	2.58783E-07	2.5742E-07	-0.527%
AmCO3+	1.97879E-07	1.9619E-07	-0.854%
Am(OH)2+	1.45940E-07	1.4463E-07	-0.898%
NpO2CO3-	1.31864E-07	1.3213E-07	0.202%
CaCO3(aq)	1.18619E-07	1.1856E-07	-0.050%
H+	1.00308E-07	9.9956E-08	-0.351%
OH-	8.98769E-08	9.0263E-08	0.430%
Th(OH)4(aq)	5.57711E-08	5.5701E-08	-0.126%
Th(OH)3(CO3)-	5.15516E-08	5.1524E-08	-0.054%
AmCl++	4.59275E-08	4.5888E-08	-0.086%
Am(CO3)4(5-)	1.60985E-08	2.2041E-08	36.913%
HSO4-	2.16002E-08	2.1251E-08	-1.617%
Am(SO4)2-	8.74018E-09	8.4099E-09	-3.779%
AmCl2+	6.10551E-09	6.0558E-09	-0.814%
NpO2OH(aq)	9.73231E-10	9.7389E-10	0.068%
Am(CO3)2-	6.59647E-10	6.5874E-10	-0.137%
NpO2(CO3)2---	1.77684E-10	1.8993E-10	6.892%
Th(SO4)3--	1.93712E-10	1.8465E-10	-4.678%
Am(CO3)3---	7.14978E-11	7.6008E-11	6.308%
Th(SO4)2(aq)	1.29590E-11	1.2401E-11	-4.306%
NpO2(CO3)3(5-)	2.61117E-12	3.6579E-12	40.087%
Am(OH)3(aq)	8.11210E-13	8.1394E-13	0.337%
NpO2(OH)2-	9.59026E-15	9.6381E-15	0.499%
Th++++	3.46745E-15	3.5739E-15	3.070%

Table 5.11-3 compares results for solute species activity coefficients. In many instances, these are within the usual 1% acceptance criterion. Again, however, there are large differences for the three very highly charged species: $Th(CO_3)_5^{6-}$ (-39.687%), $NpO_2(CO_3)_3^{5-}$ (-27.747%) and $Am(CO_3)_4^{5-}$ (-26.146%). These reduced activity coefficients correlate with the higher molalities. The likely reasons are those noted above.

Table 5.11-3. Test Case #10 (f24vc8) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.789	1.78649	-0.140%
Na+	0.7683	0.76718	-0.145%
Mg++	0.9613	0.95631	-0.519%
K+	0.3464	0.34578	-0.179%
SO4--	0.033102	0.03269	-1.248%

B(OH)3(aq)	1.558	1.55812	0.007%
Ca++	0.5208	0.51785	-0.567%
Br-	0.2666	0.26656	-0.014%
MgB(OH)4+	1.466	1.46420	-0.123%
B(OH)4-	0.1219	0.12198	0.068%
HCO3-	0.4773	0.47709	-0.044%
CO2(aq)	2.747	2.74726	0.010%
CaB(OH)4+	0.9193	0.91833	-0.105%
MgOH+	0.3158	0.31427	-0.485%
B3O3(OH)4-	0.4153	0.41572	0.101%
MgCO3(aq)	1.000	1.00000	0.000%
NpO2+	1.458	1.45579	-0.151%
CO3--	0.006174	0.0061094	-1.046%
Th(CO3)5(6-)	9.2552E-23	5.5821E-23	-39.687%
AmSO4+	0.3103	0.31254	0.721%
Am+++	0.1313	0.12820	-2.358%
B4O5(OH)4--	0.0048178	0.004776	-0.859%
AmOH++	0.021723	0.021727	0.018%
AmCO3+	0.5099	0.51192	0.396%
Am(OH)2+	0.00069794	0.00070372	0.828%
NpO2CO3-	0.067484	0.067453	-0.046%
CaCO3(aq)	1.000	1.00000	0.000%
H+	3.053	3.04789	-0.167%
OH-	0.2778	0.27778	-0.007%
Th(OH)4(aq)	1.000	1.00000	0.000%
Th(OH)3(CO3)-	0.2666	0.26656	-0.014%
AmCl++	32.13	31.805	-1.010%
Am(CO3)4(5-)	4.6852E-19	3.4602E-19	-26.146%
HSO4-	1.948	1.94491	-0.159%
Am(SO4)2-	0.097859	0.098197	0.346%
AmCl2+	264.3	263.21	-0.413%
NpO2OH(aq)	0.1091	0.10912	0.017%
Am(CO3)2-	0.1196	0.11989	0.246%
NpO2(CO3)2---	0.000013155	0.000012391	-5.809%
Th(SO4)3--	0.019448	0.019271	-0.911%
Am(CO3)3---	1.7177E-06	1.6252E-06	-5.387%
Th(SO4)2(aq)	29.41	29.404	-0.022%
NpO2(CO3)3(5-)	6.7787E-13	4.8978E-13	-27.747%
Am(OH)3(aq)	0.031179	0.031189	0.032%
NpO2(OH)2-	0.016235	0.016241	0.034%
Th++++	0.1351	0.12859	-4.820%

Table 5.11-4 compares results for saturation indices (log Q/K) for the relevant minerals. These results are similar in character to those seen for Test Case #4 (Table 5.4-6). That is, some of these differences are greater than can be explained by the limited precision of the FMT output. Note that four minerals are saturated: magnesite, AmOHCO$_{3(c)}$, ThO$_{2(am)}$, and KNpO$_2$CO$_3$. Note that

$AmOHCO_{3(c)}$ and $KNpO_2CO_3$ appear instead of $Am(OH)_{3(s)}$ and NpO_2OH(aged) that are added to the original brine.

Table 5.11-4. Test Case #10 (f24vc8) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Minerals	FMT	EQ3/6	Δ
AmOHCO3(c)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Magnesite	0.00000	0.00000	0.00000
Halite	-0.366	-0.36690	-0.00090
Sylvite	-0.418	-0.41920	-0.00120
Anhydrite	-0.548	-0.55549	-0.00749
Gypsum	-0.569	-0.57753	-0.00853
Dolomite	-0.828	-0.82865	-0.00065
B(OH)3	-1.47	-1.47127	-0.00127
Syngenite	-1.49	-1.50936	-0.01936
Epsomite	-1.62	-1.63457	-0.01457
Calcite	-1.67	-1.67105	-0.00105
Hexahydrite	-1.75	-1.76035	-0.01035
Aragonite	-1.86	-1.85785	0.00215
Arcanite	-2.14	-2.14366	-0.00366
Glauberite	-2.13	-2.14744	-0.01744
Thenardite	-2.18	-2.18685	-0.00685
NaAm(CO3)2.6H2O(c)	-2.25	-2.24825	0.00175
Kainite	-2.35	-2.36150	-0.01150
Carnallite	-2.36	-2.36381	-0.00381
Am(OH)3(s)	-2.40	-2.39495	0.00505
Mirabilite	-2.44	-2.44874	-0.00874
Kieserite	-2.66	-2.67166	-0.01166
Polyhalite	-2.89	-2.92561	-0.03561
Bischofite	-2.96	-2.96950	-0.00950
Picromerite/Schoenite	-2.97	-2.98771	-0.01771
Nesquehonite	-3.03	-3.02746	0.00254
Leonite	-3.08	-3.09597	-0.01597
NpO2OH(aged)	-3.18	-3.18156	-0.00156
Bloedite	-3.27	-3.28247	-0.01247
Aphthitalite/Glaserite	-3.30	-3.31441	-0.01441
Nahcolite	-3.59	-3.59385	-0.00385
NpO2OH(am)	-3.88	-3.88166	-0.00166
Brucite	-4.15	-4.14515	0.00485
2[NaNpO2CO3.7/2H2O]	-4.42	-4.42353	-0.00353
Labile_Salt	-4.41	-4.43443	-0.02443
Teepleite(20C)	-4.56	-4.55656	0.00344
Na_Metaborate	-4.73	-4.72849	0.00151
Kalicinite	-5.00	-5.00105	-0.00105

Borax	-5.67	-5.66791	0.00209
K-Pentaborate(30C)	-5.84	-5.84017	-0.00017
Mg2Cl(OH)3.4H2O	-5.96	-5.96119	-0.00119
CaCl2.4H2O	-6.23	-6.23422	-0.00422
Na3NpO2(CO3)2	-6.34	-6.33491	0.00509
Na_Pentaborate	-6.46	-6.46119	-0.00119
Th(SO4)2.Na2SO4.6H2O	-6.56	-6.58368	-0.02368
K3NpO2(CO3)2	-6.75	-6.75272	-0.00272

Table 5.11-5 compares results for the moles of precipitated minerals. These are within the usual 1% acceptance criterion, with the exception of $ThO_{2(am)}$,. This correlates with higher dissolved Th in the EQ3/6 output due to the increased molality of the species $Th(CO_3)_5^{6-}$.

Table 5.11-5. Test Case #10 (f24vc8) Calculated Moles of Minerals Precipitated, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
AmOHCO3(c)	8.02638E-06	8.0359E-06	0.119%
ThO2(am)	9.29381E-06	8.8930E-06	-4.313%
KNpO2CO3	3.88794E-06	3.8986E-06	0.274%
Magnesite	0.00488301	0.0048809	-0.043%

The results of the two codes are not in very good agreement. However, the EQ3/6 run was repeated in a one-off test case f24vc8_P75 in which EQ3/6 used the same J(x) approximation (Pitzer, 1975) as FMT. The results of this were compared with FMT using the spreadsheet f24vc8_P75. Table 5.11-6 shows the results for solute species molalities. The situation is somewhat improved. The difference for the most abundant Th species ($Th(CO_3)_5^{6-}$) is reduced from +66.953% (Table 5.11-2) to +46.321%. The next two most prominent exceptions are also somewhat improved: $NpO_2(CO_3)_3^{5-}$ (from +40.087% to 27.736%) and $Am(CO_3)_4^{5-}$ (from +36.913% to 24.881%). Obviously there was a significant effect in using different J(x) functions, but other factors are also in play.

Table 5.11-6. Test Case #10 One-Off (f24vc8_P75) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	5.83002	5.8296	-0.007%
Na+	2.00001	1.9999	-0.005%
Mg++	1.55394	1.5538	-0.009%
K+	0.839998	0.83994	-0.007%
SO4--	0.0435994	0.043597	-0.006%
B(OH)3(aq)	0.0202218	0.020220	-0.009%
Ca++	0.0163812	0.016380	-0.007%
Br-	0.0109000	0.010899	-0.009%
MgB(OH)4+	0.00115083	0.0011504	-0.037%
B(OH)4-	0.000369294	0.00037035	0.286%
HCO3-	0.000137539	0.00013751	-0.021%

CO2(aq)	2.09793E-05	2.0886E-05	-0.445%
CaB(OH)4+	1.86770E-05	1.8662E-05	-0.080%
MgOH+	1.81841E-05	1.8254E-05	0.384%
B3O3(OH)4-	1.26756E-05	1.2731E-05	0.437%
MgCO3(aq)	1.24349E-05	1.2434E-05	-0.007%
NpO2+	5.97904E-06	5.9642E-06	-0.248%
CO3--	1.58974E-06	1.6054E-06	0.985%
Th(CO3)5(6-)	5.98665E-07	8.7597E-07	46.321%
AmSO4+	6.72412E-07	6.5651E-07	-2.365%
Am+++	6.21005E-07	6.2411E-07	0.500%
B4O5(OH)4--	3.66918E-07	3.7210E-07	1.412%
AmOH++	2.58783E-07	2.5742E-07	-0.527%
AmCO3+	1.97879E-07	1.9613E-07	-0.884%
Am(OH)2+	1.45940E-07	1.4458E-07	-0.932%
NpO2CO3-	1.31864E-07	1.3199E-07	0.096%
CaCO3(aq)	1.18619E-07	1.1856E-07	-0.050%
H+	1.00308E-07	9.9925E-08	-0.382%
OH-	8.98769E-08	9.0194E-08	0.353%
Th(OH)4(aq)	5.57711E-08	5.5698E-08	-0.131%
Th(OH)3(CO3)-	5.15516E-08	5.1483E-08	-0.133%
AmCl++	4.59275E-08	4.5923E-08	-0.010%
Am(CO3)4(5-)	1.60985E-08	2.0104E-08	24.881%
HSO4-	2.16002E-08	2.1365E-08	-1.089%
Am(SO4)2-	8.74018E-09	8.5072E-09	-2.666%
AmCl2+	6.10551E-09	6.0632E-09	-0.693%
NpO2OH(aq)	9.73231E-10	9.7360E-10	0.038%
Am(CO3)2-	6.59647E-10	6.5825E-10	-0.212%
NpO2(CO3)2---	1.77684E-10	1.8522E-10	4.241%
Th(SO4)3--	1.93712E-10	1.8693E-10	-3.501%
Am(CO3)3---	7.14978E-11	7.4146E-11	3.704%
Th(SO4)2(aq)	1.29590E-11	1.2553E-11	-3.133%
NpO2(CO3)3(5-)	2.61117E-12	3.3354E-12	27.736%
Am(OH)3(aq)	8.11210E-13	8.1393E-13	0.335%
NpO2(OH)2-	9.59026E-15	9.6279E-15	0.392%
Th++++	3.46745E-15	3.4758E-15	0.241%

Table 5.11-7 shows the results for solute species activity coefficients. These are basically again complementary to the molality effects. The magnitude of the largest differences is reduced, but this is still quite prominent in the case of the very highly charged species.

Table 5.11-7. Test Case #10 One-Off (f24vc8_P75) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.789	1.78608	-0.163%
Na+	0.7683	0.76807	-0.030%
Mg++	0.9613	0.95786	-0.358%

K+	0.3464	0.34618	-0.064%
SO4--	0.033102	0.032832	-0.815%
B(OH)3(aq)	1.558	1.55812	0.007%
Ca++	0.5208	0.51880	-0.384%
Br-	0.2666	0.26656	-0.014%
MgB(OH)4+	1.466	1.46589	-0.008%
B(OH)4-	0.1219	0.12198	0.068%
HCO3-	0.4773	0.47698	-0.067%
CO2(aq)	2.747	2.74726	0.010%
CaB(OH)4+	0.9193	0.91939	0.010%
MgOH+	0.3158	0.31463	-0.371%
B3O3(OH)4-	0.4153	0.41562	0.078%
MgCO3(aq)	1.000	1.00000	0.000%
NpO2+	1.458	1.45747	-0.036%
CO3--	0.006174	0.0061362	-0.612%
Th(CO3)5(6-)	9.2552E-23	6.3358E-23	-31.544%
AmSO4+	0.3103	0.31290	0.837%
Am+++	0.1313	0.12975	-1.182%
B4O5(OH)4--	0.0048178	0.0047973	-0.425%
AmOH++	0.021723	0.021762	0.180%
AmCO3+	0.5099	0.51251	0.511%
Am(OH)2+	0.00069794	0.00070453	0.944%
NpO2CO3-	0.067484	0.067453	-0.046%
CaCO3(aq)	1.000	1.00000	0.000%
H+	3.053	3.05141	-0.052%
OH-	0.2778	0.27778	-0.007%
Th(OH)4(aq)	1.000	1.00000	0.000%
Th(OH)3(CO3)-	0.2666	0.26656	-0.014%
AmCl++	32.13	31.857	-0.851%
Am(CO3)4(5-)	4.6852E-19	3.7766E-19	-19.393%
HSO4-	1.948	1.94491	-0.159%
Am(SO4)2-	0.097859	0.098197	0.346%
AmCl2+	264.3	263.51	-0.298%
NpO2OH(aq)	0.1091	0.10912	0.017%
Am(CO3)2-	0.1196	0.11987	0.223%
NpO2(CO3)2---	0.000013155	0.000012671	-3.682%
Th(SO4)3--	0.019448	0.019355	-0.477%
Am(CO3)3---	1.7177E-06	1.6619E-06	-3.250%
Th(SO4)2(aq)	29.41	29.404	-0.022%
NpO2(CO3)3(5-)	6.7787E-13	5.3456E-13	-21.141%
Am(OH)3(aq)	0.031179	0.031189	0.032%
NpO2(OH)2-	0.016235	0.016237	0.011%
Th++++	0.1351	0.13268	-1.793%

Since the differences due to using different J(x) functions have been eliminated and large though smaller discrepancies for the very highly charged species still exist, the likely main culprit is the effect of higher ionic strength in the EQ3/6 results due to the different treatment of NegIon. Although this could affect the activity coefficients in several ways, most of the effect probably goes through the Debye-Hückel term in the activity coefficients. That term (in the log activity coefficient) is proportional to the square of the charge number and is approximately proportional to the square root of the ionic strength. This term strongly reduces the activity coefficient as the ionic strength increases.

One could try to further run these differences to ground. However, it is not very feasible to do so, given that the problem would need to be redefined to eliminate the known inconsistencies in the code inputs and to also eliminate the NegIon effect (as was concluded for the related Test Case #4). We will not attempt that here. Rather, we will simply declare the remaining differences sufficiently well explained. We will run to ground the next test case (#11), which is somewhat similar in nature and which is more significant to WIPP PA. Also, it does not involve the use of NegIon.

5.12 Test Case #11 – Solubility of Am(III), Th(IV), and Np(V) in WIPP GWB brine

5.12.1 Test Overview

This test case is to compare CRA-2004 PABC values of Am(III), Th(IV) and Np(V) in GWB predicted by FMT with those calculated by EQ3/6. This problem is taken from Brush (2005). The GWB brine is first created. Then it is reacted with 1.0 mole of $Am(OH)_3(s)$, $ThO_2(am)$, $KNpO_2CO_3$, and hydromagnesite(5424) ("Hydromagnesite5424", $Mg_5(CO_3)4(OH)_2.4H_2O$) plus 10.0 moles each of anhydrite ($CaSO_4$), brucite ($Mg(OH)_2$), and halite (NaCl). This is a "type 3" problem in that the lack of a proper front-end in FMT may affect the results, including the calculated pH.

Table 5.12-1 gives the FMT inputs for the GWB brine. The inputs here are consistent with 1 L of solution (see Brush, 2005, Table 2). The four organic ligands (oxalate, acetate, EDTA, and citrate) are treated as pseudo-elements by FMT (whereas they are treated as active auxiliary basis species by EQ3/6).

Table 5.12-1. Test Case #11 (c4pgwb) FMT Inputs for GWB Brine.

Element	Moles
H	99.3736
O	50.6193
Na	3.48
K	0.458
Mg	1.00
Ca	0.014
Cl	5.51
S	0.175
B	0.155
Br	0.026
Oxalate	0.0455
Acetate	0.0106
EDTA	8.14E-06
Citrate	8.06E-04

Table 5.12-2 gives the corresponding EQ3/6 inputs for the brine. Because EQ3/6 works directly in terms of molalities, the molarity inputs must be converted to molalities before the actual speciation calculations can begin. This requires inputs for density and TDS, which are needed to compute the molarity/molality factor or molarity/molality factor. The values shown in Table 5.12-2 were calculated from the molarity data using the WIPP density model (see worksheet c4pgwb of spreadsheet Conc_density_calcs_EV2008.xls). The molarity/molality factor was used in EQ3NR to rescale the brine mass for consistency with a 1 L volume, prior to reacting it with minerals in the subsequent EQ6 run.

Table 5.12-2. Test Case #11 (c4pgwb) EQ3/6 Inputs for GWB Brine.

Basis species	Molarity
Na+	3.48
K+	0.458
Mg++	1.00
Ca++	0.014
Cl-	5.51
SO4--	0.175
HCO3-	1.0E-18
B(OH)4-	0.155
Br-	0.026
Oxalate--	0.0455
Acetate-	0.0106
EDTA----	8.14E-06
Citrate---	8.06E-04
Am+++	1.0E-18
Th++++	1.0E-18
NpO2+	1.0E-18
density, g/L	1227.52
TDS, g/L	354.0163
Molarity/molality	0.87432

It is noted that the density, TDS, and molarity/molality values obtained from the spreadsheet calculation take the compositional data at face value. There is no speciation calculation in this calculation. Since EQ3NR performs a full speciation calculation, the WIPP density model embedded in FMT will generally produce slightly different calculated results. This will be addressed below in the Evaluation section.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	c4pgwb.6i
EQ6 output files:	c4pgwb.6o, c4pgwb.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_cra1bc_gwb_hmg_orgs_007.in; fmt_cra1bc_gwb_hmg_orgs_007.inguess
FMT output files:	fmt_cra1bc_gwb_hmg_orgs_007.out; fmt_cra1bc_gwb_hmg_orgs_007.for088

5.12.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.12.3 Evaluation

Code outputs were assembled into the spreadsheet c4pgwb.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.12-3 compares the density, TDS, and molarity/molality values input to EQ3NR against the output values. The output values are slightly different because they were computed using a full speciation model. These differences (<1%) are not considered significant. It is noted that they could have been further reduced by putting the output values in the EQ3NR input file and re-running the problem.

Table 5.12-3. Test Case #11 (c4pgwb) EQ3NR Inputs and Outputs for Density, TDS, and Molarity/Molality for GWB Brine.

	Input	Output	Δ
density, g/L	1227.52	1226.1	-0.116%
TDS, g/L	354.0163	351.73	-0.646%
Molarity/molality	0.8735	0.87432	0.094%

Table 5-12-4 compares the results for the set of general parameter outputs (after the brine has been reacted with the designated minerals). These outputs are the same as those defined for the previous test cases. These results are within the general acceptance criteria, except for the cases of the solution mass and the H_2O mass. This difference occurred because the EQ6 run started with 1 L of brine instead of a mass scaled to the usual 1000 g H_2O. The brine mass was deliberately rescaled to 1 L to match the FMT inputs. It was not realized until later that FMT increased the initial brine mass scaled to 1000 g H_2O before reacting the brine with the designated minerals. This is actually not problematic, because in both code runs the masses of the minerals were sufficient to saturate the system. The absolute amounts of the added minerals that dissolved and the absolute amounts remaining will be different, but the intensive system descriptors will be the same. It is noted that the ionic strength reported by EQ3/6 is slightly higher than that reported by FMT. NegIon, however, is not used in this test case.

Table 5.12-4. Test Case #11 (c4pgwb) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1293.458658	1126.9899	-12.870%
H2O mass, g	914.2900833	795.80553	-12.959%
Ionic strength, m	7.663835	7.689	0.328%
density, g/L	1232.10	1232.8	0.057%
TDS, g/L	361.1827591	362.28	0.304%
a_w	0.732297	0.73194	-0.049%
x_w	0.812688	0.81243	-0.032%
λ_w	0.9011	0.90093	-0.019%
fCO2, bars	0.000003135	3.13527E-06	0.009%

pH (Pitzer)	8.6887	8.6889	0.0002
pmH	9.3347	9.3353	0.0006
pcH	9.3947	9.3955	0.0008

Table 5.12-5 compares results for solute species molalities. In some instances, the results are within the usual 1% acceptance criterion. In many cases, however, they are not. The largest discrepancies are for the very highly charged species: $Th(CO_3)_5^{6-}$ (+18.082%), $Am(CO_3)_4^{5-}$ (+13.429%), $EDTA^{4-}$ (+8.463%), and $NpO_2(CO_3)_3^{5-}$ (+7.162%). This pattern is much like what was seen in Test Case #10. The likely causes of these discrepancies are the same, except that NegIon is not responsible here for the EQ3/6 results having a slightly higher ionic strength. Note at the bottom of the table that FMT does not report values for molalities less than 1 x 10^{-24}.

Table 5.12-5. Test Case #11 (c4pgwb) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.17604	6.1773	0.020%
Na+	4.99121	4.9853	-0.118%
Mg++	0.576993	0.58059	0.623%
K+	0.562550	0.57552	2.306%
SO4--	0.262347	0.26810	2.193%
MgB(OH)4+	0.0753902	0.07658	1.578%
B(OH)4-	0.0549134	0.05570	1.432%
Br-	0.0319351	0.032671	2.304%
B(OH)3(aq)	0.0254070	0.025809	1.582%
Ca++	0.00849908	0.0084315	-0.795%
Acetate-	0.00654112	0.0067202	2.738%
MgAcetate+	0.00642842	0.0065493	1.880%
B4O5(OH)4--	0.00575374	0.0061415	6.739%
B3O3(OH)4-	0.00331851	0.0034720	4.625%
MgOH+	0.00182005	0.0018286	0.470%
CaB(OH)4+	0.00170130	0.0016995	-0.106%
MgOxalate(aq)	0.00153978	0.0015665	1.735%
MgCitrate-	0.000962646	0.00098454	2.274%
MgCO3(aq)	0.000323947	0.00032412	0.053%
CaAcetate+	4.96558E-05	4.9749E-05	0.188%
HCO3-	4.84103E-05	4.8507E-05	0.200%
CO3--	2.48257E-05	2.4956E-05	0.525%
Citrate---	1.99049E-05	2.0782E-05	4.406%
Oxalate--	1.38711E-05	1.4117E-05	1.773%
CaOxalate(aq)	1.18939E-05	1.1899E-05	0.043%
MgEDTA--	9.72185E-06	9.9472E-06	2.318%
OH-	0.000008121	8.1171E-06	-0.048%
CaCitrate-	7.43588E-06	7.4787E-06	0.576%
CaCO3(aq)	4.17958E-06	4.1123E-06	-1.610%
HAcetate(aq)	4.26585E-07	4.3790E-07	2.652%

Am(OH)2+	2.37430E-07	2.3665E-07	-0.329%
AmEDTA-	2.01094E-07	2.0570E-07	2.290%
NpO2+	1.45815E-07	1.4291E-07	-1.992%
NpO2CO3-	1.19968E-07	1.1744E-07	-2.107%
NpO2Acetate(aq)	8.44036E-08	8.4850E-08	0.529%
CaEDTA--	7.50956E-08	7.5560E-08	0.618%
Th(OH)4(aq)	5.19575E-08	5.1910E-08	-0.091%
NpO2Oxalate-	5.03499E-08	4.9949E-08	-0.796%
CO2(aq)	2.93478E-08	2.9274E-08	-0.251%
Th(OH)3(CO3)-	1.27974E-08	1.2809E-08	0.091%
NpO2OH(aq)	4.97922E-09	4.8740E-09	-2.113%
AmOH++	2.82968E-09	2.8502E-09	0.725%
HSO4-	1.33874E-09	1.3598E-09	1.573%
AmAcetate++	1.28786E-09	1.3495E-09	4.786%
NpO2(CO3)2---	1.33679E-09	1.3376E-09	0.061%
Am(OH)3(aq)	6.87418E-10	6.8965E-10	0.325%
HCitrate--	6.54933E-10	6.6894E-10	2.139%
AmCitrate(aq)	5.10997E-10	5.1886E-10	1.539%
H+	4.62711E-10	4.6209E-10	-0.134%
AmCO3+	4.32475E-10	4.3202E-10	-0.105%
NpO2Citrate--	1.71501E-10	1.7039E-10	-0.648%
Am(CO3)2-	1.53197E-10	1.5353E-10	0.217%
AmSO4+	1.43332E-10	1.4512E-10	1.247%
EDTA----	9.60883E-11	1.0422E-10	8.463%
HOxalate-	4.08059E-11	4.1334E-11	1.294%
Am(CO3)3---	3.82087E-11	3.9495E-11	3.367%
AmOxalate+	2.91986E-11	2.9083E-11	-0.396%
Am(SO4)2-	2.21879E-11	2.2937E-11	3.376%
NpO2(CO3)3(5-)	1.47730E-11	1.5831E-11	7.162%
Am+++	1.26375E-11	1.2497E-11	-1.112%
Am(CO3)4(5-)	1.09972E-11	1.2474E-11	13.429%
HEDTA---	8.88268E-12	9.3145E-12	4.861%
NpO2(OH)2-	7.28398E-12	7.1390E-12	-1.990%
AmCl++	2.11486E-12	2.1476E-12	1.548%
NpO2EDTA---	5.07797E-13	5.1881E-13	2.169%
AmCl2+	1.09730E-13	1.1069E-13	0.875%
H2EDTA--	1.10656E-14	1.1319E-14	2.290%
H2Citrate-	4.80754E-15	4.8795E-15	1.497%
NpO2HEDTA--	9.81711E-16	9.7552E-16	-0.631%
Th(CO3)5(6-)	4.55775E-16	5.3819E-16	18.082%
Th(SO4)3--	1.83058E-17	1.8933E-17	3.426%
ThEDTA(aq)	8.65338E-18	8.8017E-18	1.714%
H2Oxalate(aq)	5.87859E-19	5.9757E-19	1.652%
Th(SO4)2(aq)	3.41990E-19	3.5307E-19	3.240%
NpO2H2EDTA-	1.50741E-19	1.4692E-19	-2.535%
ThCitrate+	6.39131E-20	6.2900E-20	-1.585%

Th(Acetate)2++	8.70115E-21	9.1639E-21	5.318%
H3Citrate(aq)	2.21771E-21	2.2462E-21	1.285%
H3EDTA-	1.22934E-21	1.2464E-21	1.388%
ThAcetate+++	1.10948E-21	1.1747E-21	5.878%
ThOxalate++	1.55293E-22	1.5397E-22	-0.852%
Th++++	-----	1.2902E-24	-----
H4EDTA(aq)	-----	1.8426E-28	-----

Table 5.12-6 compares results for solute species activity coefficients. These results are largely complementary to the molality results, much as was the case for Test Case #10. The largest discrepancy is for $Th(CO_3)_5^{6-}$ (-15.220%).

Table 5.12-6. Test Case #11 (c4pgwb) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.305	1.30707	0.159%
Na+	0.9246	0.92385	-0.081%
Mg++	1.742	1.73141	-0.608%
K+	0.4298	0.42924	-0.130%
SO4--	0.021331	0.02122	-0.531%
MgB(OH)4+	1.873	1.87111	-0.101%
B(OH)4-	0.1020	0.10205	0.046%
Br-	0.2683	0.26798	-0.120%
B(OH)3(aq)	1.069	1.06782	-0.110%
Ca++	0.9135	0.90573	-0.850%
Acetate-	0.5575	0.55731	-0.033%
MgAcetate+	7.398	7.45933	0.829%
B4O5(OH)4--	0.0042179	0.004200	-0.413%
B3O3(OH)4-	0.1631	0.16315	0.034%
MgOH+	0.3065	0.30507	-0.466%
CaB(OH)4+	1.143	1.14156	-0.126%
MgOxalate(aq)	1.263	1.26299	-0.001%
MgCitrate-	0.1662	0.16482	-0.833%
MgCO3(aq)	1.000	1.00000	0.000%
CaAcetate+	7.398	7.45933	0.829%
HCO3-	0.3511	0.35035	-0.214%
CO3--	0.015308	0.015234	-0.487%
Citrate---	0.000040119	0.000038958	-2.893%
Oxalate--	0.02246	0.022449	-0.048%
CaOxalate(aq)	1.263	1.26299	-0.001%
MgEDTA--	0.1302	0.12948	-0.554%
OH-	0.4438	0.44392	0.026%
CaCitrate-	0.1662	0.16482	-0.833%
CaCO3(aq)	1.000	1.00000	0.000%
HAcetate(aq)	1.000	1.00000	0.000%

Am(OH)2+	0.00074059	0.0007430	0.328%
AmEDTA-	0.029535	0.029404	-0.445%
NpO2+	1.858	1.85524	-0.149%
NpO2CO3-	0.089249	0.089248	-0.001%
NpO2Acetate(aq)	0.2768	0.27669	-0.038%
CaEDTA--	0.1302	0.12948	-0.554%
Th(OH)4(aq)	1.000	1.00000	0.000%
NpO2Oxalate-	0.029135	0.02923	0.343%
CO2(aq)	3.522	3.53102	0.256%
Th(OH)3(CO3)-	0.2683	0.26798	-0.120%
NpO2OH(aq)	0.095666	0.09561	-0.059%
AmOH++	0.023758	0.02359	-0.691%
HSO4-	0.8149	0.81527	0.045%
AmAcetate++	0.010578	0.010371	-1.962%
NpO2(CO3)2---	0.000081462	0.000079708	-2.154%
Am(OH)3(aq)	0.009169	0.0091390	-0.327%
HCitrate--	0.006616	0.006564	-0.779%
AmCitrate(aq)	0.006638	0.0066313	-0.101%
H+	4.426	4.42996	0.090%
AmCO3+	0.7483	0.74955	0.167%
NpO2Citrate--	0.0039615	0.0039555	-0.152%
Am(CO3)2-	0.063985	0.063915	-0.110%
AmSO4+	0.4676	0.46957	0.421%
EDTA----	9.8019E-07	9.1981E-07	-6.160%
HOxalate-	0.2842	0.28536	0.410%
Am(CO3)3---	1.5457E-05	1.4973E-05	-3.133%
AmOxalate+	0.1034	0.10563	2.160%
Am(SO4)2-	0.048011	0.048006	-0.009%
NpO2(CO3)3(5-)	2.1613E-10	1.9756E-10	-8.592%
Am+++	0.5347	0.54088	1.156%
Am(CO3)4(5-)	1.2771E-13	1.1277E-13	-11.697%
HEDTA---	0.00080805	0.00078	-2.980%
NpO2(OH)2-	0.013842	0.01381	-0.207%
AmCl++	44.67	44.09608	-1.285%
NpO2EDTA---	0.017233	0.01680	-2.515%
AmCl2+	727.7	724.60279	-0.426%
H2EDTA--	0.010058	0.01000	-0.554%
H2Citrate-	0.1276	0.12741	-0.150%
NpO2HEDTA--	0.1873	0.18767	0.199%
Th(CO3)5(6-)	2.2699E-14	1.9244E-14	-15.220%
Th(SO4)3--	0.025738	0.026134	1.537%
ThEDTA(aq)	3.944	3.94548	0.038%
H2Oxalate(aq)	1.000	1.00000	0.000%
Th(SO4)2(aq)	35.95	35.97493	0.069%
NpO2H2EDTA-	0.52	0.53101	2.117%
ThCitrate+	21.6	22.24334	2.978%

Th(Acetate)2++	266.4	266.68587	0.107%
H3Citrate(aq)	1.000	1.00000	0.000%
H3EDTA-	0.2267	0.22735	0.288%
ThAcetate+++	75.98	73.67158	-3.038%
ThOxalate++	490.8	503.26879	2.541%
Th++++	0.8146	0.77875	-4.401%
H4EDTA(aq)	1.000	1.00000	0.000%

Table 5.12-7 compares results for saturation indices (log Q/K) for the relevant minerals. In a number of instances, the differences exceed both the usual acceptance criterion (0.004) and also what can be explained by the limited precision with which FMT reports saturation indices. This table provides confirmation that the brine became saturated with respect to each of the solids with which it was reacting, despite the difference in brine masses in the two code runs. As expected, magnesite ($MgCO_3$) precipitates and is thus saturated. Whewellite ($CaC_2O_4•H_2O$, calcium oxalate) does likewise.

Table 5.12-7. Test Case #11 (c4pgwb) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	2.13	2.12759	-0.00241
Magnesite	1.42	1.4161	-0.00390
Am(OH)3(s)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Anhydrite	0.00000	0.00000	0.00000
Whewellite	0.00000	0.00000	0.00000
Brucite	0.00000	0.00000	0.00000
Halite	0.00000	0.00000	0.00000
Mg2Cl(OH)3.4H2O	0.00000	0.00000	0.00000
Hydromagnesite5424	0.00000	0.00000	0.00000
Glauberite	-0.0413	-0.03609	0.00521
Gypsum	-0.0522	-0.05265	-0.00045
Calcite	-0.124	-0.13091	-0.00691
Aragonite	-0.311	-0.31771	-0.00671
AmOHCO3(c)	-0.334	-0.33410	-0.00010
Hydromagnesite4323	-0.344	-0.34347	0.00053
Syngenite	-0.534	-0.50877	0.02523
Sylvite	-0.61	-0.60003	0.00997
Thenardite	-0.636	-0.63099	0.00501
Borax	-0.699	-0.67632	0.02268
Labile_Salt	-0.808	-0.79782	0.01018
Polyhalite	-0.986	-0.95338	0.03262
Mirabilite	-1.05	-1.04593	0.00407
Epsomite	-1.32	-1.31026	0.00974
Bloedite	-1.37	-1.35637	0.01363
Hexahydrite	-1.43	-1.42074	0.00926

B(OH)3	-1.54	-1.52929	0.01071
Teepleite(20C)	-1.62	-1.61289	0.00711
Nesquehonite	-1.66	-1.65727	0.00273
Arcanite	-1.71	-1.68325	0.02675
Aphthitalite/Glaserite	-1.89	-1.84586	0.04414
Kainite	-2.17	-2.15679	0.01321
Na_Metaborate	-2.19	-2.18234	0.00766
Picromerite/Schoenite	-2.22	-2.18768	0.03232
Kieserite	-2.26	-2.25551	0.00449
Leonite	-2.30	-2.26533	0.03467
NpO2OH(aged)	-2.53	-2.53957	-0.00957
Na2Oxalate	-2.77	-2.76746	0.00254
NaAm(CO3)2.6H2O(c)	-2.77	-2.76845	0.00155
Carnallite	-3.04	-3.02708	0.01292
NpO2OH(am)	-3.23	-3.23967	-0.00967
Na3NpO2(CO3)2	-3.23	-3.24667	-0.01667
2[NaNpO2CO3.7/2H2O]	-3.41	-3.43521	-0.02521
Bischofite	-3.45	-3.45195	-0.00195
Nahcolite	-3.70	-3.70342	-0.00342
K-Tetraborate(30C)	-3.89	-3.84653	0.04347
K-Pentaborate(30C)	-4.02	-3.98197	0.03803
Na_Pentaborate	-4.10	-4.07056	0.02944
Pirssonite	-4.65	-4.65866	-0.00866
Gaylussite	-4.88	-4.88743	-0.00743
K3NpO2(CO3)2	-5.33	-5.30766	0.02234
Na2CO3.7H2O	-5.58	-5.58207	-0.00207
Natron	-5.62	-5.62404	-0.00404
Kalicinite	-5.67	-5.65835	0.01165
Thermonatrite	-5.71	-5.71092	-0.00092
Burkeite	-6.17	-6.15837	0.01163
CaCl2.4H2O	-6.56	-6.56201	-0.00201
KNaCO3.6H2O	-7.07	-7.06128	0.00872

Table 5.12-8 compares results for actinide species distributions, considering only those species needed to comprise 99% of the mass balance of any actinide. These data were key results in the Brush (2005) calculations. The differences here are small (<3%), though some instances exceed the usual 1% criterion for "linear" quantities.

The data in Table 5.12-8 help to point out that the results shown above in this section are fairly good for the things that really matter. The numerically large differences are mainly for things that do not matter that much, namely species that do not much affect the brine "medium" concentration or the mass balances for the basis species (or chemical elements). One can see in Table 5.12-6 that large differences in calculated activity coefficients (>3%) are only apparent for relatively minor species. This is reflected by complementary differences in molalities as shown in Table 5.12.7. However, there are relatively large discrepancies in the molalities of the polyborate species $B_4O_5(OH)_4^{2-}$ (6.304%) and $B_3O_3(OH)_4^-$ (+4.680%). There are no complementary discrepancies in the activity coefficients of these species. These two species are lesser but non-negligible contributors to the total concentration of borate. Their formation has a fairly high dependence on the activity of water (as implied for example by the reaction 4 $B(OH)_4^-$ + 2 H^+ = $B_4O_5(OH)_4^{2-}$ + 7 H_2O). Although there is not much difference in the activity of water calculated by the two codes (-0.049%, Table 5.12-4), the effect of this difference can be magnified considerably by the number of waters appearing in reaction. A small difference in the water activity might also have a magnified effect on the formation of a highly charged actinide complex (as implied for example by the reaction Am^{3+} + 4 HCO_3^- + 4 OH^- = $Am(CO_3)_4^{5-}$ + 4 H_2O).

Table 5.12-8. Test Case #11 (c4pgwb) Actinide Species Distributions, EQ3/6 vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	4.44684E-07	100.00%	4.4861E-07	100.00%	0.88%
Am(OH)2+	2.37430E-07	53.39%	2.3665E-07	52.75%	-0.33%
AmEDTA-	2.01094E-07	45.22%	2.0570E-07	45.85%	2.29%
AmOH++	2.82968E-09	0.64%	2.8502E-09	0.64%	0.73%
Subtotal	4.41354E-07	99.25%	4.4520E-07	99.24%	0.87%
Total NpO2+	4.07047E-07	100.00%	4.0155E-07	100.00%	-1.35%
NpO2+	1.45815E-07	35.82%	1.4291E-07	35.59%	-1.99%
NpO2CO3-	1.19968E-07	29.47%	1.1744E-07	29.25%	-2.11%
NpO2Acetate(aq)	8.44036E-08	20.74%	8.4850E-08	21.13%	0.53%
NpO2Oxalate-	5.03499E-08	12.37%	4.9949E-08	12.44%	-0.80%
NpO2OH(aq)	4.97922E-09	1.22%	4.8740E-09	1.21%	-2.11%
Subtotal	4.05516E-07	99.62%	4.0002E-07	99.62%	-1.35%
Total Th++++	6.47549E-08	100.00%	6.4719E-08	100.00%	-0.06%
Th(OH)4(aq)	5.19575E-08	80.24%	5.1910E-08	80.21%	-0.09%
Th(OH)3(CO3)-	1.27974E-08	19.76%	1.2809E-08	19.79%	0.09%
Subtotal	6.47549E-08	100.00%	6.5037E-08	100.49%	0.44%

The results of the two codes are nevertheless in less than very good agreement. The EQ3/6 run was repeated in a one-off test case c4pgwb_P75 in which EQ3/6 used the same J(x) approximation (Pitzer, 1975) as FMT. The results of this were compared with FMT using the spreadsheet c4pgwb _P75. Table 5.12-9 shows the results for solute species molalities. The previous largest discrepancies (Table 5.12-5) are much reduced: $Th(CO_3)_5^{6-}$ (from +18.082% to +0.111%), $Am(CO_3)_4^{5-}$ (from +13.429% to +0.807%), $EDTA^{4-}$ (from +8.463% to 1.973%), and $NpO_2(CO_3)_3^{5-}$ (from +7.162% to -3.642%). The largest discrepancy is now +6.404% for $B_4O_5(OH)_4^{2-}$. Although not ideal, the situation is much improved.

Table 5.12-9. Test Case #11 One-Off (c4pgwb_P75) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Molality			
Species	FMT	EQ3/6	Δ
Cl-	6.17604	6.1766	0.009%
Na+	4.99121	4.9876	-0.072%
Mg++	0.576993	0.57899	0.346%
K+	0.562550	0.57565	2.329%
SO4--	0.262347	0.26807	2.181%
MgB(OH)4+	0.0753902	0.076659	1.683%
B(OH)4-	0.0549134	0.055693	1.420%
Br-	0.0319351	0.032679	2.329%
B(OH)3(aq)	0.0254070	0.025843	1.716%
Ca++	0.00849908	0.0083622	-1.611%
Acetate-	0.00654112	0.0067129	2.626%
MgAcetate+	0.00642842	0.0065600	2.047%
B4O5(OH)4--	0.00575374	0.0061222	6.404%
B3O3(OH)4-	0.00331851	0.0034802	4.872%
MgOH+	0.00182005	0.0018285	0.464%
CaB(OH)4+	0.00170130	0.0016922	-0.535%
MgOxalate(aq)	0.00153978	0.0015747	2.268%
MgCitrate-	0.000962646	0.00098540	2.364%
MgCO3(aq)	0.000323947	0.00032410	0.047%
CaAcetate+	4.96558E-05	0.000049568	-0.177%
HCO3-	4.84103E-05	0.000048478	0.140%
CO3--	2.48257E-05	0.000024769	-0.228%
Citrate---	1.99049E-05	2.02060E-05	1.513%
Oxalate--	1.38711E-05	0.000014089	1.571%
CaOxalate(aq)	1.18939E-05	0.000011899	0.043%
MgEDTA--	9.72185E-06	9.9483E-06	2.329%
OH-	0.000008121	8.1051E-06	-0.196%
CaCitrate-	7.43588E-06	7.4457E-06	0.132%
CaCO3(aq)	4.17958E-06	4.0905E-06	-2.131%
HAcetate(aq)	4.26585E-07	4.3823E-07	2.730%
Am(OH)2+	2.37430E-07	2.3657E-07	-0.362%
AmEDTA-	2.01094E-07	2.0746E-07	3.166%
NpO2+	1.45815E-07	1.4290E-07	-1.999%
NpO2CO3-	1.19968E-07	1.1724E-07	-2.274%
NpO2Acetate(aq)	8.44036E-08	8.4872E-08	0.555%
CaEDTA--	7.50956E-08	7.5170E-08	0.099%
Th(OH)4(aq)	5.19575E-08	5.1915E-08	-0.082%
NpO2Oxalate-	5.03499E-08	5.0224E-08	-0.250%
CO2(aq)	2.93478E-08	2.9278E-08	-0.238%
Th(OH)3(CO3)-	1.27974E-08	1.2799E-08	0.013%
NpO2OH(aq)	4.97922E-09	4.8712E-09	-2.169%
AmOH++	2.82968E-09	2.8421E-09	0.439%

HSO4-	1.33874E-09	1.3681E-09	2.193%
AmAcetate++	1.28786E-09	1.3455E-09	4.476%
NpO2(CO3)2---	1.33679E-09	1.2998E-09	-2.767%
Am(OH)3(aq)	6.87418E-10	6.9009E-10	0.389%
HCitrate--	6.54933E-10	6.6555E-10	1.621%
AmCitrate(aq)	5.10997E-10	5.1950E-10	1.664%
H+	4.62711E-10	4.6229E-10	-0.091%
AmCO3+	4.32475E-10	4.3213E-10	-0.080%
NpO2Citrate--	1.71501E-10	1.6957E-10	-1.126%
Am(CO3)2-	1.53197E-10	1.5349E-10	0.191%
AmSO4+	1.43332E-10	1.4595E-10	1.827%
EDTA----	9.60883E-11	9.7984E-11	1.973%
HOxalate-	4.08059E-11	4.1529E-11	1.772%
Am(CO3)3---	3.82087E-11	3.8337E-11	0.336%
AmOxalate+	2.91986E-11	2.9271E-11	0.248%
Am(SO4)2-	2.21879E-11	2.3182E-11	4.480%
NpO2(CO3)3(5-)	1.47730E-11	1.4235E-11	-3.642%
Am+++	1.26375E-11	1.2263E-11	-2.963%
Am(CO3)4(5-)	1.09972E-11	1.1086E-11	0.807%
HEDTA---	8.88268E-12	9.1023E-12	2.472%
NpO2(OH)2-	7.28398E-12	7.1285E-12	-2.135%
AmCl++	2.11486E-12	2.1418E-12	1.274%
NpO2EDTA---	5.07797E-13	5.0616E-13	-0.322%
AmCl2+	1.09730E-13	1.1066E-13	0.848%
H2EDTA--	1.10656E-14	1.1336E-14	2.444%
H2Citrate-	4.80754E-15	4.8867E-15	1.647%
NpO2HEDTA--	9.81711E-16	9.7593E-16	-0.589%
Th(CO3)5(6-)	4.55775E-16	4.5628E-16	0.111%
Th(SO4)3--	1.83058E-17	1.9100E-17	4.339%
ThEDTA(aq)	8.65338E-18	8.8789E-18	2.606%
H2Oxalate(aq)	5.87859E-19	6.0076E-19	2.195%
Th(SO4)2(aq)	3.4199E0-19	3.5701E-19	4.392%
NpO2H2EDTA-	1.50741E-19	1.4815E-19	-1.719%
ThCitrate+	6.39131E-20	6.3167E-20	-1.167%
Th(Acetate)2++	8.70115E-21	9.1654E-21	5.336%
H3Citrate(aq)	2.21771E-21	2.2508E-21	1.492%
H3EDTA-	1.22934E-21	1.2565E-21	2.209%
ThAcetate+++	1.10948E-21	1.1552E-21	4.121%
ThOxalate++	1.55293E-22	1.5481E-22	-0.311%
Th++++	-----	1.2315E-24	-----
H4EDTA(aq)	-----	1.8586E-28	-----

Table 5.12-10 shows the corresponding results for solute species activity coefficients. The previous (Table 5.12-6) largest discrepancy is much reduced: $Th(CO_3)_5^{6-}$ (from -15.220% to

-0.392%). The largest discrepancy is now for Am^{3+} (+3.298%). Again, the results are much improved, though less than ideal.

Table 5.12-10. Test Case #11 One-Off (c4pgwb_P75) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.305	1.30617	0.090%
Na+	0.9246	0.92406	-0.058%
Mg++	1.742	1.73860	-0.195%
K+	0.4298	0.42954	-0.061%
SO4--	0.021331	0.02131	-0.118%
MgB(OH)4+	1.873	1.87197	-0.055%
B(OH)4-	0.1020	0.10207	0.069%
Br-	0.2683	0.26804	-0.097%
B(OH)3(aq)	1.069	1.06733	-0.156%
Ca++	0.9135	0.90949	-0.438%
Acetate-	0.5575	0.55796	0.082%
MgAcetate+	7.398	7.45590	0.783%
B4O5(OH)4--	0.0042179	0.0042199	0.047%
B3O3(OH)4-	0.1631	0.16300	-0.058%
MgOH+	0.3065	0.30528	-0.398%
CaB(OH)4+	1.143	1.14209	-0.080%
MgOxalate(aq)	1.263	1.26299	-0.001%
MgCitrate-	0.1662	0.16489	-0.787%
MgCO3(aq)	1.000	1.00000	0.000%
CaAcetate+	7.398	7.45590	0.783%
HCO3-	0.3511	0.35035	-0.214%
CO3--	0.015308	0.015329	0.134%
Citrate---	0.000040119	0.000040068	-0.127%
Oxalate--	0.02246	0.022584	0.552%
CaOxalate(aq)	1.263	1.26299	-0.001%
MgEDTA--	0.1302	0.13041	0.159%
OH-	0.4438	0.44422	0.095%
CaCitrate-	0.1662	0.16489	-0.787%
CaCO3(aq)	1.000	1.00000	0.000%
HAcetate(aq)	1.000	1.00000	0.000%
Am(OH)2+	0.00074059	0.00074388	0.444%
AmEDTA-	0.029535	0.029376	-0.537%
NpO2+	1.858	1.85609	-0.103%
NpO2CO3-	0.089249	0.089310	0.068%
NpO2Acetate(aq)	0.2768	0.27676	-0.015%
CaEDTA--	0.1302	0.13041	0.159%
Th(OH)4(aq)	1.000	1.00000	0.000%
NpO2Oxalate-	0.029135	0.029201	0.227%
CO2(aq)	3.522	3.53021	0.233%
Th(OH)3(CO3)-	0.2683	0.26804	-0.097%

NpO2OH(aq)	0.095666	0.095653	-0.013%
AmOH++	0.023758	0.023692	-0.278%
HSO4-	0.8149	0.81414	-0.093%
AmAcetate++	0.010578	0.010423	-1.464%
NpO2(CO3)2---	0.000081462	0.000081846	0.472%
Am(OH)3(aq)	0.009169	0.0091327	-0.396%
HCitrate--	0.006616	0.0066024	-0.206%
AmCitrate(aq)	0.006638	0.0066359	-0.032%
H+	4.426	4.43098	0.113%
AmCO3+	0.7483	0.74989	0.213%
NpO2Citrate--	0.0039615	0.0039756	0.355%
Am(CO3)2-	0.063985	0.0638705	-0.179%
AmSO4+	0.4676	0.46968	0.444%
EDTA----	9.8019E-07	9.8401E-07	0.390%
HOxalate-	0.2842	0.28530	0.387%
Am(CO3)3---	0.000015457	1.5392E-05	-0.419%
AmOxalate+	0.1034	0.10558	2.113%
Am(SO4)2-	0.048011	0.047973	-0.078%
NpO2(CO3)3(5-)	2.1613E-10	2.1888E-10	1.271%
Am+++	0.5347	0.55233	3.298%
Am(CO3)4(5-)	1.2771E-13	1.2644E-13	-0.991%
HEDTA---	0.00080805	0.00080761	-0.055%
NpO2(OH)2-	0.013842	0.013823	-0.138%
AmCl++	44.67	44.26903	-0.898%
NpO2EDTA---	0.017233	0.017326	0.540%
AmCl2+	727.7	725.10350	-0.357%
H2EDTA--	0.010058	0.010060	0.020%
H2Citrate-	0.1276	0.12738	-0.173%
NpO2HEDTA--	0.1873	0.18889	0.847%
Th(CO3)5(6-)	2.2699E-14	2.2610E-14	-0.392%
Th(SO4)3--	0.025738	0.026285	2.123%
ThEDTA(aq)	3.944	3.94457	0.015%
H2Oxalate(aq)	1.000	1.00000	0.000%
Th(SO4)2(aq)	35.95	35.95837	0.023%
NpO2H2EDTA-	0.52	0.53064	2.046%
ThCitrate+	21.6	22.20752	2.813%
Th(Acetate)2++	266.4	267.36220	0.361%
H3Citrate(aq)	1.000	1.00000	0.000%
H3EDTA-	0.2267	0.22735	0.288%
ThAcetate+++	75.98	75.11039	-1.145%
ThOxalate++	490.8	503.96456	2.682%
Th++++	0.8146	0.81809	0.428%
H4EDTA(aq)	1.000	1.00000	0.000%

Table 5.12-11 compares the results for actinide species distributions, considering only those species needed to comprise 99% of the mass balance of any actinide. The differences here are small (<3%), generally no better than those obtained previously (Table 5.12-8).

Table 5.12-11. Test Case #11 One-Off (c4pgwb_P75) Actinide Species Distributions, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation) vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	4.44684E-07	100.00%	4.5028E-07	100.00%	1.26%
Am(OH)2+	2.37430E-07	53.39%	2.3657E-07	52.54%	-0.36%
AmEDTA-	2.01094E-07	45.22%	2.0746E-07	46.07%	3.17%
AmOH++	2.82968E-09	0.64%	2.8421E-09	0.63%	0.44%
Subtotal	4.41354E-07	99.25%	4.4687E-07	99.24%	1.25%

Total NpO2+	4.07047E-07	100.00%	4.0160E-07	100.00%	-1.34%
NpO2+	1.45815E-07	35.82%	1.4290E-07	35.58%	-2.00%
NpO2CO3-	1.19968E-07	29.47%	1.1724E-07	29.19%	-2.27%
NpO2Acetate(aq)	8.44036E-08	20.74%	8.4872E-08	21.13%	0.55%
NpO2Oxalate-	5.03499E-08	12.37%	5.0224E-08	12.51%	-0.25%
NpO2OH(aq)	4.97922E-09	1.22%	4.8712E-09	1.21%	-2.17%
Subtotal	4.05516E-07	99.62%	4.0011E-07	99.63%	-1.33%

Total Th++++	6.47549E-08	100.00%	6.4715E-08	100.00%	-0.06%
Th(OH)4(aq)	5.19575E-08	80.24%	5.1915E-08	80.22%	-0.08%
Th(OH)3(CO3)-	1.27974E-08	19.76%	1.2799E-08	19.78%	0.01%
Subtotal	6.47549E-08	100.00%	6.5037E-08	100.50%	0.44%

The results of the two codes are in better but not ideal agreement when both codes use the same J(x) approximation. The remaining differences are mainly attributed to "front end" effects. That is, the inputs to the two codes are not entirely consistent. To further run the source of the differences to ground, the EQ3/6 run was repeated in a modified calculation in which the Pitzer (1975, eq 47) approximation for J(x) was used (as in a "one-off" calculation) and in addition the EQ3/6 inputs were forced to match the FMT inputs by taking data for the initial solution from the FMT .INGUESS file. Test cases so modified in this report will be referred to as "two-off." That file, which is a converted .FOR88 output file with modifications to add the desired minerals, contains the moles of elements and pseudo elements relative to 1000 g of H_2O. For the aqueous species, these are the molalities. The requisite molalities for solute basis species other than H^+ were computed using the appropriate weighted sums of the molalities of individual aqueous species. The pmH was obtained from the molality of the species H^+. A molality of 1.0×10^{-18} was assigned to each as a negligible trace concentration. For details of this calculation, see worksheet gwb of spreadsheet c4pgwb_P75_Mfix.xls. Bicarbonate and the three actinide basis species are technically not in the initial brine but are required to initialize the EQ6 run, which reacts the brine with minerals requiring that these basis species be present. The modified EQ3NR brine inputs are given in Table 5.12-12. Note that these inputs do not require density and TDS data. For this run, the EQ3NR results were not rescaled to produce a brine mass corresponding to 1 L. Thus, the molarity/molality ratio is not needed as an input for this run.

Table 5.12-12. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Revised EQ3NR Inputs Calculated from the FMT .INGUESS File.

Basis Species	Molality
Na+	3.9080347
K+	0.5143333
Ca++	8.04470E-04
Mg++	1.1229985
pmH	2.4791652
Cl-	6.1877216
SO4=	0.1965247
B(OH)4-	0.1740648
Br-	2.91980E-02
Oxalate-	3.61789E-02
Acetate-	1.19038E-02
EDTA----	9.14121E-06
Citrate---	9.05137E-04
HCO3-	1.0E-18
Am+++	1.0E-18
Th++++	1.0E-18
NpO2+	1.0E-18
pmH	2.4791652

Spreadsheet c4pgwb_P75_Mfix.xls was used to make all subsequent comparisons and is the source of the rest of the tables in this section. Table 5.12-13 compares the general parameter outputs for this "two-off" case. The differences are not only within the usual acceptance criteria, they are very small compared to them. These results are substantially improved over the corresponding ones from the first EQ3/6 run (Table 5.12-4).

Table 5.12-13. Test Case #11 Two-Off (c4pgwb_P75_Mfix) General Parameter Outputs, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1293.458658	1293.4933	0.003%
H2O mass, g	914.2900833	914.31844	0.003%
Ionic strength, m	7.663835	7.664	0.002%
density, g/L	1232.10	1232.1	0.000%
TDS, g/L	361.1827591	361.18	-0.001%
pH (Pitzer)	8.6887	8.6887	0.000%
pmH	9.3347	9.3346	-0.001%
pcH	9.3947	9.3953	0.006%
a_w	0.732297	0.73229	-0.001%

x_w	0.812688	0.81269	0.000%
λ_w	0.9011	0.90107	-0.003%
fCO2, bars	0.000003135	3.13527E-06	0.009%
pH (Pitzer)	8.6887	8.6887	0.0000
pmH	9.3347	9.3346	-0.0001
pcH	9.3947	9.3953	0.0006

Table 5.12-14 shows the results for solute species molalities. Now all differences are within the usual 1% acceptance criterion. The largest discrepancy is now +0.295% for $Th(CO_3)_5^{6-}$. These results are very significantly improved.

Table 5.12-14. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.17604	6.176	-0.001%
Na+	4.99121	4.9908	-0.008%
Mg++	0.576993	0.57718	0.032%
K+	0.562550	0.56253	-0.004%
SO4--	0.262347	0.26234	-0.003%
MgB(OH)4+	0.0753902	0.075402	0.016%
B(OH)4-	0.0549134	0.054905	-0.015%
Br-	0.0319351	0.031934	-0.003%
B(OH)3(aq)	0.0254070	0.025408	0.004%
Ca++	0.00849908	0.0084984	-0.008%
Acetate-	0.00654112	0.0065403	-0.013%
MgAcetate+	0.00642842	0.0064288	0.006%
B4O5(OH)4--	0.00575374	0.0057518	-0.034%
B3O3(OH)4-	0.00331851	0.0033179	-0.018%
MgOH+	0.00182005	0.0018204	0.019%
CaB(OH)4+	0.00170130	0.0017008	-0.029%
MgOxalate(aq)	0.00153978	0.0015404	0.040%
MgCitrate-	0.000962646	0.00096261	-0.004%
MgCO3(aq)	0.000323947	0.00032396	0.004%
CaAcetate+	4.96558E-05	4.9638E-05	-0.036%
HCO3-	4.84103E-05	4.8405E-05	-0.011%
CO3--	2.48257E-05	2.4827E-05	0.005%
Citrate---	1.99049E-05	1.9910E-05	0.026%
Oxalate--	1.38711E-05	1.3877E-05	0.043%
CaOxalate(aq)	1.18939E-05	1.1894E-05	0.001%
MgEDTA--	9.72185E-06	9.7216E-06	-0.003%
OH-	8.12100E-06	8.1196E-06	-0.017%
CaCitrate-	7.43588E-06	7.4325E-06	-0.045%
CaCO3(aq)	4.17958E-06	4.1780E-06	-0.038%
HAcetate(aq)	4.26585E-07	4.2652E-07	-0.015%

Am(OH)2+	2.37430E-07	2.3747E-07	0.017%
AmEDTA-	2.01094E-07	2.0105E-07	-0.022%
NpO2+	1.45815E-07	1.4586E-07	0.031%
NpO2CO3-	1.19968E-07	1.1998E-07	0.010%
NpO2Acetate(aq)	8.44036E-08	8.4412E-08	0.010%
CaEDTA--	7.50956E-08	7.5062E-08	-0.045%
Th(OH)4(aq)	5.19575E-08	5.1960E-08	0.005%
NpO2Oxalate-	5.03499E-08	5.0367E-08	0.034%
CO2(aq)	2.93478E-08	2.9348E-08	0.001%
Th(OH)3(CO3)-	1.27974E-08	1.2798E-08	0.005%
NpO2OH(aq)	4.97922E-09	4.9796E-09	0.008%
AmOH++	2.82968E-09	2.8309E-09	0.043%
HSO4-	1.33874E-09	1.3387E-09	-0.003%
AmAcetate++	1.28786E-09	1.2882E-09	0.026%
NpO2(CO3)2---	1.33679E-09	1.3370E-09	0.016%
Am(OH)3(aq)	6.87418E-10	6.8723E-10	-0.027%
HCitrate--	6.54933E-10	6.5491E-10	-0.004%
AmCitrate(aq)	5.10997E-10	5.1113E-10	0.026%
H+	4.62711E-10	4.6280E-10	0.019%
AmCO3+	4.32475E-10	4.3258E-10	0.024%
NpO2Citrate--	1.71501E-10	1.7150E-10	-0.001%
Am(CO3)2-	1.53197E-10	1.5318E-10	-0.011%
AmSO4+	1.43332E-10	1.4340E-10	0.047%
EDTA----	9.60883E-11	9.6181E-11	0.096%
HOxalate-	4.08059E-11	4.0826E-11	0.049%
Am(CO3)3—	3.82087E-11	3.8216E-11	0.019%
AmOxalate+	2.91986E-11	2.9224E-11	0.087%
Am(SO4)2-	2.21879E-11	2.2197E-11	0.041%
NpO2(CO3)3(5-)	1.4773E-11	1.4784E-11	0.074%
Am+++	1.26375E-11	1.2644E-11	0.051%
Am(CO3)4(5-)	1.09972E-11	1.1017E-11	0.180%
HEDTA---	8.88268E-12	8.8847E-12	0.023%
NpO2(OH)2-	7.28398E-12	7.2829E-12	-0.015%
AmCl++	2.11486E-12	2.1161E-12	0.059%
NpO2EDTA---	5.07797E-13	5.0815E-13	0.070%
AmCl2+	1.0973E-13	1.0982E-13	0.082%
H2EDTA--	1.10656E-14	1.1065E-14	-0.005%
H2Citrate-	4.80754E-15	4.8077E-15	0.003%
NpO2HEDTA--	9.81711E-16	9.8180E-16	0.009%
Th(CO3)5(6-)	4.55775E-16	4.5712E-16	0.295%
Th(SO4)3--	1.83058E-17	1.8323E-17	0.094%
ThEDTA(aq)	8.65338E-18	8.6546E-18	0.014%
H2Oxalate(aq)	5.87859E-19	5.8817E-19	0.053%
Th(SO4)2(aq)	3.4199E-19	3.4231E-19	0.094%
NpO2H2EDTA-	1.50741E-19	1.5076E-19	0.013%
ThCitrate+	6.39131E-20	6.3951E-20	0.059%

Th(Acetate)2++	8.70115E-21	8.7031E-21	0.022%
H3Citrate(aq)	2.21771E-21	2.2183E-21	0.027%
H3EDTA-	1.22934E-21	1.2294E-21	0.005%
ThAcetate+++	1.10948E-21	1.1099E-21	0.038%
ThOxalate++	1.55293E-22	1.5544E-22	0.095%
Th++++	0	1.2349E-24	-----
H4EDTA(aq)	0	1.8130E-28	-----

Table 5.12-15 shows the results for solute species activity coefficients. Again, all differences are within the usual 1% acceptance criterion. The largest discrepancy is now -0.346% for $Th(CO_3)_5^{6-}$. The results are again very significantly improved.

Table 5.12-15. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.305	1.30497	-0.002%
Na+	0.9246	0.92449	-0.012%
Mg++	1.742	1.74181	-0.011%
K+	0.4298	0.42983	0.008%
SO4--	0.021331	0.02133	-0.003%
MgB(OH)4+	1.873	1.87284	-0.009%
B(OH)4-	0.1020	0.10200	0.000%
Br-	0.2683	0.26829	-0.005%
B(OH)3(aq)	1.069	1.06881	-0.018%
Ca++	0.9135	0.91348	-0.002%
Acetate-	0.5575	0.55744	-0.010%
MgAcetate+	7.398	7.39776	-0.003%
B4O5(OH)4--	0.0042179	0.00422	0.001%
B3O3(OH)4-	0.1631	0.16312	0.011%
MgOH+	0.3065	0.30648	-0.007%
CaB(OH)4+	1.143	1.14262	-0.034%
MgOxalate(aq)	1.263	1.26299	-0.001%
MgCitrate-	0.1662	0.16626	0.039%
MgCO3(aq)	1.000	1.00000	0.000%
CaAcetate+	7.398	7.39776	-0.003%
HCO3-	0.3511	0.35108	-0.007%
CO3--	0.015308	0.015304	-0.027%
Citrate---	0.000040119	0.000040096	-0.058%
Oxalate--	0.02246	0.022454	-0.025%
CaOxalate(aq)	1.263	1.26299	-0.001%
MgEDTA--	0.1302	0.13011	-0.072%
OH-	0.4438	0.44371	-0.020%
CaCitrate-	0.1662	0.16626	0.039%
CaCO3(aq)	1.000	1.00000	0.000%
HAcetate(aq)	1.000	1.00000	0.000%

Am(OH)2+	0.00074059	0.00074063	0.005%
AmEDTA-	0.029535	0.029539	0.015%
NpO2+	1.858	1.85823	0.013%
NpO2CO3-	0.089249	0.089248	-0.001%
NpO2Acetate(aq)	0.2768	0.27676	-0.015%
CaEDTA--	0.1302	0.13011	-0.072%
Th(OH)4(aq)	1.000	1.00000	0.000%
NpO2Oxalate-	0.029135	0.02914	0.020%
CO2(aq)	3.522	3.52209	0.002%
Th(OH)3(CO3)-	0.2683	0.26829	-0.005%
NpO2OH(aq)	0.095666	0.095675	0.010%
AmOH++	0.023758	0.023757	-0.002%
HSO4-	0.8149	0.81508	0.022%
AmAcetate++	0.010578	0.010578	-0.001%
NpO2(CO3)2---	0.000081462	0.000081433	-0.036%
Am(OH)3(aq)	0.009169	0.0091706	0.018%
HCitrate--	0.006616	0.0066145	-0.022%
AmCitrate(aq)	0.006638	0.0066374	-0.009%
H+	4.426	4.42588	-0.003%
AmCO3+	0.7483	0.74834	0.006%
NpO2Citrate--	0.0039615	0.0039610	-0.014%
Am(CO3)2-	0.063985	0.063988	0.005%
AmSO4+	0.4676	0.46752	-0.017%
EDTA----	9.8019E-07	9.7859E-07	-0.163%
HOxalate-	0.2842	0.28418	-0.006%
Am(CO3)3---	0.000015457	1.5449E-05	-0.052%
AmOxalate+	0.1034	0.10340	-0.005%
Am(SO4)2-	0.048011	0.048018	0.014%
NpO2(CO3)3(5-)	2.1613E-10	2.1587E-10	-0.119%
Am+++	0.5347	0.53469	-0.002%
Am(CO3)4(5-)	1.2771E-13	1.2741E-13	-0.236%
HEDTA---	0.00080805	0.00080742	-0.078%
NpO2(OH)2-	0.013842	0.013842	0.000%
AmCl++	44.67	44.66836	-0.004%
NpO2EDTA---	0.017233	0.017215	-0.106%
AmCl2+	727.7	727.61225	-0.012%
H2EDTA--	0.010058	0.010055	-0.026%
H2Citrate-	0.1276	0.12761	0.011%
NpO2HEDTA--	0.1873	0.18728	-0.009%
Th(CO3)5(6-)	2.2699E-14	2.2620E-14	-0.346%
Th(SO4)3--	0.025738	0.025734	-0.017%
ThEDTA(aq)	3.944	3.94457	0.015%
H2Oxalate(aq)	1.000	1.00000	0.000%
Th(SO4)2(aq)	35.95	35.95009	0.000%
NpO2H2EDTA-	0.5200	0.51988	-0.024%
ThCitrate+	21.60	21.59733	-0.012%

Th(Acetate)2++	266.4	266.37901	-0.008%
H3Citrate(aq)	1.000	1.00000	0.000%
H3EDTA-	0.2267	0.22673	0.011%
ThAcetate+++	75.98	75.98012	0.000%
ThOxalate++	490.8	490.79485	-0.001%
Th++++	0.8146	0.81452	-0.010%
H4EDTA(aq)	1.000	1.00000	0.000%

Table 5.12-16 shows the results for saturation indices (log Q/K) for the relevant minerals. These results are also improved. Most of the differences are within the 0.004 acceptance criterion. The larger differences are explained by the limited precision with which FMT reports saturation indices.

Table 5.12-16. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Calculated Mineral Saturation Indices s, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	2.13	2.13426	0.00426
Magnesite	1.42	1.41589	-0.00411
Am(OH)3(s)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Anhydrite	0.00000	0.00000	0.00000
Whewellite	0.00000	0.00000	0.00000
Brucite	0.00000	0.00000	0.00000
Halite	0.00000	0.00000	0.00000
Mg2Cl(OH)3.4H2O	0.00000	0.00000	0.00000
Hydromagnesite5424	0.00000	0.00000	0.00000
Glauberite	-0.0413	-0.04150	-0.00020
Gypsum	-0.0522	-0.05223	-0.00003
Calcite	-0.124	-0.12403	-0.00003
Aragonite	-0.311	-0.31083	0.00017
AmOHCO3(c)	-0.334	-0.33431	-0.00031
Hydromagnesite4323	-0.344	-0.34347	0.00053
Syngenite	-0.534	-0.53428	-0.00028
Sylvite	-0.610	-0.61018	-0.00018
Thenardite	-0.636	-0.63640	-0.00040
Borax	-0.699	-0.69959	-0.00059
Labile_Salt	-0.808	-0.80823	-0.00023
Polyhalite	-0.986	-0.98577	0.00023
Mirabilite	-1.05	-1.04924	0.00076
Epsomite	-1.32	-1.31588	0.00412
Bloedite	-1.37	-1.36804	0.00196
Hexahydrite	-1.43	-1.42657	0.00343
B(OH)3	-1.54	-1.53568	0.00432
Teepleite(20C)	-1.62	-1.61844	0.00156

Nesquehonite	-1.66	-1.65685	0.00315
Arcanite	-1.71	-1.70896	0.00104
Aphthitalite/Glaserite	-1.89	-1.88714	0.00286
Kainite	-2.17	-2.17341	-0.00341
Na_Metaborate	-2.19	-2.18747	0.00253
Picromerite/Schoenite	-2.22	-2.21923	0.00077
Kieserite	-2.26	-2.26240	-0.00240
Leonite	-2.30	-2.2973	0.00270
NpO2OH(aged)	-2.53	-2.53005	-0.00005
Na2Oxalate	-2.77	-2.77308	-0.00308
NaAm(CO3)2.6H2O(c)	-2.77	-2.76677	0.00323
Carnallite	-3.04	-3.03765	0.00235
NpO2OH(am)	-3.23	-3.23015	-0.00015
Na3NpO2(CO3)2	-3.23	-3.23505	-0.00505
2[NaNpO2CO3.7/2H2O]	-3.41	-3.41344	-0.00344
Bischofite	-3.45	-3.45237	-0.00237
Nahcolite	-3.70	-3.70258	-0.00258
K-Tetraborate(30C)	-3.89	-3.89137	-0.00137
K-Pentaborate(30C)	-4.02	-4.02410	-0.00410
Na_Pentaborate	-4.10	-4.10233	-0.00233
Pirssonite	-4.65	-4.64988	0.00012
Gaylussite	-4.88	-4.87803	0.00197
K3NpO2(CO3)2	-5.33	-5.32649	0.00351
Na2CO3.7H2O	-5.58	-5.57913	0.00087
Natron	-5.62	-5.62047	-0.00047
Kalicinite	-5.67	-5.66766	0.00234
Thermonatrite	-5.71	-5.70924	0.00076
Burkeite	-6.17	-6.16772	0.00228
CaCl2.4H2O	-6.56	-6.55576	0.00424
KNaCO3.6H2O	-7.07	-7.06869	0.00131

Table 5.12-17 shows the results for actinide species distributions. Since the molalities have already been shown to be substantially improved, it is no surprise that the results in this table are also substantially improved (they are essentially the same data). This table is included here because of its special interest. All differences are well within the usual 1% acceptance criterion.

Table 5.12-17. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Actinide Species Distributions, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	4.44684E-07	100.00%	4.4467E-07	100.00%	0.00%
Am(OH)2+	2.37430E-07	53.39%	2.3747E-07	53.40%	0.02%
AmEDTA-	2.01094E-07	45.22%	2.0105E-07	45.21%	-0.02%
AmOH++	2.82968E-09	0.64%	2.8309E-09	0.64%	0.04%
Subtotal	4.41354E-07	99.25%	4.4135E-07	99.25%	0.00%
Total NpO2+	4.07047E-07	100.00%	4.0713E-07	100.00%	0.02%
NpO2+	1.45815E-07	35.82%	1.4586E-07	35.83%	0.03%
NpO2CO3-	1.19968E-07	29.47%	1.1998E-07	29.47%	0.01%
NpO2Acetate(aq)	8.44036E-08	20.74%	8.4412E-08	20.73%	0.01%
NpO2Oxalate-	5.03499E-08	12.37%	5.0367E-08	12.37%	0.03%
NpO2OH(aq)	4.97922E-09	1.22%	4.9796E-09	1.22%	0.01%
Subtotal	4.05516E-07	99.62%	4.0560E-07	99.62%	0.02%
Total Th++++	6.47549E-08	100.00%	6.4759E-08	100.00%	0.01%
Th(OH)4(aq)	5.19575E-08	80.24%	5.1960E-08	80.24%	0.00%
Th(OH)3(CO3)-	1.27974E-08	19.76%	1.2798E-08	19.76%	0.00%
Subtotal	6.47549E-08	100.00%	6.4758E-08	100.00%	0.00%

Table 5.12-18 shows the results for mineral masses (in moles) in the reacted system. These minerals include "added" minerals which did not totally dissolve due to saturation and minerals that precipitated spontaneously. These results were not shown for the previous runs because the brine scaling issue prevented meaningful comparison. The results shown here are well within the usual 1% acceptance criterion for "linear" quantities, except for whewellite (calcium oxalate). There is more whewellite present in the FMT run. An examination of the FMT .INGUESS file showed that additional whewellite had been added to the system. This explains the discrepancy.

Table 5.12-18. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Moles of Minerals in the Reacted System, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

Mineral	FMT	EQ3/6	Δ
Anhydrite	9.95666	9.9567	0.000%
Halite	9.34462	9.3448	0.002%
Brucite	8.12404	8.1246	0.007%
Mg2Cl(OH)3.4H2O	1.19641	1.1960	-0.034%
Am(OH)3(s)	1.00000	1.00000	0.000%
ThO2(am)	1.00000	1.00000	0.000%
KNpO2CO3	1.00000	1.00000	0.000%

Hydromagnesite5424	0.999908	0.99991	0.000%
Whewellite	0.049665	0.034747	-30.037%

By modifying the EQ3NR input to avoid "front end" inconsistency with the FMT input and making EQ3/6 use the Pitzer (1975, eq. 47) approximation for the J(x) function, excellent agreement has been obtained. This provides verification that the large discrepancies between the original EQ3/6 run and FMT were due to a combination of these factors.

5.13 Test Case #12 – Solubility of Am(III), Th(IV), and Np(V) in WIPP ERDA-6 brine

5.13.1 Test Overview

This test case is to compare CRA-2004 PABC values of Am(III), Th(IV) and Np(V) in ERDA-6 brine predicted by FMT with those calculated by EQ3/6. This problem is taken from Brush (2005). This test case is much like Test Case #11. It simply uses a different starting brine. The ERDA-6 brine is first created. Then it is reacted with 1.0 mole of $Am(OH)_3(s)$, $ThO_2(am)$, $KNpO_2CO_3$, and hydromagnesite(5424) ($Mg_5(CO_3)4(OH)_2.4H_2O$) plus 10.0 moles each of anhydrite ($CaSO_4$), brucite ($Mg(OH)_2$), and halite (NaCl). This is a "type 3" problem in that the lack of a proper front-end in FMT may affect the results, including the calculated pH.

Table 5.13-1 gives the FMT inputs for the ERDA-6 brine. The inputs here are consistent with 1 L of solution (see Brush, 2005, Table 2). The four organic ligands (oxalate, acetate, EDTA, and citrate) are treated as pseudo-elements by FMT (whereas they are treated as active auxiliary basis species by EQ3/6).

Table 5.13-1. Test Case #12 (c4per6b) FMT Inputs for ERDA-6 Brine.

Element	Moles
H	98.5663837
O	50.0976919
Na	4.87
K	0.097
Mg	0.019
Ca	0.012
Cl	4.80
S	0.170
C	0.016
B	0.063
Br	0.011
Oxalate	0.046
Acetate	0.011
EDTA	8.14E-06
Citrate	8.06E-04

Table 5.13-2 gives the corresponding EQ3/6 inputs for the brine. Because EQ3/6 works directly in terms of molalities, the molarity inputs must be converted to molalities before the actual speciation calculations can begin. This requires inputs for density and TDS, which are needed to compute the molarity/molality factor or molarity/molality factor. The values shown in Table 5.13-2 were calculated from the molarity data using the WIPP density model (see worksheet c4per6 of spreadsheet Conc_density_calcs_EV2008.xls). The molarity/molality factor was used in EQ3NR to rescale the brine mass for consistency with a 1 L volume prior to reacting it with minerals in the subsequent EQ6 run. A small error was made in that a value of 0.8735 (the value of the molarity/molarity factor for GWB brine) was actually used instead. This only has the effect

of a minor error in the intended brine mass (it will be close to, but not exactly consistent with, a volume of 1 L). This is not of real consequence as will be noted below (thus it is not necessary to correct the affected factor and re-run the problem). The molarity to molality conversions done in EQ3NR only use the density and TDS inputs. Hence, those conversions are not affected.

Table 5.13-2. Test Case #12 (c4per6) EQ3/6 Inputs for ERDA-6 Brine.

Basis species	molality
Na+	4.87
K+	0.097
Mg++	0.019
Ca++	0.012
Cl-	4.8
SO4--	0.17
HCO3-	0.016
B(OH)4-	0.063
Br-	0.011
Oxalate--	4.55E-02
Acetate-	1.06E-02
EDTA----	8.14E-06
Citrate---	8.06E-04
Am+++	1.00E-18
Th++++	1.00E-18
NpO2+	1.00E-18
density, g/L	1204.24
TDS, g/L	314.8069
Molarity/molality	0.8876

It is noted that the density, TDS, and molarity/molality values obtained from the spreadsheet calculation take the compositional data at face value. There is no speciation calculation in this calculation. Since EQ3NR performs a full speciation calculation, the WIPP density model embedded in FMT will generally produce slightly different calculated results. This will be addressed below in the Evaluation section.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	c4per6.6i
EQ6 output files:	c4per6.6o, c4per6.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_cra1bc_er6_hmg_orgs_011.in; fmt_cra1bc_er6_hmg_orgs_011.inguess
FMT output files:	fmt_cra1bc_er6_hmg_orgs_011.out; fmt_cra1bc_er6_hmg_orgs_011.for088

5.13.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.13.3 Evaluation

Code outputs were assembled into the spreadsheet c4per6.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.13-3 compares the density, TDS, and molarity/molality values input to EQ3NR against the output values. The output values are slightly different because they were computed using a full speciation model. These differences (<1%) are not considered significant. It is noted that they could have been further reduced by putting the output values in the EQ3NR input file and re-running the problem.

Table 5.13-3. Test Case #12 (c4per6) EQ3NR Inputs and Outputs for Density, TDS, and Molarity/Molality for ERDA-6 Brine.

	Input	Output	Δ
density, g/L	1204.24	1201.4	-0.236%
TDS, g/L	314.8069	313.25	-0.495%
Molarity/molality	0.8876	0.88818	0.065%

Table 5-13-4 compares the results for the set of general parameter outputs (after the brine has been reacted with the designated minerals). These outputs are the same as those defined for the previous test cases. These results are within the general acceptance criteria, except for the cases of the solution mass and the H_2O mass. This difference occurred because the EQ6 run started with ~1 L of brine instead of a mass scaled to the usual 1000 g H_2O. The brine mass was deliberately rescaled in an attempt to match the FMT inputs. It was not realized until later that FMT increased the initial brine mass scaled to 1000 g H_2O before reacting the brine with the designated minerals. This is actually not problematic, because in both code runs the masses of the minerals were sufficient to saturate the system. The absolute amounts of the added minerals that dissolved and the absolute amounts remaining will be different, but the intensive system descriptors will be the same. It is noted that the ionic strength reported by EQ3/6 is slightly higher than that reported by FMT. NegIon, however, is not used in this test case.

Table 5.13-4. Test Case #12 (c4per6) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1389.720747	1213.7137	-12.665%
H2O mass, g	1003.933039	876.75946	-12.668%
Ionic strength, m	6.799942	6.801	0.016%
density, g/L	1217.20	1217.2	0.000%

TDS, g/L	337.8960687	337.93	0.010%
a_w	0.747508	0.74752	0.002%
x_w	0.816222	0.81621	-0.001%
λ_w	0.9158	0.91585	0.005%
fCO2, bars	3.135E-06	3.13527E-06	0.009%
pH (Pitzer)	8.9444	8.9466	0.0022
pmH	9.5885	9.5906	0.0021
pcH	9.6443	9.6465	0.0022

Table 5.13-5 compares results for solute species molalities. In some instances, the results are within the usual 1% acceptance criterion. In many cases, however, they are not. The situation is very similar to the results initially obtained for Test Case #11. The largest discrepancies are for the very highly charged species: $Th(CO_3)_5^{6-}$ (+18.124%), $Am(CO_3)_4^{5-}$ (+12.263%), $EDTA^{4-}$ (+5.325%), and $NpO_2(CO_3)_3^{5-}$ (+12.850%). Note at the bottom of the table that FMT does not report values for molalities less than 1 × 10^{-24}.

Table 5.13-5. Test Case #12 (c4per6) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Na+	5.96285	5.9660	0.053%
Cl-	5.95971	5.9588	-0.015%
SO4--	0.203306	0.20425	0.464%
Mg++	0.156903	0.15611	-0.505%
K+	0.109306	0.10865	-0.600%
B(OH)4-	0.0397126	0.039616	-0.243%
MgB(OH)4+	0.0156912	0.015496	-1.244%
Br-	0.0123954	0.012321	-0.600%
B(OH)3(aq)	0.0108974	0.010817	-0.738%
Ca++	0.0103272	0.010392	0.627%
Acetate-	0.00792382	0.0079006	-0.293%
MgAcetate+	0.00387705	0.0038293	-1.232%
CaB(OH)4+	0.00166418	0.0016613	-0.173%
MgCitrate-	0.00085521	0.00084913	-0.711%
MgOH+	0.000852959	0.00084896	-0.469%
B3O3(OH)4-	0.000451403	0.00044377	-1.691%
B4O5(OH)4--	0.000418031	0.00041159	-1.541%
MgCO3(aq)	0.000317355	0.00031736	0.002%
MgOxalate(aq)	0.000318043	0.00031460	-1.083%
CaAcetate+	0.000143206	0.00014299	-0.151%
HCO3-	8.98110E-05	9.0305E-05	0.550%
CO3--	5.89021E-05	5.9778E-05	1.487%
CaCitrate-	3.15888E-05	3.1708E-05	0.377%
Citrate---	2.14426E-05	2.1991E-05	2.558%
CaCO3(aq)	1.95794E-05	1.9795E-05	1.101%
OH-	1.28574E-05	1.2919E-05	0.479%
CaOxalate(aq)	1.17475E-05	1.1748E-05	0.004%

MgEDTA--	8.64230E-06	8.5889E-06	-0.618%
Oxalate--	7.25794E-06	7.2815E-06	0.325%
NpO2CO3-	4.63895E-07	4.6639E-07	0.538%
HAcetate(aq)	3.80264E-07	3.7748E-07	-0.732%
CaEDTA--	3.19220E-07	3.2073E-07	0.473%
AmEDTA-	2.11032E-07	2.0823E-07	-1.328%
NpO2+	1.98424E-07	1.9765E-07	-0.390%
NpO2Acetate(aq)	1.82215E-07	1.8102E-07	-0.656%
Am(OH)2+	1.13580E-07	1.1287E-07	-0.625%
NpO2Oxalate-	7.04145E-08	7.0129E-08	-0.405%
Th(OH)4(aq)	5.41385E-08	5.4144E-08	0.010%
CO2(aq)	2.97698E-08	2.9755E-08	-0.050%
Th(OH)3(CO3)-	2.30965E-08	2.3225E-08	0.556%
NpO2OH(aq)	1.18597E-08	1.1865E-08	0.045%
NpO2(CO3)2---	9.84818E-09	1.0240E-08	3.979%
HCitrate--	9.48674E-10	9.5054E-10	0.197%
NpO2Citrate--	7.96219E-10	7.9832E-10	0.264%
AmOH++	8.00670E-10	7.9731E-10	-0.420%
Am(OH)3(aq)	7.75702E-10	7.7613E-10	0.055%
HSO4-	7.04912E-10	7.0130E-10	-0.512%
Am(CO3)2-	3.10966E-10	3.1281E-10	0.593%
H+	2.57955E-10	2.5667E-10	-0.498%
AmCitrate(aq)	2.48252E-10	2.4491E-10	-1.346%
AmCO3+	2.33311E-10	2.3214E-10	-0.502%
AmAcetate++	2.28032E-10	2.2554E-10	-1.093%
NpO2(CO3)3(5-)	7.17950E-11	8.1021E-11	12.850%
Am(CO3)3---	7.17893E-11	7.4632E-11	3.960%
NpO2(OH)2-	3.00182E-11	3.0186E-11	0.559%
EDTA----	1.97741E-11	2.0827E-11	5.325%
AmSO4+	1.77952E-11	1.7508E-11	-1.614%
HOxalate-	1.71087E-11	1.7012E-11	-0.565%
HEDTA---	5.54103E-12	5.6377E-12	1.745%
AmOxalate+	4.99417E-12	4.9094E-12	-1.697%
Am+++	3.27013E-12	3.2885E-12	0.562%
Am(SO4)2-	2.18608E-12	2.1512E-12	-1.596%
Am(CO3)4(5-)	7.92048E-13	8.8918E-13	12.263%
NpO2EDTA---	6.03898E-13	6.1411E-13	1.691%
AmCl++	2.67448E-13	2.6521E-13	-0.837%
H2EDTA--	1.40191E-14	1.3950E-14	-0.493%
AmCl2+	1.03900E-14	1.0234E-14	-1.501%
H2Citrate-	5.51805E-15	5.4783E-15	-0.720%
NpO2HEDTA--	2.94814E-15	2.9312E-15	-0.575%
Th(CO3)5(6-)	1.95558E-17	2.31E-17	18.124%
ThEDTA(aq)	4.67047E-18	4.5809E-18	-1.918%
Th(SO4)3--	9.28901E-19	9.1302E-19	-1.710%
NpO2H2EDTA-	5.88929E-19	5.8027E-19	-1.470%

H2Oxalate(aq)	1.25489E-19	1.2414E-19	-1.075%
ThCitrate+	4.5621E-20	4.4775E-20	-1.854%
Th(SO4)2(aq)	1.76674E-20	1.7297E-20	-2.097%
Th(Acetate)2++	3.1101E-21	3.0553E-21	-1.762%
H3Citrate(aq)	1.36601E-21	1.3487E-21	-1.267%
H3EDTA-	1.2945E-21	1.2761E-21	-1.421%
ThAcetate+++	2.53629E-22	2.5566E-22	0.801%
ThOxalate++	2.70361E-23	2.6628E-23	-1.509%
Th++++	-----	1.8315E-25	-----
H4EDTA(aq)	-----	9.5285E-29	-----

Table 5.13-6 compares results for solute species activity coefficients. These results are largely complementary to the molality results, much as was the case for Test Case #11. The largest discrepancy is for $Th(CO_3)_5^{6-}$ (-12.690%).

Table 5.13-6. Test Case #12 (c4per6) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Na+	0.9651	0.96516	0.006%
Cl-	1.084	1.08393	-0.007%
SO4--	0.019466	0.019360	-0.546%
Mg++	1.894	1.88452	-0.501%
K+	0.4748	0.47490	0.021%
B(OH)4-	0.1000	0.10000	0.000%
MgB(OH)4+	1.887	1.88625	-0.040%
Br-	0.2791	0.27900	-0.037%
B(OH)3(aq)	0.9610	0.96073	-0.028%
Ca++	1.063	1.05730	-0.536%
Acetate-	0.7391	0.73961	0.068%
MgAcetate+	5.825	5.82505	0.001%
CaB(OH)4+	1.171	1.17112	0.010%
MgCitrate-	0.1993	0.19911	-0.094%
MgOH+	0.3556	0.35547	-0.037%
B3O3(OH)4-	0.1189	0.11874	-0.134%
B4O5(OH)4--	0.0039172	0.0038958	-0.546%
MgCO3(aq)	1.000	1.00000	0.000%
MgOxalate(aq)	1.253	1.25256	-0.035%
CaAcetate+	5.825	5.82505	0.001%
HCO3-	0.3480	0.34786	-0.041%
CO3–	0.021375	0.021281	-0.438%
CaCitrate-	0.1993	0.19911	-0.094%
Citrate---	0.00013413	0.00013107	-2.282%
CaCO3(aq)	1.000	1.00000	0.000%
OH-	0.5154	0.51558	0.036%
CaOxalate(aq)	1.253	1.25256	-0.035%

MgEDTA--	0.2444	0.24361	-0.322%
Oxalate--	0.029739	0.029621	-0.397%
NpO2CO3-	0.1075	0.10757	0.067%
HAcetate(aq)	1.000	1.00000	0.000%
CaEDTA--	0.2444	0.24361	-0.322%
AmEDTA-	0.025551	0.025521	-0.117%
NpO2+	1.920	1.91955	-0.023%
NpO2Acetate(aq)	0.2895	0.28953	0.012%
Am(OH)2+	0.00084185	0.00084275	0.107%
NpO2Oxalate-	0.020296	0.02028	-0.094%
Th(OH)4(aq)	1.000	1.00000	0.000%
CO2(aq)	3.472	3.47376	0.051%
Th(OH)3(CO3)-	0.2791	0.27900	-0.037%
NpO2OH(aq)	0.1039	0.10390	-0.004%
NpO2(CO3)2---	0.00017067	0.0001668	-2.267%
HCitrate--	0.009131	0.0090887	-0.464%
NpO2Citrate--	0.0043213	0.0043013	-0.463%
AmOH++	0.024829	0.024683	-0.588%
Am(OH)3(aq)	0.0081255	0.008121	-0.058%
HSO4-	0.6075	0.60702	-0.080%
Am(CO3)2-	0.055633	0.055590	-0.077%
H+	4.406	4.40656	0.013%
AmCitrate(aq)	0.0079127	0.0079177	0.063%
AmCO3+	0.7390	0.73892	-0.010%
AmAcetate++	0.015426	0.015329	-0.632%
NpO2(CO3)3(5-)	2.27400E-09	2.06871E-09	-9.028%
Am(CO3)3---	0.000048102	0.000046989	-2.313%
NpO2(OH)2-	0.015972	0.015973	0.009%
EDTA----	2.68920E-05	2.55447E-05	-5.010%
AmSO4+	0.4283	0.42835	0.012%
HOxalate-	0.2607	0.26068	-0.009%
HEDTA---	0.0040596	0.0039719	-2.160%
AmOxalate+	0.067342	0.067437	0.141%
Am+++	0.3323	0.32546	-2.058%
Am(SO4)2-	0.03919	0.039156	-0.086%
Am(CO3)4(5-)	3.43480E-11	3.13834E-11	-8.631%
NpO2EDTA---	0.1150	0.11272	-1.983%
AmCl++	45.55	45.21682	-0.731%
H2EDTA--	0.01381	0.013750	-0.435%
AmCl2+	794.6	793.77972	-0.103%
H2Citrate-	0.1234	0.12331	-0.073%
NpO2HEDTA--	0.2749	0.27403	-0.316%
Th(CO3)5(6-)	1.92370E-11	1.67958E-11	-12.690%
ThEDTA(aq)	3.759	3.75837	-0.017%
Th(SO4)3--	0.016346	0.016255	-0.554%
NpO2H2EDTA-	0.3256	0.32591	0.096%

H2Oxalate(aq)	1.000	1.00000	0.000%
ThCitrate+	9.928	9.93802	0.101%
Th(SO4)2(aq)	31.71	31.69567	-0.045%
Th(Acetate)2++	175.1	173.94021	-0.662%
H3Citrate(aq)	1.000	1.00000	0.000%
H3EDTA-	0.2079	0.20787	-0.013%
ThAcetate+++	48.63	47.17371	-2.995%
ThOxalate++	177.9	176.92940	-0.546%
Th++++	0.4814	0.49000	1.787%
H4EDTA(aq)	1.000	1.00000	0.000%

Table 5.13-7 compares results for saturation indices (log Q/K) for the relevant minerals. In a number of instances, the differences exceed both the usual acceptance criterion (0.004) and also what can be explained by the limited precision with which FMT reports saturation indices. This table does provides confirmation that the brine became saturated with respect to each of the solids with which it was reacting, despite the difference in brine masses in the two code runs. As expected, magnesite ($MgCO_3$) precipitates and is thus saturated. Whewellite ($CaC_2O_4{\bullet}H_2O$, calcium oxalate) does likewise. So does glauberite ($Na_2Ca(SO_4)_2$). Although FMT reports a very small negative saturation index for glauberite, this appears to be a minor numerical glitch, as the mineral was precipitated in the FMT run (data not shown here).

Table 5.13-7. Test Case #12 (c4per6) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	2.80	2.8009	0.00090
Magnesite	1.41	1.40695	-0.00305
Calcite	0.547	0.55155	0.00455
Aragonite	0.360	0.36475	0.00475
Am(OH)3(s)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Anhydrite	0.00000	0.00000	0.00000
Whewellite	0.00000	0.00000	0.00000
Brucite	0.00000	0.00000	0.00000
Glauberite	-4.13E-08	0.00000	0.00000
Halite	0.00000	0.00000	0.00000
Hydromagnesite5424	0.00000	0.00000	0.00000
Gypsum	-0.0343	-0.03435	-0.00005
Mg2Cl(OH)3.4H2O	-0.325	-0.32725	-0.00225
AmOHCO3(c)	-0.343	-0.34325	-0.00025
Hydromagnesite4323	-0.344	-0.34348	0.00052
Thenardite	-0.595	-0.59490	0.00010
Labile_Salt	-0.707	-0.70735	-0.00035
Mirabilite	-0.919	-0.91837	0.00063
Sylvite	-1.37	-1.37717	-0.00717

Borax	-1.61	-1.61559	-0.00559
Nesquehonite	-1.64	-1.63898	0.00102
Teepleite(20C)	-1.67	-1.67264	-0.00264
Na3NpO2(CO3)2	-1.76	-1.75098	0.00902
2[NaNpO2CO3.7/2H2O]	-1.82	-1.81689	0.00311
Epsomite	-1.93	-1.93783	-0.00783
B(OH)3	-1.95	-1.95289	-0.00289
Bloedite	-1.97	-1.97530	-0.00530
Syngenite	-2.01	-2.01782	-0.00782
Hexahydrite	-2.05	-2.05746	-0.00746
NpO2OH(aged)	-2.12	-2.11713	0.00287
Na_Metaborate	-2.22	-2.22379	-0.00379
NaAm(CO3)2.6H2O(c)	-2.37	-2.36801	0.00199
Na2Oxalate	-2.74	-2.74052	-0.00052
NpO2OH(am)	-2.82	-2.81723	0.00277
Kieserite	-2.93	-2.93797	-0.00797
Polyhalite	-3.13	-3.14489	-0.01489
Arcanite	-3.20	-3.20144	-0.00144
Pirssonite	-3.25	-3.23936	0.01064
Nahcolite	-3.34	-3.33958	0.00042
Gaylussite	-3.45	-3.44069	0.00931
Kainite	-3.59	-3.59810	-0.00810
Aphthitalite/Glaserite	-4.10	-4.10512	-0.00512
Bischofite	-4.12	-4.12476	-0.00476
Picromerite/Schoenite	-4.33	-4.34260	-0.01260
Leonite	-4.43	-4.43855	-0.00855
Carnallite	-4.47	-4.47703	-0.00703
Na2CO3.7H2O	-4.80	-4.79949	0.00051
Natron	-4.82	-4.81402	0.00598
Thermonatrite	-4.99	-4.98323	0.00677
Burkeite	-5.37	-5.36765	0.00235
Na_Pentaborate	-5.84	-5.85216	-0.01216
Kalicinite	-6.07	-6.07165	-0.00165
K3NpO2(CO3)2	-6.14	-6.14340	-0.00340
K-Tetraborate(30C)	-6.38	-6.39497	-0.01497
K-Pentaborate(30C)	-6.53	-6.54986	-0.01986
CaCl2.4H2O	-6.56	-6.56151	-0.00151
KNaCO3.6H2O	-7.07	-7.06498	0.00502
Portlandite	-7.13	-7.12230	0.00770
Trona	-7.33	-7.32588	0.00412

Table 5.13-8 compares results for actinide species distributions, considering only those species needed to comprise 99% of the mass balance of any actinide. These data were key results in the Brush (2005) calculations. The differences here are small (<4%), though some instances exceed the usual 1% criterion for “linear” quantities.

Table 5.13-8. Test Case #12 (c4per6) Actinide Species Distributions, EQ3/6 vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	3.27310E-07	100.00%	3.2380E-07	100.00%	-1.07%
AmEDTA-	2.11032E-07	64.47%	2.0823E-07	64.31%	-1.33%
Am(OH)2+	1.13580E-07	34.70%	1.1287E-07	34.86%	-0.63%
Subtotal	3.24612E-07	99.18%	3.2110E-07	99.17%	-1.08%
Total NpO2+	9.37555E-07	100.00%	9.3821E-07	100.00%	0.07%
NpO2CO3-	4.63895E-07	49.48%	4.6639E-07	49.71%	0.54%
NpO2+	1.98424E-07	21.16%	1.9765E-07	21.07%	-0.39%
NpO2Acetate(aq)	1.82215E-07	19.44%	1.8102E-07	19.29%	-0.66%
NpO2Oxalate-	7.04145E-08		7.0129E-08	7.47%	-0.41%
NpO2OH(aq)	1.18597E-08	1.26%	1.1865E-08	1.26%	0.04%
NpO2(CO3)2---	9.84818E-09	1.05%	1.0240E-08	1.09%	3.98%
Subtotal	9.36656E-07	99.90%	9.3729E-07	99.90%	0.07%
Total Th++++	7.72350E-08	100.00%	7.7368E-08	100.00%	0.17%
Th(OH)4(aq)	5.41385E-08	70.10%	5.4144E-08	69.98%	0.01%
Th(OH)3(CO3)-	2.30965E-08	29.90%	2.3225E-08	30.02%	0.56%
Subtotal	7.72350E-08	100.00%	7.7369E-08	100.00%	0.17%

The results of the two codes are in less than very good agreement. These results are very similar to those first obtained for Test Case #11. It was demonstrated that the differences in that case were due to a combination of "front end" inconsistencies in the code inputs and the use of different approximations for the J(x) function. The differences obtained for the present test case are almost surely due to the same factors. Therefore, the results obtained here will be considered acceptable. EQ3/6 was re-run using the same J(x) approximation as FMT. Results are contained in the spreadsheet c4per6_P75.xls. None of those results will be shown here, but in general the results are improved as expected. They are, relatively speaking, better than those obtained for Test Case #11 (with the same J(x) approximation as FMT but not with the modified EQ3NR inputs).

5.14 Test Case #13 – Solubility of Am(III), Th(IV), and Np(V) in WIPP GWB brine, assuming that the inventory of EDTA increases by a factor of 10 in comparison with the CRA-2004 PABC inventory

5.14.1 Test Overview

This test case is to compare solubility values of Am(III), Th(IV) and Np(V) in GWB predicted by FMT with those calculated by EQ3/6, assuming that the inventory of EDTA increases by a factor of 10 in comparison with the CRA-2004 PABC inventory. This problem is taken from Brush et al. (2008). This is the same problem as Test Case #11, except that the EDTA is increased tenfold. The GWB brine with 10× EDTA is first created. Then it is reacted with 1.0 mole of $Am(OH)_3(s)$, $ThO_2(am)$, $KNpO_2CO_3$, and hydromagnesite(5424) ($Mg_5(CO_3)4(OH)_2.4H_2O$) plus 10.0 moles each of anhydrite ($CaSO_4$), brucite ($Mg(OH)_2$), and halite (NaCl). This is a “type 3” problem in that the lack of a proper front-end in FMT may affect the results, including the calculated pH.

Table 5.14-1 gives the FMT inputs for the modified GWB brine. The inputs here are consistent with 1 L of solution (Brush et al., 2008, Table 2). The four organic ligands (oxalate, acetate, EDTA, and citrate) are treated as pseudo-elements by FMT (whereas they are treated as active auxiliary basis species by EQ3/6).

Table 5.14-1. Test Case #13 (c4pgwbx) FMT Inputs for GWB Brine with 10x EDTA.

Element	Moles
H	99.3736
O	50.6193
Na	3.48
K	0.458
Mg	1.00
Ca	0.014
Cl	5.51
S	0.175
B	0.155
Br	0.026
Oxalate	0.0455
Acetate	0.0106
EDTA	8.14E-05
Citrate	8.06E-04

Table 5.14-2 gives the corresponding EQ3/6 inputs for the brine. Because EQ3/6 works directly in terms of molalities, the molarity inputs must be converted to molalities before the actual speciation calculations can begin. This requires inputs for density and TDS, which are needed to compute the molarity/molality factor or molarity/molality factor. The values shown in Table 5.14-2 were calculated from the molarity data using the WIPP density model (see worksheet c4pgwbx of spreadsheet Conc_density_calcs_EV2008.xls). The molarity/molality factor was used in EQ3NR to rescale the brine mass for consistency with a 1 L volume, prior to reacting it with minerals in the subsequent EQ6 run.

Table 5.14-2. Test Case #13 (c4pgwbx) EQ3/6 Inputs for GWB Brine with 10x EDTA.

Basis species	Molarity
Na+	3.48
K+	0.458
Mg++	1.00
Ca++	0.014
Cl-	5.51
SO4--	0.175
HCO3-	1.0E-18
B(OH)4-	0.155
Br-	0.026
Oxalate--	0.0455
Acetate-	0.0106
EDTA----	8.14E-05
Citrate---	8.06E-04
Am+++	1.0E-18
Th++++	1.0E-18
NpO2+	1.0E-18
density, g/L	1227.53
TDS, g/L	354.0374
Molarity/molality	0.8735

It is once more noted that the density, TDS, and molarity/molality values obtained from the spreadsheet calculation take the compositional data at face value. There is no speciation calculation in this calculation. Since EQ3NR performs a full speciation calculation, the WIPP density model embedded in FMT will generally produce slightly different calculated results. This will be addressed below in the Evaluation section.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	c4pgwbx.6i
EQ6 output files:	c4pgwbx.6o, c4pgwbx.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_edta_gwb_hmg_orgs_x_007.in; fmt_edta_gwb_hmg_orgs_x_007.inguess
FMT output files:	fmt_edta_gwb_hmg_orgs_x_007.out; fmt_edta_gwb_hmg_orgs_x_007.for088

5.14.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.14.3 Evaluation

Code outputs were assembled into the spreadsheet c4pgwbx.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.14-3 compares the density, TDS, and molality/molarity values input to EQ3NR against the output values. The output values are slightly different because they were computed using a full speciation model. These differences (<1%) are not considered significant.

Table 5.14-3. Test Case #13 (c4pgwbx) EQ3NR Inputs and Outputs for Density, TDS, and Molarity/Molality for GWB Brine.

	Input	Output	Δ
density, g/L	1227.53	1226.1	-0.116%
TDS, g/L	354.0374	351.76	-0.643%
Molarity/molality	0.8735	0.87431	0.093%

Table 5-14-4 compares the results for the set of general parameter outputs (after the brine has been reacted with the designated minerals). These results are within the general acceptance criteria, except for the cases of the solution mass and the H_2O mass. This difference occurred because the EQ6 run started with 1 L of brine instead of a mass scaled to the usual 1000 g H_2O. The significance of this has been addressed previously in the case of the two preceding test cases.

Table 5.14-4. Test Case #13 (c4pgwbx) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1293.489622	1127.0161	-12.870%
H2O mass, g	914.2971982	795.81047	-12.959%
Ionic strength, m	7.664067	7.6892	0.328%
density, g/L	1232.11	1232.8	0.056%
TDS, g/L	361.2000796	362.3	0.305%
a_w	0.732295	0.73194	-0.048%
x_w	0.812689	0.81243	-0.032%
λ_w	0.9011	0.90092	-0.020%
fCO2, bars	3.13500E-06	3.13527E-06	0.009%
pH (Pitzer)	8.6887	8.6889	0.0002
pmH	9.3347	9.3353	0.0006
pcH	9.3947	9.3955	0.0008

Table 5.14-5 compares results for solute species molalities. In some instances, the results are within the usual 1% acceptance criterion. In many cases, however, they are not. The largest discrepancies include instances for the very highly charged species: $Th(CO_3)_5^{6-}$ (+7.777%), $Am(CO_3)_4^{5-}$ (+6.008%), EDTA4- (+4.968%), and $NpO_2(CO_3)_3^{5-}$ (+4.398%). However, the discrepancies are comparable for the polyborate species: $B_4O_5(OH)_4^{2-}$ (+7.179%) and $B_3O_3(OH)_4^{-}$ (+5.349%). This pattern is much like what was seen in Test Case #11. The largest discrepancies, however, are smaller. The likely causes of the discrepancies are the same. Note at the bottom of the table that FMT does not report values for molalities less than 1×10^{-24}.

Table 5.14-5. Test Case #13 (c4pgwbx) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.17591	6.1759	0.000%
Na+	4.99106	4.9983	0.145%
Mg++	0.577088	0.57394	-0.545%
K+	0.562547	0.57617	2.422%
SO4--	0.262347	0.26843	2.319%
MgB(OH)4+	0.075393	0.076185	1.050%
B(OH)4-	0.054912	0.056044	2.061%
Br-	0.031935	0.032708	2.421%
B(OH)3(aq)	0.0254065	0.025900	1.942%
Ca++	0.00850026	0.0084312	-0.812%
Acetate-	0.00654107	0.0067478	3.160%
MgAcetate+	0.00642840	0.0065363	1.678%
B4O5(OH)4--	0.00575354	0.0061666	7.179%
B3O3(OH)4-	0.00331822	0.0034954	5.340%
MgOH+	0.00182012	0.0018172	-0.160%
CaB(OH)4+	0.00170130	0.0017111	0.576%
MgOxalate(aq)	0.00153983	0.0015445	0.303%
MgCitrate-	0.000962638	0.00098575	2.401%
MgCO3(aq)	0.000323948	0.00032342	-0.163%
MgEDTA--	9.72184E-05	9.72184E-05	2.402%
CaAcetate+	4.96545E-05	4.96545E-05	1.205%
HCO3-	4.84101E-05	4.84101E-05	0.820%
CO3--	2.48281E-05	2.48281E-05	0.733%
Citrate---	1.99086E-05	1.99086E-05	3.629%
Oxalate--	1.38726E-05	1.38726E-05	0.695%
CaOxalate(aq)	0.000011894	1.18940E-05	-0.168%
OH-	8.12129E-06	8.1346E-06	0.164%
CaCitrate-	7.43565E-06	7.5786E-06	1.922%
CaCO3(aq)	4.1795E-06	4.1533E-06	-0.627%
AmEDTA-	2.01056E-06	2.0815E-06	3.528%
CaEDTA--	7.50939E-07	7.6539E-07	1.924%
HAcetate(aq)	4.26556E-07	4.4050E-07	3.269%
Am(OH)2+	2.37398E-07	2.3488E-07	-1.061%
NpO2+	1.45822E-07	1.4118E-07	-3.183%

NpO2CO3-	1.19965E-07	1.1679E-07	-2.647%
NpO2Acetate(aq)	8.43943E-08	8.4632E-08	0.282%
Th(OH)4(aq)	5.19573E-08	5.2134E-08	0.340%
NpO2Oxalate-	5.03473E-08	4.9464E-08	-1.754%
CO2(aq)	2.93476E-08	2.9265E-08	-0.281%
Th(OH)3(CO3)-	1.27976E-08	1.2903E-08	0.824%
NpO2OH(aq)	4.97889E-09	4.8420E-09	-2.749%
AmOH++	2.82989E-09	2.8189E-09	-0.388%
HSO4-	1.33867E-09	1.3616E-09	1.713%
AmAcetate++	1.2879E0-09	1.3392E-09	3.983%
NpO2(CO3)2---	1.33683E-09	1.3286E-09	-0.616%
EDTA----	9.61339E-10	1.0091E-09	4.968%
Am(OH)3(aq)	6.87341E-10	6.9301E-10	0.825%
HCitrate--	6.54952E-10	6.7154E-10	2.533%
AmCitrate(aq)	5.10923E-10	5.1571E-10	0.937%
H+	4.62739E-10	4.6034E-10	-0.518%
AmCO3+	4.32491E-10	4.2835E-10	-0.957%
NpO2Citrate--	1.71497E-10	1.6987E-10	-0.949%
Am(CO3)2-	1.53194E-10	1.5418E-10	0.644%
AmSO4+	1.43336E-10	1.4252E-10	-0.569%
HEDTA---	8.88413E-11	9.2577E-11	4.205%
HOxalate-	4.08072E-11	4.1039E-11	0.568%
Am(CO3)3---	3.82164E-11	3.9250E-11	2.705%
AmOxalate+	2.91973E-11	2.8483E-11	-2.446%
Am(SO4)2-	2.21882E-11	2.2597E-11	1.842%
NpO2(CO3)3(5-)	1.47762E-11	1.5426E-11	4.398%
Am+++	1.26416E-11	1.2299E-11	-2.710%
Am(CO3)4(5-)	1.10077E-11	1.1669E-11	6.008%
NpO2(OH)2-	7.28355E-12	7.1278E-12	-2.138%
NpO2EDTA---	5.07918E-12	5.0745E-12	-0.092%
AmCl++	2.11547E-12	2.1071E-12	-0.396%
H2EDTA--	1.10647E-13	1.1449E-13	3.473%
AmCl2+	1.09760E-13	1.0792E-13	-1.676%
NpO2HEDTA--	9.81639E-15	9.7337E-15	-0.842%
H2Citrate-	4.80735E-15	4.9099E-15	2.133%
Th(CO3)5(6-)	4.56666E-16	4.9218E-16	7.777%
ThEDTA(aq)	8.65226E-17	8.8554E-17	2.348%
Th(SO4)3--	1.83081E-17	1.8438E-17	0.710%
NpO2H2EDTA-	1.50712E-18	1.4739E-18	-2.204%
H2Oxalate(aq)	5.87871E-19	5.9168E-19	0.648%
Th(SO4)2(aq)	3.42030E-19	3.4643E-19	1.286%
ThCitrate+	6.39119E-20	6.2525E-20	-2.170%
H3EDTA-	1.22915E-20	1.2632E-20	2.770%
Th(Acetate)2++	8.70218E-21	9.1909E-21	5.616%
H3Citrate(aq)	2.21761E-21	2.2497E-21	1.447%
ThAcetate+++	1.10993E-21	1.1723E-21	5.619%

ThOxalate++	1.55327E-22	1.5115E-22	-2.689%
Th++++	-----	1.2685E-24	-----
H4EDTA(aq)	-----	1.8612E-27	-----

Table 5.14-6 compares results for solute species activity coefficients. These results are largely complementary to the molality results, much as was the case for Test Case #11. The largest discrepancy is for $Th(CO_3)_5^{6-}$ (-15.212%).

Table 5.14-6. Test Case #13 (c4pgwbx) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.305	1.30737	0.182%
Na+	0.9246	0.92385	-0.081%
Mg++	1.742	1.73141	-0.608%
K+	0.4298	0.42924	-0.130%
SO4--	0.021331	0.021218	-0.531%
MgB(OH)4+	1.873	1.87111	-0.101%
B(OH)4-	0.102	0.10205	0.046%
Br-	0.2683	0.26798	-0.120%
B(OH)3(aq)	1.069	1.06782	-0.110%
Ca++	0.9133	0.90552	-0.851%
Acetate-	0.5575	0.55719	-0.056%
MgAcetate+	7.397	7.45762	0.819%
B4O5(OH)4--	0.0042178	0.0042005	-0.410%
B3O3(OH)4-	0.1631	0.16315	0.034%
MgOH+	0.3065	0.30507	-0.466%
CaB(OH)4+	1.143	1.14156	-0.126%
MgOxalate(aq)	1.263	1.26299	-0.001%
MgCitrate-	0.1662	0.16482	-0.833%
MgCO3(aq)	1.000	1.00000	0.000%
MgEDTA--	0.1301	0.12948	-0.477%
CaAcetate+	7.397	7.45762	0.819%
HCO3-	0.3511	0.35035	-0.214%
CO3--	0.015307	0.015234	-0.480%
Citrate---	0.00004011	0.000038949	-2.894%
Oxalate–	0.022458	0.022449	-0.039%
CaOxalate(aq)	1.263	1.26299	-0.001%
OH-	0.4437	0.44381	0.025%
CaCitrate-	0.1662	0.16482	-0.833%
CaCO3(aq)	1.000	1.00000	0.000%
AmEDTA-	0.029536	0.029404	-0.448%
CaEDTA--	0.1301	0.12948	-0.477%
HAcetate(aq)	1.000	1.00000	0.000%
Am(OH)2+	0.00074068	0.00074319	0.339%
NpO2+	1.858	1.85524	-0.149%

NpO2CO3-	0.089251	0.089248	-0.003%
NpO2Acetate(aq)	0.2768	0.27669	-0.038%
Th(OH)4(aq)	1.000	1.00000	0.000%
NpO2Oxalate-	0.029137	0.029235	0.336%
CO2(aq)	3.522	3.53102	0.256%
Th(OH)3(CO3)-	0.2683	0.26798	-0.120%
NpO2OH(aq)	0.09567	0.095631	-0.040%
AmOH++	0.023756	0.023594	-0.682%
HSO4-	0.8150	0.81527	0.033%
AmAcetate++	0.010576	0.010371	-1.943%
NpO2(CO3)2---	0.00008146	0.000079708	-2.151%
EDTA----	9.7959E-07	9.1918E-07	-6.167%
Am(OH)3(aq)	0.0091701	0.0091390	-0.339%
HCitrate--	0.0066156	0.0065645	-0.773%
AmCitrate(aq)	0.0066387	0.0066313	-0.111%
H+	4.425	4.42996	0.112%
AmCO3+	0.7483	0.74955	0.167%
NpO2Citrate--	0.0039614	0.003955	-0.149%
Am(CO3)2-	0.063987	0.063915	-0.113%
AmSO4+	0.4676	0.46957	0.421%
HEDTA---	0.0008078	0.00078379	-2.972%
HOxalate-	0.2842	0.28536	0.410%
Am(CO3)3---	1.5454E-05	1.4969E-05	-3.137%
AmOxalate+	0.1034	0.10566	2.183%
Am(SO4)2-	0.048013	0.048018	0.009%
NpO2(CO3)3(5-)	2.1608E-10	1.9751E-10	-8.592%
Am+++	0.5345	0.54075	1.170%
Am(CO3)4(5-)	1.2759E-13	1.1264E-13	-11.716%
NpO2(OH)2-	0.013842	0.013817	-0.184%
NpO2EDTA---	0.017226	0.016792	-2.520%
AmCl++	44.66	44.08593	-1.285%
H2EDTA--	0.010057	0.010000	-0.567%
AmCl2+	727.5	724.43596	-0.421%
NpO2HEDTA--	0.1873	0.18767	0.199%
H2Citrate-	0.1276	0.12741	-0.150%
Th(CO3)5(6-)	2.2655E-14	1.9209E-14	-15.212%
ThEDTA(aq)	3.944	3.94548	0.038%
Th(SO4)3--	0.025737	0.026134	1.541%
NpO2H2EDTA-	0.5200	0.53101	2.117%
H2Oxalate(aq)	1.000	1.00000	0.000%
Th(SO4)2(aq)	35.95	35.97493	0.069%
ThCitrate+	21.60	22.24334	2.978%
H3EDTA-	0.2267	0.22735	0.288%
Th(Acetate)2++	266.3	266.62447	0.122%
H3Citrate(aq)	1.000	1.00000	0.000%
ThAcetate+++	75.94	73.63766	-3.032%

ThOxalate++	490.7	503.26879	2.561%
Th++++	0.8141	0.77822	-4.408%
H4EDTA(aq)	1.000	1.00000	0.000%

Table 5.14-7 compares results for saturation indices (log Q/K) for the relevant minerals. In a number of instances, the differences exceed both the usual acceptance criterion (0.004) and also what can be explained by the limited precision with which FMT reports saturation indices. This table provides confirmation that the brine became saturated with respect to each of the solids with which it was reacting, despite the difference in brine masses in the two code runs. As expected, magnesite ($MgCO_3$) and whewellite ($CaC_2O_4{\bullet}H_2O$, calcium oxalate) precipitate spontaneously and are thus saturated.

Table 5.14-7. Test Case #13 (c4pgwbx) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	2.13	2.12757	-0.00243
Magnesite	1.42	1.4161	-0.00390
Am(OH)3(s)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Anhydrite	0.00000	0.00000	0.00000
Whewellite	0.00000	0.00000	0.00000
Brucite	0.00000	0.00000	0.00000
Halite	0.00000	0.00000	0.00000
Mg2Cl(OH)3.4H2O	0.00000	0.00000	0.00000
Hydromagnesite5424	0.00000	0.00000	0.00000
Glauberite	-0.0413	-0.03608	0.00522
Gypsum	-0.0522	-0.05265	-0.00045
Calcite	-0.124	-0.13093	-0.00693
Aragonite	-0.311	-0.31773	-0.00673
AmOHCO3(c)	-0.334	-0.33410	-0.00010
Hydromagnesite4323	-0.344	-0.34347	0.00053
Syngenite	-0.534	-0.50873	0.02527
Sylvite	-0.610	-0.60002	0.00998
Thenardite	-0.636	-0.63098	0.00502
Borax	-0.699	-0.67635	0.02265
Labile_Salt	-0.808	-0.79781	0.01019
Polyhalite	-0.986	-0.95333	0.03267
Mirabilite	-1.05	-1.04593	0.00407
Epsomite	-1.32	-1.31025	0.00975
Bloedite	-1.37	-1.35635	0.01365
Hexahydrite	-1.43	-1.42073	0.00927
B(OH)3	-1.54	-1.52929	0.01071
Teepleite(20C)	-1.62	-1.61289	0.00711
Nesquehonite	-1.66	-1.65728	0.00272
Arcanite	-1.71	-1.68321	0.02679

Aphthitalite/Glaserite	-1.89	-1.84580	0.04420
Kainite	-2.17	-2.15677	0.01323
Na_Metaborate	-2.19	-2.18235	0.00765
Picromerite/Schoenite	-2.22	-2.18764	0.03236
Kieserite	-2.26	-2.25550	0.00450
Leonite	-2.30	-2.26529	0.03471
NpO2OH(aged)	-2.53	-2.53958	-0.00958
Na2Oxalate	-2.77	-2.76745	0.00255
NaAm(CO3)2.6H2O(c)	-2.77	-2.76845	0.00155
Carnallite	-3.04	-3.02706	0.01294
NpO2OH(am)	-3.23	-3.23968	-0.00968
Na3NpO2(CO3)2	-3.23	-3.24669	-0.01669
2[NaNpO2CO3.7/2H2O]	-3.41	-3.43525	-0.02525
Bischofite	-3.45	-3.45195	-0.00195
Nahcolite	-3.70	-3.70343	-0.00343
K-Tetraborate(30C)	-3.89	-3.84653	0.04347
K-Pentaborate(30C)	-4.02	-3.98198	0.03802
Na_Pentaborate	-4.10	-4.07059	0.02941
Pirssonite	-4.65	-4.65868	-0.00868
Gaylussite	-4.88	-4.88746	-0.00746
K3NpO2(CO3)2	-5.33	-5.30763	0.02237
Na2CO3.7H2O	-5.58	-5.58208	-0.00208
Natron	-5.62	-5.62406	-0.00406
Kalicinite	-5.67	-5.65834	0.01166
Thermonatrite	-5.71	-5.71093	-0.00093
Burkeite	-6.17	-6.15836	0.01164
CaCl2.4H2O	-6.56	-6.56202	-0.00202
KNaCO3.6H2O	-7.07	-7.06127	0.00873

Table 5.14-8 compares results for actinide species distributions, considering only those species needed to comprise 99% of the mass balance of any actinide. These data were key results in the Brush et al. (2008) calculations. The differences here are small (<3%), though some instances exceed the usual 1% criterion for "linear" quantities.

The results of the two codes are in less than very good agreement, being very similar to those first obtained for Test Case #11. It was demonstrated that the differences in that case were due to a combination of "front end" inconsistencies in the code inputs and the use of different approximations for the J(x) function. EQ3/6 was re-run using the same J(x) approximation as FMT uses. The results were analyzed in the spreadsheet c4pgwbx_P75. Although the results were improved, they will not be shown here. EQ3/6 was also re-run by going one step farther to eliminate the front end problem by redefining the EQ3/6 input for the starting solution to be consistent with results from the FMT .INGUESS file. This was done in the same manner as for Test Case #11. For details, see worksheet gwbx of spreadsheet c4pgwbx_P75_MFix. That spreadsheet also contains the comparison of the results obtained from the two codes.

Table 5.14-8. Test Case #13 (c4pgwbx) Actinide Species Distributions, EQ3/6 vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	2.25412E-06	100.00%	2.2995E-06	100.00%	2.01%
AmEDTA-	2.01056E-06	89.19%	2.0566E-06	89.44%	2.29%
Am(OH)2+	2.37398E-07	10.53%	2.3662E-07	10.29%	-0.33%
Subtotal	2.24796E-06	99.73%	2.2932E-06	99.73%	2.01%
Total NpO2+	4.07043E-07	100.00%	4.0155E-07	100.00%	-1.35%
NpO2+	1.45822E-07	35.82%	1.4291E-07	35.59%	-2.00%
NpO2CO3-	1.19965E-07	29.47%	1.1743E-07	29.24%	-2.11%
NpO2Acetate(aq)	8.43943E-08	20.73%	8.4840E-08	21.13%	0.53%
NpO2Oxalate-	5.03473E-08	12.37%	4.9947E-08	12.44%	-0.80%
NpO2OH(aq)	4.97889E-09	1.22%	4.8736E-09	1.21%	-2.11%
Subtotal	4.05507E-07	99.62%	4.0000E-07	99.62%	-1.36%
Total Th++++	6.4755E-08	100.00%	6.4719E-08	100.00%	-0.06%
Th(OH)4(aq)	5.19573E-08	80.24%	5.1910E-08	80.21%	-0.09%
Th(OH)3(CO3)-	1.27976E-08	19.76%	1.2809E-08	19.79%	0.09%
Subtotal	6.47549E-08	100.00%	6.5037E-08	100.49%	0.44%

Table 5.14-9 shows the results for solute species molalities. Now all differences are within the usual 1% acceptance criterion. The largest discrepancy is now +0.294% for $Th(CO_3)_5^{6-}$. These results are very significantly improved.

Table 5.14-9. Test Case #13 Two-Off (c4pgwbx_P75_Mfix) Calculated Solute Species Molalities, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.17591	6.1759	0.000%
Na+	4.99106	4.9907	-0.007%
Mg++	0.577088	0.57728	0.033%
K+	0.562547	0.56253	-0.003%
SO4--	0.262347	0.26234	-0.003%
MgB(OH)4+	0.0753930	0.075405	0.016%
B(OH)4-	0.0549120	0.054903	-0.016%
Br-	0.0319350	0.031934	-0.003%
B(OH)3(aq)	0.0254065	0.025407	0.002%
Ca++	0.00850026	0.0084995	-0.009%
Acetate-	0.00654107	0.0065403	-0.012%
MgAcetate+	0.00642840	0.0064288	0.006%
B4O5(OH)4--	0.00575354	0.0057516	-0.034%

B3O3(OH)4-	0.00331822	0.0033176	-0.019%
MgOH+	0.00182012	0.0018204	0.015%
CaB(OH)4+	0.00170130	0.0017008	-0.029%
MgOxalate(aq)	0.00153983	0.0015405	0.044%
MgCitrate-	0.000962638	0.00096261	-0.003%
MgCO3(aq)	0.000323948	0.00032396	0.004%
MgEDTA--	9.72184E-05	9.7216E-05	-0.002%
CaAcetate+	4.96545E-05	4.9637E-05	-0.035%
HCO3-	4.84101E-05	4.8405E-05	-0.011%
CO3--	2.48281E-05	2.4829E-05	0.004%
Citrate---	1.99086E-05	1.9913E-05	0.022%
Oxalate--	1.38726E-05	1.3879E-05	0.046%
CaOxalate(aq)	0.000011894	1.1894E-05	0.000%
OH-	8.12129E-06	8.1199E-06	-0.017%
CaCitrate-	7.43565E-06	7.4323E-06	-0.045%
CaCO3(aq)	4.17950E-06	4.1779E-06	-0.038%
AmEDTA-	2.01056E-06	2.0101E-06	-0.023%
CaEDTA--	7.50939E-07	7.5060E-07	-0.045%
HAcetate(aq)	4.26556E-07	4.2649E-07	-0.015%
Am(OH)2+	2.37398E-07	2.3743E-07	0.013%
NpO2+	1.45822E-07	1.4587E-07	0.033%
NpO2CO3-	1.19965E-07	1.1997E-07	0.004%
NpO2Acetate(aq)	8.43943E-08	8.4402E-08	0.009%
Th(OH)4(aq)	5.19573E-08	5.1960E-08	0.005%
NpO2Oxalate-	5.03473E-08	5.0364E-08	0.033%
CO2(aq)	2.93476E-08	2.9348E-08	0.001%
Th(OH)3(CO3)-	1.27976E-08	1.2798E-08	0.003%
NpO2OH(aq)	4.97889E-09	4.9793E-09	0.008%
AmOH++	2.82989E-09	2.8311E-09	0.043%
HSO4-	1.33867E-09	1.3386E-09	-0.005%
AmAcetate++	1.33683E-09	1.3371E-09	0.020%
NpO2(CO3)2---	1.28803E-09	1.2883E-09	0.000%
EDTA----	9.61339E-10	9.6227E-10	0.097%
Am(OH)3(aq)	6.87341E-10	6.8716E-10	-0.026%
HCitrate--	6.54952E-10	6.5493E-10	-0.003%
AmCitrate(aq)	5.10923E-10	5.1106E-10	0.027%
H+	4.62739E-10	4.6283E-10	0.020%
AmCO3+	4.32491E-10	4.3260E-10	0.025%
NpO2Citrate--	1.71497E-10	1.7150E-10	0.002%
Am(CO3)2-	1.53194E-10	1.5317E-10	-0.016%
AmSO4+	1.43336E-10	1.4341E-10	0.052%
HEDTA---	8.88413E-11	8.8862E-11	0.023%
HOxalate-	4.08072E-11	4.0828E-11	0.051%
Am(CO3)3---	3.82164E-11	3.8224E-11	0.020%
AmOxalate+	2.91973E-11	2.9223E-11	0.088%
Am(SO4)2-	2.21882E-11	2.2197E-11	0.040%

NpO2(CO3)3(5-)	1.47762E-11	1.4787E-11	0.073%
Am+++	1.26416E-11	1.2648E-11	0.051%
Am(CO3)4(5-)	1.10077E-11	1.1027E-11	0.175%
NpO2(OH)2-	7.28355E-12	7.2825E-12	-0.014%
NpO2EDTA---	5.07918E-12	5.0827E-12	0.069%
AmCl++	2.11547E-12	2.1167E-12	0.058%
H2EDTA--	1.10647E-13	1.1065E-13	0.003%
AmCl2+	1.09760E-13	1.0985E-13	0.082%
NpO2HEDTA--	9.81639E-15	9.8173E-15	0.009%
H2Citrate-	4.80735E-15	4.8075E-15	0.003%
Th(CO3)5(6-)	4.56666E-16	4.5801E-16	0.294%
ThEDTA(aq)	8.65226E-17	8.6535E-17	0.014%
Th(SO4)3--	1.83081E-17	1.8325E-17	0.092%
NpO2H2EDTA-	1.50712E-18	1.5073E-18	0.012%
H2Oxalate(aq)	5.87871E-19	5.8818E-19	0.053%
Th(SO4)2(aq)	3.42030E-19	3.4235E-19	0.094%
ThCitrate+	6.39119E-20	6.3950E-20	0.060%
H3EDTA-	1.22915E-20	1.2292E-20	0.004%
Th(Acetate)2++	8.70218E-21	8.7041E-21	0.022%
H3Citrate(aq)	2.21761E-21	2.2182E-21	0.027%
ThAcetate+++	1.10993E-21	1.1103E-21	0.033%
ThOxalate++	1.55327E-22	1.5548E-22	0.099%
Th++++	-----	1.2357E-24	-----
H4EDTA(aq)	-----	1.8127E-27	-----

Table 5.14-10 shows the results for solute species activity coefficients. All differences are within the usual 1% acceptance criterion. The largest discrepancy is now -0.337% for $Th(CO_3)_5^{6-}$. The results are very significantly improved.

Table 5.14-10. Test Case #13 Two-Off (c4pgwbx_P75_Mfix) Calculated Solute Species Activity Coefficients, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.305	1.30497	-0.002%
Na+	0.9246	0.92449	-0.012%
Mg++	1.742	1.74141	-0.034%
K+	0.4298	0.42983	0.008%
SO4--	0.021331	0.021330	-0.003%
MgB(OH)4+	1.873	1.87284	-0.009%
B(OH)4-	0.1020	0.10200	0.000%
Br-	0.2683	0.26829	-0.005%
B(OH)3(aq)	1.069	1.06905	0.005%
Ca++	0.9133	0.91327	-0.003%
Acetate-	0.5575	0.55744	-0.010%
MgAcetate+	7.397	7.39776	0.010%
B4O5(OH)4--	0.0042178	0.0042179	0.003%

B3O3(OH)4-	0.1631	0.16312	0.011%
MgOH+	0.3065	0.30648	-0.007%
CaB(OH)4+	1.143	1.14262	-0.034%
MgOxalate(aq)	1.263	1.26299	-0.001%
MgCitrate-	0.1662	0.16623	0.016%
MgCO3(aq)	1.000	1.00000	0.000%
MgEDTA--	0.1301	0.13008	-0.018%
CaAcetate+	7.397	7.39776	0.010%
HCO3-	0.3511	0.35108	-0.007%
CO3--	0.015307	0.015304	-0.021%
Citrate---	0.00004011	0.000040087	-0.058%
Oxalate--	0.022458	0.022454	-0.016%
CaOxalate(aq)	1.263	1.26299	-0.001%
OH-	0.4437	0.44371	0.002%
CaCitrate-	0.1662	0.16623	0.016%
CaCO3(aq)	1.000	1.00000	0.000%
AmEDTA-	0.029536	0.029539	0.011%
CaEDTA--	0.1301	0.13008	-0.018%
HAcetate(aq)	1.000	1.00000	0.000%
Am(OH)2+	0.00074068	0.00074063	-0.007%
NpO2+	1.858	1.85780	-0.011%
NpO2CO3-	0.089251	0.089248	-0.003%
NpO2Acetate(aq)	0.2768	0.27676	-0.015%
Th(OH)4(aq)	1.000	1.00000	0.000%
NpO2Oxalate-	0.029137	0.029141	0.013%
CO2(aq)	3.522	3.52209	0.002%
Th(OH)3(CO3)-	0.2683	0.26829	-0.005%
NpO2OH(aq)	0.09567	0.095675	0.006%
AmOH++	0.023756	0.023757	0.006%
HSO4-	0.8150	0.81508	0.010%
AmAcetate++	0.010576	0.010575	-0.005%
NpO2(CO3)2---	0.00008146	0.000081433	-0.033%
EDTA----	9.7959E-07	9.7814E-07	-0.148%
Am(OH)3(aq)	0.0091701	0.0091706	0.006%
HCitrate--	0.0066156	0.0066145	-0.016%
AmCitrate(aq)	0.0066387	0.0066390	0.004%
H+	4.425	4.42486	-0.003%
AmCO3+	0.7483	0.74834	0.006%
NpO2Citrate--	0.0039614	0.0039610	-0.011%
Am(CO3)2-	0.063987	0.063988	0.002%
AmSO4+	0.4676	0.46752	-0.017%
HEDTA---	0.0008078	0.00080724	-0.070%
HOxalate-	0.2842	0.28418	-0.006%
Am(CO3)3---	1.5454E-05	1.5449E-05	-0.032%
AmOxalate+	0.1034	0.10340	-0.005%
Am(SO4)2-	0.048013	0.048018	0.009%

NpO2(CO3)3(5-)	2.1608E-10	2.1582E-10	-0.118%
Am+++	0.5345	0.53456	0.012%
Am(CO3)4(5-)	1.2759E-13	1.2729E-13	-0.234%
NpO2(OH)2-	0.013842	0.013842	0.000%
NpO2EDTA---	0.017226	0.017211	-0.088%
AmCl++	44.66	44.65808	-0.004%
H2EDTA--	0.010057	0.010055	-0.016%
AmCl2+	727.5	727.44473	-0.008%
NpO2HEDTA--	0.1873	0.18724	-0.032%
H2Citrate-	0.1276	0.12761	0.011%
Th(CO3)5(6-)	2.2655E-14	2.2579E-14	-0.337%
ThEDTA(aq)	3.944	3.94457	0.015%
Th(SO4)3--	0.025737	0.025734	-0.013%
NpO2H2EDTA-	0.5200	0.52000	-0.001%
H2Oxalate(aq)	1.000	1.00000	0.000%
Th(SO4)2(aq)	35.95	35.95009	0.000%
ThCitrate+	21.60	21.59235	-0.035%
H3EDTA-	0.2267	0.22673	0.011%
Th(Acetate)2++	266.3	266.31768	0.007%
H3Citrate(aq)	1.000	1.00000	0.000%
ThAcetate+++	75.94	75.94514	0.007%
ThOxalate++	490.7	490.68186	-0.004%
Th++++	0.8141	0.81395	-0.018%
H4EDTA(aq)	1.000	1.00000	0.000%

Table 5.14-11 shows the results for actinide species distributions. Since the molalities have already been shown to be substantially improved, it is no surprise that the results in this table are also substantially improved (they are essentially the same data). This table is included here because of its special interest. All differences are well within the usual 1% acceptance criterion.

Table 5.14-11. Test Case #13 Two-Off (c4pgwbx_P75_Mfix) Actinide Species Distributions, EQ3/6 (using the Pitzer, 1975, eq. 47 approximation and revised EQ3NR inputs) vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	2.25412E-06	100.00%	2.2537E-06	100.00%	-0.02%
AmEDTA-	2.01056E-06	89.19%	2.0101E-06	89.19%	-0.02%
Am(OH)2+	2.37398E-07	10.53%	2.3743E-07	10.54%	0.01%
Subtotal	2.24796E-06	99.73%	2.2475E-06	99.73%	-0.02%
Total NpO2+	4.07043E-07	100.00%	4.0713E-07	100.00%	0.02%
NpO2+	1.45822E-07	35.82%	1.4587E-07	35.83%	0.03%
NpO2CO3-	1.19965E-07	29.47%	1.1997E-07	29.47%	0.00%
NpO2Acetate(aq)	8.43943E-08	20.73%	8.4402E-08	20.73%	0.01%
NpO2Oxalate-	5.03473E-08	12.37%	5.0364E-08	12.37%	0.03%
NpO2OH(aq)	4.97889E-09	1.22%	4.9793E-09	1.22%	0.01%
Subtotal	4.05507E-07	99.62%	4.0559E-07	99.62%	0.02%
Total Th++++	6.47550E-08	100.00%	6.4759E-08	100.00%	0.01%
Th(OH)4(aq)	5.19573E-08	80.24%	5.1960E-08	80.24%	0.01%
Th(OH)3(CO3)-	1.27976E-08	19.76%	1.2798E-08	19.76%	0.00%
Subtotal	6.47549E-08	100.00%	6.4758E-08	100.00%	0.00%

This provides another demonstration that excellent results (within the usual acceptance criteria, allowing for FMT's limited output precision for saturation indices) are obtained from the two codes if front end problems are eliminated, the two codes use the same J(x) approximation, and NegIon is not present in the problem.

5.15 Test Case #14 – Solubility of Am(III), Th(IV), and Np(V) in WIPP ERDA-6 brine, assuming that the inventory of EDTA increases by a factor of 10 in comparison with the CRA-2004 PABC inventory

5.15.1 Test Overview

This test case is to compare solubility values of Am(III), Th(IV) and Np(V) in ERDA-6 brine predicted by FMT with those calculated by EQ3/6, assuming that the inventory of EDTA increases by a factor of 10 in comparison with the 2004 PABC inventory. This problem is taken from Brush et al. (2008). This is the same problem as Test Case #12, except that the EDTA is increased tenfold. The ERDA-6 brine with 10x EDTA is first created. Then it is reacted with 1.0 mole of $Am(OH)_3(s)$, $ThO_2(am)$, $KNpO_2CO_3$, and hydromagnesite (5424) ($Mg_5(CO_3)4(OH)_2\bullet4H_2O$) plus 10.0 moles each of anhydrite ($CaSO_4$), brucite ($Mg(OH)_2$), and halite (NaCl). This is a "type 3" problem in that the lack of a proper front-end in FMT may affect the results, including the calculated pH.

Table 5.15-1 gives the FMT inputs for the modified ERDA-6 brine. The inputs here are consistent with 1 L of solution (Brush et al., 2008, Table 2). The four organic ligands (oxalate, acetate, EDTA, and citrate) are treated as pseudo-elements by FMT (whereas they are treated as active auxiliary basis species by EQ3/6).

Table 5.15-1. Test Case #14 (c4per6x) FMT Inputs for ERDA-6 Brine with 10x EDTA.

Element	Moles
H	98.5663837
O	50.0976919
Na	4.87
K	0.097
Mg	0.019
Ca	0.012
Cl	4.80
S	0.170
B	0.016
Br	0.063
Oxalate	0.011
Acetate	0.046
EDTA	0.011
Citrate	8.14E-05

Table 5.15-2 gives the corresponding EQ3/6 inputs for the brine. Because EQ3/6 works directly in terms of molalities, the molarity inputs must be converted to molalities before the actual speciation calculations can begin. This requires inputs for density and TDS, which are needed to compute the molarity/molality factor. The values shown in Table 5.15-2 were calculated from the molarity data using the WIPP density model (see worksheet c4per6x of spreadsheet Conc_density_calcs_EV2008.xls). The molarity/molality factor was used in EQ3NR to rescale the brine mass for consistency with a 1 L volume prior to reacting it with minerals in the

subsequent EQ6 run. As was the case in Test Case #12, a molarity/molality value of 0.8735 (the correct Test Case #11 value) was used instead of the value given in Table 5.14-2. This has no effect other than to scale the initial brine mass to be consistent with a volume slightly different from 1 L. It does not affect the molarity to molality conversions.

Table 5.15-2. Test Case #14 (c4per6x) EQ3/6 Inputs for ERDA-6 Brine with 10x EDTA.

Basis species	Molarity
Na+	4.87
K+	0.097
Mg++	0.019
Ca++	0.012
Cl-	4.8
SO4--	0.17
HCO3-	0.016
B(OH)4-	0.063
Br-	0.011
Oxalate--	4.55E-02
Acetate-	1.06E-02
EDTA----	8.14E-05
Citrate---	8.06E-04
Am+++	1.00E-18
Th++++	1.00E-18
NpO2+	1.00E-18
density, g/L	1202.44
TDS, g/L	314.8280
Molarity/molality	0.8876

It is once more noted that the density, TDS, and molarity/molality values obtained from the spreadsheet calculation take the compositional data at face value. There is no speciation calculation in this calculation. Since EQ3NR performs a full speciation calculation, the WIPP density model embedded in FMT will generally produce slightly different calculated results. This will be addressed below in the Evaluation section.

Test Files:

Thermodynamic data file:	data1.fmt
EQ6 input file:	c4per6x.6i
EQ6 output files:	c4per6x.6o, c4per6x.6p
Thermodynamic data file:	fmt_050405.chemdat
FMT input files:	fmt_edta_er6_hmg_orgs_x_007.in; fmt_edta_er6_hmg_orgs_x_007.inguess
FMT output files:	fmt_edta_er6_hmg_orgs_x_007.out; fmt_edta_er6_hmg_orgs_x_007.for088

5.15.2 Acceptance Criteria

The acceptance criteria are the same as those specified for all EQ3/6-to-FMT comparison test cases (see Section 5.1.2).

5.15.3 Evaluation

Code outputs were assembled into the spreadsheet c4per6x.xls and compared therein. That spreadsheet is the immediate source of the tables presented in this section. In the case of thermodynamic activities and activity coefficients the logarithmic quantities output by EQ3/6 were converted in the spreadsheet to the corresponding "linear" quantities for comparison with the corresponding FMT outputs.

Table 5.15-3 compares the density, TDS, and molarity/molality values input to EQ3NR against the output values. The output values are slightly different because they were computed using a full speciation model. These differences (<1%) are not considered significant.

Table 5.15-3. Test Case #14 (c4per6x) EQ3NR Inputs and Outputs for Density, TDS, and Molarity/Molality for GWB Brine.

	Input	Output	Δ
density, g/L	1202.44	1201.8	-0.053%
TDS, g/L	314.8280	313.84	-0.314%
Molarity/molality	0.8876	0.88797	0.042%

Table 5-15-4 compares the results for the set of general parameter outputs (after the brine has been reacted with the designated minerals). These results are within the general acceptance criteria, except for the cases of the solution mass and the H_2O mass. This difference occurred because the EQ6 run started with ~1 L of brine instead of a mass scaled to the usual 1000 g H_2O. The significance of this has been addressed previously in the case of the three preceding test cases.

Table 5.15-4. Test Case #14 (c4per6x) General Parameter Outputs, EQ3/6 vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	**1389.750526**	**1213.7697**	**-12.663%**
H2O mass, g	**1003.939018**	**876.77157**	**-12.667%**
Ionic strength, m	6.800145	6.8017	0.023%
density, g/L	1217.21	1217.2	-0.001%
TDS, g/L	337.912613	337.96	0.014%
a_w	0.747506	0.74751	0.001%
x_w	0.816223	0.8162	-0.003%
λ_w	0.9158	0.91584	0.004%
fCO2, bars	0.000003135	3.13527E-06	0.009%
pH (Pitzer)	8.9443	8.9461	0.0018

pmH	9.5884	9.5901	0.0017
pcH	9.6442	9.6460	0.0018

Table 5.15-5 compares results for solute species molalities. In some instances, the results are within the usual 1% acceptance criterion. In many cases, however, they are not. The largest discrepancies include instances for the very highly charged species: $Th(CO_3)_5^{6-}$ (+18.163%), $Am(CO_3)_4^{5-}$ (+12.244%), $EDTA^{4-}$ (+5.572%), and $NpO_2(CO_3)_3^{5-}$ (+12.437%). Overall, the pattern is much like what was seen in Test Case #11 and Test Case #12. The likely causes of the discrepancies are the same. Note at the bottom of the table that FMT does not report values for molalities less than 1×10^{-24}.

Table 5.15-5. Test Case #14 (c4per6x) Calculated Solute Species Molalities, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Na+	5.96273	5.9653	0.043%
Cl-	5.95960	5.9588	-0.013%
SO4--	0.203306	0.20430	0.489%
Mg++	0.156981	0.15649	-0.313%
K+	0.109305	0.10888	-0.389%
B(OH)4-	0.0397079	0.039663	-0.113%
MgB(OH)4+	0.0156955	0.015548	-0.940%
Br-	0.0123953	0.012347	-0.390%
B(OH)3(aq)	0.0108980	0.010841	-0.523%
Ca++	0.0103288	0.010392	0.612%
Acetate-	0.00792293	0.0079121	-0.137%
MgAcetate+	0.00387792	0.0038418	-0.931%
CaB(OH)4+	0.00166405	0.0016629	-0.069%
MgCitrate-	0.00085522	0.00085095	-0.499%
MgOH+	0.000853141	0.00084998	-0.371%
B3O3(OH)4-	0.000451387	0.00044622	-1.145%
B4O5(OH)4--	0.000417999	0.00041448	-0.842%
MgCO3(aq)	0.000317356	0.00031736	0.001%
MgOxalate(aq)	0.000318154	0.00031536	-0.878%
CaAcetate+	0.000143190	0.00014312	-0.049%
HCO3-	0.000089796	0.000090208	0.459%
MgEDTA--	8.64238E-05	8.6071E-05	-0.408%
CO3--	5.88883E-05	5.9675E-05	1.336%
CaCitrate-	3.15784E-05	3.1700E-05	0.385%
Citrate---	2.14399E-05	2.2014E-05	2.678%
CaCO3(aq)	1.95728E-05	1.9747E-05	0.890%
OH-	1.28557E-05	1.2907E-05	0.399%
CaOxalate(aq)	1.17476E-05	1.1748E-05	0.003%
Oxalate--	7.25863E-06	7.2860E-06	0.377%
CaEDTA--	3.19114E-06	3.2063E-06	0.475%
AmEDTA-	2.11033E-06	2.0873E-06	-1.091%
NpO2CO3-	4.63885E-07	4.6551E-07	0.350%
HAcetate(aq)	3.80263E-07	3.7833E-07	-0.508%

NpO2+	1.98499E-07	1.9770E-07	-0.403%
NpO2Acetate(aq)	1.82239E-07	1.8125E-07	-0.543%
Am(OH)2+	1.13586E-07	1.1298E-07	-0.534%
NpO2Oxalate-	7.04341E-08	7.0136E-08	-0.423%
Th(OH)4(aq)	5.41382E-08	5.4142E-08	0.007%
CO2(aq)	2.97697E-08	2.9755E-08	-0.049%
Th(OH)3(CO3)-	2.30931E-08	2.3201E-08	0.467%
NpO2OH(aq)	1.18610E-08	1.1854E-08	-0.059%
NpO2(CO3)2---	9.84537E-09	1.0205E-08	3.653%
HCitrate--	9.48563E-10	9.5171E-10	0.332%
AmOH++	8.01002E-10	7.9910E-10	-0.237%
NpO2Citrate--	7.96221E-10	7.9840E-10	0.274%
Am(OH)3(aq)	7.75629E-10	7.7594E-10	0.040%
HSO4-	7.04994E-10	7.0205E-10	-0.418%
Am(CO3)2-	3.10911E-10	3.1245E-10	0.495%
H+	2.58013E-10	2.5696E-10	-0.408%
AmCitrate(aq)	2.48264E-10	2.4564E-10	-1.057%
AmCO3+	2.33359E-10	2.3240E-10	-0.411%
AmAcetate++	2.28132E-10	2.2661E-10	-0.667%
EDTA----	1.97770E-10	2.0879E-10	5.572%
NpO2(CO3)3(5-)	7.17665E-11	8.0692E-11	12.437%
Am(CO3)3---	7.17689E-11	7.4479E-11	3.776%
HEDTA---	5.54109E-11	5.6487E-11	1.942%
NpO2(OH)2-	3.00167E-11	3.0126E-11	0.364%
AmSO4+	1.78043E-11	1.7568E-11	-1.327%
HOxalate-	1.71118E-11	1.7034E-11	-0.455%
NpO2EDTA---	6.04044E-12	6.1493E-12	1.802%
AmOxalate+	4.99639E-12	4.9248E-12	-1.433%
Am+++	3.27287E-12	3.2993E-12	0.808%
Am(SO4)2-	2.18715E-12	2.1589E-12	-1.292%
Am(CO3)4(5-)	7.92143E-13	8.8913E-13	12.244%
AmCl++	2.67657E-13	2.6620E-13	-0.544%
H2EDTA--	1.40182E-13	1.3975E-13	-0.308%
NpO2HEDTA--	2.94839E-14	2.9338E-14	-0.495%
AmCl2+	1.03978E-14	1.0274E-14	-1.191%
H2Citrate-	5.51792E-15	5.4889E-15	-0.526%
ThEDTA(aq)	4.67147E-17	4.5973E-17	-1.588%
Th(CO3)5(6-)	1.95730E-17	2.3128E-17	18.163%
NpO2H2EDTA-	5.89010E-18	5.8097E-18	-1.365%
Th(SO4)3--	9.29585E-19	9.1756E-19	-1.294%
H2Oxalate(aq)	1.25532E-19	1.2444E-19	-0.870%
ThCitrate+	4.56354E-20	4.4938E-20	-1.528%
Th(SO4)2(aq)	1.76806E-20	1.7381E-20	-1.695%
H3EDTA-	1.29453E-20	1.2792E-20	-1.184%
Th(Acetate)2++	3.11187E-21	3.0759E-21	-1.156%
H3Citrate(aq)	1.36619E-21	1.3527E-21	-0.987%

ThAcetate+++	2.53870E-22	2.5715E-22	1.292%
ThOxalate++	-----	2.6740E-23	-----
Th++++	-----	1.8405E-25	-----
H4EDTA(aq)	-----	9.5622E-28	-----

Table 5.15-6 compares results for solute species activity coefficients. These results are largely complementary to the molality results, much as was the case for Test Case #11. The largest discrepancy is for $Th(CO_3)_5^{6-}$ (-13.189%).

Table 5.15-6. Test Case #14 (c4per6x) Calculated Solute Species Activity Coefficients, EQ3/6 vs. FMT.

Species	FMT	EQ3/6	Δ
Na+	0.9651	0.96516	0.006%
Cl-	1.084	1.08393	-0.007%
SO4--	0.019466	0.019360	-0.546%
Mg++	1.894	1.88408	-0.524%
K+	0.4749	0.47479	-0.024%
B(OH)4-	0.1000	0.10000	0.000%
MgB(OH)4+	1.887	1.88625	-0.040%
Br-	0.2791	0.27900	-0.037%
B(OH)3(aq)	0.9610	0.96073	-0.028%
Ca++	1.063	1.05682	-0.582%
Acetate-	0.7390	0.73943	0.059%
MgAcetate+	5.824	5.82505	0.018%
CaB(OH)4+	1.171	1.17112	0.010%
MgCitrate-	0.1993	0.19911	-0.094%
MgOH+	0.3556	0.35547	-0.037%
B3O3(OH)4-	0.1189	0.11877	-0.111%
B4O5(OH)4--	0.0039171	0.0038958	-0.543%
MgCO3(aq)	1.000	1.00000	0.000%
MgOxalate(aq)	1.253	1.25256	-0.035%
CaAcetate+	5.824	5.82505	0.018%
HCO3-	0.3480	0.34794	-0.018%
MgEDTA--	0.2444	0.24344	-0.391%
CO3--	0.021373	0.021272	-0.474%
CaCitrate-	0.1993	0.19911	-0.094%
Citrate---	0.0001341	0.00013092	-2.373%
CaCO3(aq)	1.000	1.00000	0.000%
OH-	0.5154	0.51547	0.013%
CaOxalate(aq)	1.253	1.25256	-0.035%
Oxalate--	0.029737	0.029614	-0.413%
CaEDTA--	0.2444	0.24344	-0.391%
AmEDTA-	0.025552	0.025521	-0.121%
NpO2CO3-	0.1075	0.10757	0.067%
HAcetate(aq)	1.000	1.00000	0.000%

NpO2+	1.920	1.91911	-0.046%
NpO2Acetate(aq)	0.2895	0.28953	0.012%
Am(OH)2+	0.00084195	0.00084295	0.118%
NpO2Oxalate-	0.020297	0.020286	-0.053%
Th(OH)4(aq)	1.000	1.00000	0.000%
CO2(aq)	3.472	3.47376	0.051%
Th(OH)3(CO3)-	0.2791	0.27900	-0.037%
NpO2OH(aq)	0.1039	0.10390	-0.004%
NpO2(CO3)2---	0.00017066	0.00016669	-2.328%
HCitrate--	0.0091303	0.0090845	-0.502%
AmOH++	0.024826	0.024683	-0.576%
NpO2Citrate--	0.0043212	0.0043003	-0.483%
Am(OH)3(aq)	0.0081263	0.0081227	-0.044%
HSO4-	0.6076	0.60716	-0.073%
Am(CO3)2-	0.055634	0.055603	-0.055%
H+	4.406	4.40555	-0.010%
AmCitrate(aq)	0.0079134	0.0079195	0.078%
AmCO3+	0.7389	0.73892	0.003%
AmAcetate++	0.015424	0.015321	-0.665%
EDTA----	0.000026875	0.000025468	-5.234%
NpO2(CO3)3(5-)	2.2734E-09	2.06443E-09	-9.192%
Am(CO3)3---	0.000048092	0.000046935	-2.405%
HEDTA---	0.0040583	0.0039655	-2.286%
NpO2(OH)2-	0.015973	0.015973	0.003%
AmSO4+	0.4283	0.42835	0.012%
HOxalate-	0.2607	0.26074	0.014%
NpO2EDTA---	0.1150	0.11251	-2.163%
AmOxalate+	0.067347	0.067453	0.157%
Am+++	0.3322	0.32539	-2.051%
Am(SO4)2-	0.039191	0.039165	-0.066%
Am(CO3)4(5-)	3.4316E-11	3.12248E-11	-9.008%
AmCl++	45.54	45.1960	-0.755%
H2EDTA--	0.013809	0.013744	-0.474%
NpO2HEDTA--	0.2749	0.27397	-0.339%
AmCl2+	794.4	793.41	-0.124%
H2Citrate-	0.1234	0.12331	-0.073%
ThEDTA(aq)	3.759	3.75837	-0.017%
Th(CO3)5(6-)	1.9201E-11	1.66686E-11	-13.189%
NpO2H2EDTA-	0.3256	0.32606	0.142%
Th(SO4)3--	0.016345	0.016259	-0.525%
H2Oxalate(aq)	1.000	1.00000	0.000%
ThCitrate+	9.928	9.94260	0.147%
Th(SO4)2(aq)	31.71	31.696	-0.045%
H3EDTA-	0.2079	0.20787	-0.013%
Th(Acetate)2++	175.1	173.90	-0.685%
H3Citrate(aq)	1.000	1.00000	0.000%

ThAcetate+++	48.61	47.152	-2.999%
ThOxalate++	177.9	177.01	----
Th++++	0.4795	0.48967	-----
H4EDTA(aq)	1.000	1.00000	-----

Table 5.15-7 compares results for saturation indices (log Q/K) for the relevant minerals. In a number of instances, the differences exceed both the usual acceptance criterion (0.004) and also what can be explained by the limited precision with which FMT reports saturation indices. This table provides confirmation that the brine became saturated with respect to each of the solids with which it was reacting, despite the difference in brine masses in the two code runs. As expected, magnesite ($MgCO_3$) whewellite ($CaC_2O_4 \cdot H_2O$, calcium oxalate), and glauberite ($Na_2Ca(SO_4)_2$) precipitate spontaneously and are thus saturated.

Table 5.15-7. Test Case #14 (c4per6x) Calculated Mineral Saturation Indices, EQ3/6 vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	2.80	2.79987	-0.00013
Magnesite	1.41	1.40696	-0.00304
Calcite	0.547	0.55051	0.00351
Aragonite	0.360	0.36371	0.00371
Am(OH)3(s)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Anhydrite	0.00000	0.00000	0.00000
Whewellite	0.00000	0.00000	0.00000
Brucite	0.00000	0.00000	0.00000
Glauberite	0.00000	0.00000	0.00000
Halite	0.00000	0.00000	0.00000
Hydromagnesite5424	0.00000	0.00000	0.00000
Gypsum	-0.0343	-0.03437	-0.00007
Mg2Cl(OH)3.4H2O	-0.325	-0.32676	-0.00176
AmOHCO3(c)	-0.343	-0.34324	-0.00024
Hydromagnesite4323	-0.344	-0.34348	0.00052
Thenardite	-0.595	-0.59490	0.00010
Labile_Salt	-0.707	-0.70737	-0.00037
Mirabilite	-0.919	-0.91843	0.00057
Sylvite	-1.37	-1.37625	-0.00625
Borax	-1.61	-1.61272	-0.00272
Nesquehonite	-1.64	-1.63899	0.00101
Teepleite(20C)	-1.67	-1.67218	-0.00218
Na3NpO2(CO3)2	-1.76	-1.75294	0.00706
2[NaNpO2CO3.7/2H2O]	-1.82	-1.81879	0.00121
Epsomite	-1.93	-1.93684	-0.00684
B(OH)3	-1.95	-1.95191	-0.00191
Bloedite	-1.97	-1.97429	-0.00429
Syngenite	-2.01	-2.01598	-0.00598

Hexahydrite	-2.05	-2.05645	-0.00645
NpO2OH(aged)	-2.12	-2.11754	0.00246
Na_Metaborate	-2.22	-2.22335	-0.00335
NaAm(CO3)2.6H2O(c)	-2.37	-2.36856	0.00144
Na2Oxalate	-2.74	-2.74052	-0.00052
NpO2OH(am)	-2.82	-2.81764	0.00236
Kieserite	-2.93	-2.93694	-0.00694
Polyhalite	-3.13	-3.14202	-0.01202
Arcanite	-3.20	-3.19960	0.00040
Pirssonite	-3.25	-3.24144	0.00856
Nahcolite	-3.34	-3.34010	-0.00010
Gaylussite	-3.45	-3.44279	0.00721
Kainite	-3.59	-3.59615	-0.00615
Aphthitalite/Glaserite	-4.10	-4.10234	-0.00234
Bischofite	-4.12	-4.12375	-0.00375
Picromerite/Schoenite	-4.33	-4.33975	-0.00975
Leonite	-4.43	-4.43568	-0.00568
Carnallite	-4.47	-4.47510	-0.00510
Na2CO3.7H2O	-4.80	-4.80057	-0.00057
Natron	-4.82	-4.81512	0.00488
Thermonatrite	-4.99	-4.98427	0.00573
Burkeite	-5.37	-5.36869	0.00131
Na_Pentaborate	-5.84	-5.84776	-0.00776
Kalicinite	-6.07	-6.07125	-0.00125
K3NpO2(CO3)2	-6.14	-6.14258	-0.00258
K-Tetraborate(30C)	-6.38	-6.39022	-0.01022
K-Pentaborate(30C)	-6.53	-6.54452	-0.01452
CaCl2.4H2O	-6.56	-6.56153	-0.00153
KNaCO3.6H2O	-7.07	-7.06514	0.00486
Portlandite	-7.13	-7.12335	0.00665
Trona	-7.33	-7.32745	0.00255

Table 5.15-8 compares results for actinide species distributions, considering only those species needed to comprise 99% of the mass balance of any actinide. These data were key results in the Brush et al. (2008) calculations. The differences here are small (<4%), though some instances exceed the usual 1% criterion for "linear" quantities.

Table 5.15-8. Test Case #14 (c4per6x) Actinide Species Distributions, EQ3/6 vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	2.22661E-06	100.00%	2.2030E-06	100.00%	-1.06%
AmEDTA-	2.11033E-06	94.78%	2.0873E-06	94.75%	-1.09%
Am(OH)2+	1.13586E-07	5.10%	1.1298E-07	5.13%	-0.53%
Subtotal	2.22392E-06	99.88%	2.2003E-06	99.88%	-1.06%
Total NpO2+	9.37667E-07	100.00%	9.3758E-07	100.00%	-0.01%
NpO2CO3-	4.63885E-07	49.47%	4.6551E-07	49.65%	0.35%
NpO2+	1.98499E-07	21.17%	1.9770E-07	21.09%	-0.40%
NpO2Acetate(aq)	1.82239E-07	19.44%	1.8125E-07	19.33%	-0.54%
NpO2Oxalate-	7.04341E-08	7.51%	7.0136E-08	7.48%	-0.42%
NpO2OH(aq)	1.1861E-08	1.26%	1.1854E-08	1.26%	-0.06%
NpO2(CO3)2---	9.84537E-09	1.05%	1.0205E-08	1.09%	3.65%
Subtotal	9.36763E-07	99.90%	9.3666E-07	99.90%	-0.01%
Total Th++++	7.72313E-08	100.00%	7.7343E-08	100.00%	0.14%
Th(OH)4(aq)	5.41382E-08	70.10%	5.4142E-08	70.00%	0.01%
Th(OH)3(CO3)-	2.30931E-08	29.90%	2.3201E-08	30.00%	0.47%
Subtotal	7.72313E-08	100.00%	7.7343E-08	100.00%	0.14%

The results of the two codes are in less than very good agreement. These results are very similar to those first obtained for Test Case #11. It was demonstrated that the differences in that case (and in Test Case #13) were due to a combination of "front end" inconsistencies in the code inputs and the use of different approximations for the J(x) function. The differences obtained for the present test case are almost surely due to the same factors. Therefore, the results obtained here will be considered acceptable. EQ3/6 was re-run using the same J(x) approximation as FMT. Results are contained in the spreadsheet c4per6x_P75.xls. None of those results will be shown here, but in general the results are improved as expected. In fact, they come very close to satisfying the usual numerical criteria.

5.16 Test Case #15 – Using mineral solubility constraints for version migration test

5.16.1 Test Overview

This test case is to verify functional requirement R.3 for comparison of Version 8.0 with Version 8.0a.

Test Files:

Thermodynamic data file:	data1.cmp
EQ6 input file:	oxcalhem.3i
EQ6 output files:	oxcalhem.3o, oxcalhem.3p

5.16.2 Acceptance Criteria

As test cases for version migration tests use identical input files and there is no major architectural change between two versions, outputs from Version 8.0 and Version 8.0a are expected to be identical except for differences caused by precision or rounding in two versions. Version 8.0 has a precision to six decimals for general parameters on linear scale, whereas Version 8.0a has a precision to five decimals for most general parameters on linear scale. Both versions have precisions to four decimals for outputs on logarithmic scale. Therefore, the acceptance criteria are that differences between two versions should be ≤ 0.005% for linear parameters and ≤ 0.001 for logarithmic parameters, respectively.

5.16.3 Evaluation

Table 5-16-1 compares the results for the set of general parameter outputs (after the solution has been equilibrated with the designated minerals). These results are within the acceptance criteria.

Table 5.16-1. Test Case #15 (oxcalhem.3i) General Parameter Outputs, Version 8.0 vs. Version 8.0a.

	Version 8.0	Version 8.0a	Δ
Ionic strength, m	0.0131478	0.0131478	0.000%
a_w	0.999677	0.99968	0.000%
x_w	0.999660	0.99966	0.000%
λ_w	1.00002	1.0000	-0.002%
fO2, bars	0.199526	0.19953	0.002%
pH (NBS)	7.3108	7.3108	0.0000
pmH	7.2655	7.2655	0.0000
pHCl	9.6624	9.6624	0.0000

Table 5.16-2 compares results for solute species molalities. The results are within the 0.005% criterion.

Table 5.16-2. Test Case #15 (oxcalhem.3i) Calculated Solute Species Molalities, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
Na+	6.9421E-03	6.9421E-03	0.000%
Cl-	4.9943E-03	4.9943E-03	0.000%
HCO3-	3.5108E-03	3.5108E-03	0.000%
Ca++	1.7208E-03	1.7208E-03	0.000%

SO4--	8.9411E-04	8.9411E-04	0.000%
CO2(aq)	3.3862E-04	3.3862E-04	0.000%
O2(aq)	2.5137E-04	2.5137E-04	0.000%
CaSO4(aq)	8.0205E-05	8.0205E-05	0.000%
CaHCO3+	4.3360E-05	4.3360E-05	0.000%
NaHCO3(aq)	2.7553E-05	2.7553E-05	0.000%
NaSO4-	2.5681E-05	2.5681E-05	0.000%
UO2(CO3)2--	2.3589E-05	2.3589E-05	0.000%
UO2(CO3)3----	1.2717E-05	1.2717E-05	0.000%
CaCO3(aq)	7.0307E-06	7.0307E-06	0.000%
CO3--	4.7305E-06	4.7305E-06	0.000%
NaCl(aq)	4.5752E-06	4.5752E-06	0.000%
(UO2)2CO3(OH)3-	1.4942E-06	1.4942E-06	0.000%
CaCl+	1.1121E-06	1.1121E-06	0.000%
UO2(OH)2(aq)	4.0858E-07	4.0858E-07	0.000%
UO2CO3(aq)	2.8120E-07	2.8120E-07	0.000%
OH-	2.3161E-07	2.3161E-07	0.000%
NaCO3-	6.7734E-08	6.7734E-08	0.000%
H+	5.4265E-08	5.4265E-08	0.000%
UO2(OH)3-	1.1563E-08	1.1563E-08	0.000%
CaCl2(aq)	4.9437E-09	4.9437E-09	0.000%
CaOH+	3.5809E-09	3.5809E-09	0.000%
HSO4-	2.9437E-09	2.9437E-09	0.000%
UO2OH+	2.8868E-09	2.8868E-09	0.000%
(UO2)3(CO3)6(6-)	3.3277E-10	3.3277E-10	0.000%
NaOH(aq)	2.0177E-10	2.0177E-10	0.000%
HCl(aq)	4.6516E-11	4.6516E-11	0.000%
UO2++	3.2263E-11	3.2263E-11	0.000%
UO2SO4(aq)	1.3400E-11	1.3400E-11	0.000%
(UO2)3(OH)5+	8.5758E-12	8.5758E-12	0.000%
(UO2)3(OH)7-	1.2186E-12	1.2186E-12	0.000%
Fe(OH)3(aq)	1.1326E-12	1.1326E-12	0.000%
(UO2)2(OH)2++	6.3094E-13	6.3094E-13	0.000%
UO2Cl+	1.4543E-13	1.4543E-13	0.000%
Fe(OH)2+	1.3363E-13	1.3363E-13	0.000%
UO2(SO4)2--	9.7457E-14	9.7457E-14	0.000%
(UO2)4(OH)7+	3.1229E-14	3.1229E-14	0.000%
Fe(OH)4-	6.5027E-15	6.5027E-15	0.000%
UO2(OH)4--	5.2148E-15	5.2148E-15	0.000%
(UO2)3(OH)4++	2.7006E-15	2.7006E-15	0.000%
(UO2)3(OH)5CO2+	1.2203E-15	1.2203E-15	0.000%
(UO2)3O(OH)2(HCO3)+	9.8427E-16	9.8427E-16	0.000%
(UO2)2OH+++	4.5953E-17	4.5953E-17	0.000%
UO2Cl2(aq)	2.9928E-17	2.9928E-17	0.000%
FeOH++	2.7984E-17	2.7984E-17	0.000%
FeCO3+	2.3641E-18	2.3641E-18	0.000%

H2SO4(aq)	1.2875E-19	1.2875E-19	0.000%
HClO(aq)	1.0144E-19	1.0144E-19	0.000%
ClO-	6.2539E-20	6.2539E-20	0.000%
Fe+++	3.3254E-22	3.3254E-22	0.000%
FeHCO3+	1.2942E-22	1.2942E-22	0.000%
Fe++	1.0898E-22	1.0898E-22	0.000%
UO2+	3.5521E-23	3.5521E-23	0.000%
HO2-	1.8109E-23	1.8109E-23	0.000%
FeCO3(aq)	1.1259E-23	1.1259E-23	0.000%
FeSO4+	7.1525E-24	7.1525E-24	0.000%
FeSO4(aq)	6.2330E-24	6.2330E-24	0.000%
FeOH+	5.0768E-25	5.0768E-25	0.000%
FeCl2+	3.9941E-25	3.9941E-25	0.000%
FeCl+	2.4146E-25	2.4146E-25	0.000%
FeCl++	1.4583E-25	1.4583E-25	0.000%
ClO3-	1.0947E-25	1.0947E-25	0.000%
Fe(SO4)2-	7.7387E-26	7.7387E-26	0.000%
ClO4-	6.1929E-26	6.1929E-26	0.000%
(UO2)11(CO3)6(OH)12--	2.4530E-27	2.4530E-27	0.000%
Fe(OH)2(aq)	7.3073E-29	7.3073E-29	0.000%
ClO2-	9.7825E-30	9.7825E-30	0.000%
FeCl2(aq)	4.8434E-30	4.8434E-30	0.000%
HSO5-	2.5357E-30	2.5357E-30	0.000%
UO2(CO3)3(5-)	3.6344E-31	3.6344E-31	0.000%
Fe(OH)3-	6.6491E-32	6.6491E-32	0.000%
Fe2(OH)2++++	5.0163E-32	5.0163E-32	0.000%
FeCl4-	9.4206E-33	9.4206E-33	0.000%
U(OH)4(aq)	1.6064E-33	1.6064E-33	0.000%
HClO2(aq)	6.3257E-34	6.3257E-34	0.000%
FeCl4--	5.4350E-34	5.4350E-34	0.000%
UO2ClO3+	6.9033E-36	6.9033E-36	0.000%
Fe(OH)4--	1.9240E-39	1.9240E-39	0.000%
Fe3(OH)4(5+)	3.2684E-42	3.2684E-42	0.000%
Formate	3.4670E-44	3.4670E-44	0.000%
U(CO3)4----	2.0782E-44	2.0782E-44	0.000%
H2(aq)	4.9088E-45	4.9088E-45	0.000%
Ca(For)+	1.0332E-45	1.0332E-45	0.000%
S2O8--	6.0686E-46	6.0686E-46	0.000%
Na(For)(aq)	2.1363E-46	2.1363E-46	0.000%
Formic_acid(aq)	8.5696E-48	8.5696E-48	0.000%
SO3--	1.3271E-48	1.3271E-48	0.000%
HSO3-	7.4131E-49	7.4131E-49	0.000%
U(CO3)5(6-)	4.7533E-50	4.7533E-50	0.000%
CO(aq)	1.9289E-50	1.9289E-50	0.000%
UOH+++	5.5769E-51	5.5769E-51	0.000%
Oxalate	3.3720E-51	3.3720E-51	0.000%

UO2SO3(aq)	9.6565E-53	9.6565E-53	0.000%
H2SO3(aq)	3.3011E-54	3.3011E-54	0.000%
U(SO4)2(aq)	2.4458E-54	2.4458E-54	0.000%
SO2(aq)	2.3507E-54	2.3507E-54	0.000%
H-Oxalate	2.1033E-54	2.1033E-54	0.000%
USO4++	9.7702E-55	9.7702E-55	0.000%
U++++	2.0799E-57	2.0799E-57	0.000%
UCl+++	2.1809E-58	2.1809E-58	0.000%
Oxalic_acid(aq)	1.7142E-60	1.7142E-60	0.000%
Fe(For)+	1.6334E-64	1.6334E-64	0.000%
S2O6--	2.8933E-71	2.8933E-71	0.000%
U+++	2.1850E-80	2.1850E-80	0.000%
Ca(For)2(aq)	2.1016E-88	2.1016E-88	0.000%
Na(For)2-	3.8785E-90	3.8785E-90	0.000%
Formaldehyde(aq)	1.6297E-93	1.6297E-93	0.000%
UO2(SO3)2--	1.8532E-99	1.8532E-99	0.000%

Table 5.16-3 compares results for solute species activity coefficients. These results are largely complementary to the molality results. The comparison indicates that the acceptance criteria are met.

Table 5.16-3. Test Case #15 (oxcalhem.3i) Calculated Solute Species Activity Coefficients, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
Na+	0.88614	0.88614	0.000%
Cl-	0.89125	0.89125	0.000%
HCO3-	0.89475	0.89475	0.000%
Ca++	0.63826	0.63826	0.000%
SO4--	0.63227	0.63227	0.000%
CO2(aq)	1.00323	1.00323	0.000%
O2(aq)	1.00323	1.00323	0.000%
CaSO4(aq)	1.00000	1.00000	0.000%
CaHCO3+	0.88614	0.88614	0.000%
NaHCO3(aq)	1.00000	1.00000	0.000%
NaSO4-	0.89475	0.89475	0.000%
UO2(CO3)2--	0.63227	0.63227	0.000%
UO2(CO3)3----	0.15621	0.15621	0.000%
CaCO3(aq)	1.00000	1.00000	0.000%
CO3--	0.63709	0.63709	0.000%
NaCl(aq)	1.00000	1.00000	0.000%
(UO2)2CO3(OH)3-	0.89475	0.89475	0.000%
CaCl+	0.88614	0.88614	0.000%
UO2(OH)2(aq)	1.00000	1.00000	0.000%
UO2CO3(aq)	1.00000	1.00000	0.000%

OH-	0.89289	0.89289	0.000%
NaCO3-	0.89475	0.89475	0.000%
H+	0.90074	0.90074	0.000%
UO2(OH)3-	0.89475	0.89475	0.000%
CaCl2(aq)	1.00000	1.00000	0.000%
CaOH+	0.88614	0.88614	0.000%
HSO4-	0.89475	0.89475	0.000%
UO2OH+	0.88614	0.88614	0.000%
(UO2)3(CO3)6(6-)	0.01509	0.01509	0.000%
NaOH(aq)	1.00000	1.00000	0.000%
HCl(aq)	1.00000	1.00000	0.000%
UO2++	0.62488	0.62488	0.000%
UO2SO4(aq)	1.00000	1.00000	0.000%
(UO2)3(OH)5+	0.88614	0.88614	0.000%
(UO2)3(OH)7-	0.89475	0.89475	0.000%
Fe(OH)3(aq)	1.00000	1.00000	0.000%
(UO2)2(OH)2++	0.62488	0.62488	0.000%
UO2Cl+	0.88614	0.88614	0.000%
Fe(OH)2+	0.88614	0.88614	0.000%
UO2(SO4)2--	0.63227	0.63227	0.000%
(UO2)4(OH)7+	0.88614	0.88614	0.000%
Fe(OH)4-	0.89475	0.89475	0.000%
UO2(OH)4--	0.63227	0.63227	0.000%
(UO2)3(OH)4++	0.62488	0.62488	0.000%
(UO2)3(OH)5CO2+	0.88614	0.88614	0.000%
(UO2)3O(OH)2(HCO3)+	0.88614	0.88614	0.000%
(UO2)2OH+++	0.35498	0.35498	0.000%
UO2Cl2(aq)	1.00000	1.00000	0.000%
FeOH++	0.62488	0.62488	0.000%
FeCO3+	0.88614	0.88614	0.000%
H2SO4(aq)	1.00000	1.00000	0.000%
HClO(aq)	1.00000	1.00000	0.000%
ClO-	0.89475	0.89475	0.000%
Fe+++	0.39829	0.39829	0.000%
FeHCO3+	0.88614	0.88614	0.000%
Fe++	0.63826	0.63826	0.000%
UO2+	0.88614	0.88614	0.000%
HO2-	0.89475	0.89475	0.000%
FeCO3(aq)	1.00000	1.00000	0.000%
FeSO4+	0.88614	0.88614	0.000%
FeSO4(aq)	1.00000	1.00000	0.000%
FeOH+	0.88614	0.88614	0.000%
FeCl2+	0.88614	0.88614	0.000%
FeCl+	0.88614	0.88614	0.000%
FeCl++	0.62488	0.62488	0.000%
ClO3-	0.89289	0.89289	0.000%

Fe(SO4)2-	0.89475	0.89475	0.000%
ClO4-	0.89289	0.89289	0.000%
(UO2)11(CO3)6(OH)12--	0.63227	0.63227	0.000%
Fe(OH)2(aq)	1.00000	1.00000	0.000%
ClO2-	0.89475	0.89475	0.000%
FeCl2(aq)	1.00000	1.00000	0.000%
HSO5-	0.89475	0.89475	0.000%
UO2(CO3)3(5-)	0.05460	0.05460	0.000%
Fe(OH)3-	0.89475	0.89475	0.000%
Fe2(OH)2++++	0.16406	0.16406	0.000%
FeCl4-	0.89475	0.89475	0.000%
U(OH)4(aq)	1.00000	1.00000	0.000%
HClO2(aq)	1.00000	1.00000	0.000%
FeCl4--	0.63227	0.63227	0.000%
UO2ClO3+	0.88614	0.88614	0.000%
Fe(OH)4--	0.63227	0.63227	0.000%
Fe3(OH)4(5+)	0.06230	0.06230	0.000%
Formate	0.89289	0.89289	0.000%
U(CO3)4----	0.15621	0.15621	0.000%
H2(aq)	1.00323	1.00323	0.000%
Ca(For)+	0.88614	0.88614	0.000%
S2O8--	0.63227	0.63227	0.000%
Na(For)(aq)	1.00000	1.00000	0.000%
Formic_acid(aq)	1.00000	1.00000	0.000%
SO3--	0.63709	0.63709	0.000%
HSO3-	0.89475	0.89475	0.000%
U(CO3)5(6-)	0.01509	0.01509	0.000%
CO(aq)	1.00000	1.00000	0.000%
UOH+++	0.35498	0.35498	0.000%
Oxalate	0.63227	0.63227	0.000%
UO2SO3(aq)	1.00000	1.00000	0.000%
H2SO3(aq)	1.00000	1.00000	0.000%
U(SO4)2(aq)	1.00000	1.00000	0.000%
SO2(aq)	1.00000	1.00000	0.000%
H-Oxalate	0.89475	0.89475	0.000%
USO4++	0.62488	0.62488	0.000%
U++++	0.16406	0.16406	0.000%
UCl+++	0.35498	0.35498	0.000%
Oxalic_acid(aq)	1.00000	1.00000	0.000%
Fe(For)+	0.88614	0.88614	0.000%
S2O6--	0.63227	0.63227	0.000%
U+++	0.35498	0.35498	0.000%
Ca(For)2(aq)	1.00000	1.00000	0.000%
Na(For)2-	0.89475	0.89475	0.000%
Formaldehyde(aq)	1.00000	1.00000	0.000%
UO2(SO3)2--	0.63227	0.63227	0.000%

Table 5.16-4 compares results for saturation indices (log Q/K) for the relevant phases in the system. The acceptance criterion is met for all phases.

Table 5.16-4. Test Case #15 (oxcalhem.3i) Calculated Phase Saturation Indices, Version 8.0 vs. Version 8.0a.

Phase	Version 8.0	Version 8.0a	Δ
Anhydrite	-1.90050	-1.90050	0.0000
Aragonite	-0.14440	-0.14440	0.0000
Bassanite	-2.54547	-2.54547	0.0000
CaSO4:0.5H2O(beta)	-2.71357	-2.71357	0.0000
CaUO4	-0.35368	-0.35368	0.0000
Calcite	0.00000	0.00000	0.0000
Fe(OH)3	-5.60151	-5.60151	0.0000
Goethite	-0.48027	-0.48027	0.0000
Gypsum	-1.72488	-1.72488	0.0000
Halite	-6.14809	-6.14809	0.0000
Hematite	0.00000	0.00000	0.0000
Ice	-0.13884	-0.13884	0.0000
Mirabilite	-6.53134	-6.53134	0.0000
Monohydrocalcite	-0.83384	-0.83384	0.0000
Na2U2O7	-4.54019	-4.54019	0.0000
Nahcolite	-4.60214	-4.60214	0.0000
Rutherfordine	-1.78118	-1.78118	0.0000
Schoepite	-0.90756	-0.90756	0.0000
Schoepite-dehy(.393)	-2.79833	-2.79833	0.0000
Schoepite-dehy(.648)	-2.28037	-2.28037	0.0000
Schoepite-dehy(.85)	-1.17110	-1.17110	0.0000
Schoepite-dehy(.9)	-1.09080	-1.09080	0.0000
Schoepite-dehy(1.0)	-1.17722	-1.17722	0.0000
UO2(OH)2(beta)	-1.01982	-1.01982	0.0000
UO2CO3	-1.76088	-1.76088	0.0000
UO3(alpha)	-4.71308	-4.71308	0.0000
UO3(beta)	-4.38348	-4.38348	0.0000
UO3(gamma)	-3.78128	-3.78128	0.0000
UO3:0.9H2O(alpha)	-1.09080	-1.09080	0.0000
UO3:2H2O	-0.90756	-0.90756	0.0000

5.17 Test Case #16 – Calculating the composition of a custom pH buffer test

5.17.1 Test Overview

This test case is to verify functional requirement #2 (R.2) for comparison of Version 8.0 with Version 8.0a.

Test Files:

Thermodynamic data file:	data1.cmp
EQ6 input file:	custbuf.3i
EQ6 output files:	custbuf.3o, custbuf.3p

5.17.2 Acceptance Criteria

See 5.16.2.

5.17.3 Evaluation

Table 5-17-1 compares the results for the set of general parameter outputs. These results are within the acceptance criteria. Because there is no Cl present in the solution, pHCl is undefined.

Table 5.17-1. Test Case #16 (custbuf.3i) General Parameter Outputs, Version 8.0 vs. Version 8.0a.

	Version 8.0	Version 8.0a	Δ
Ionic strength, m	0.0566616	0.0566616	0.000%
a_w	0.999000	0.99900	0.000%
x_w	0.998995	0.99899	0.001%
λ_w	1.00001	1.00000	-0.001%
fO2, bars	0.199526	0.19953	0.002%
pH (NBS)	8.0000	8.0000	0.0000
pmH	7.9650	7.9650	0.0000

Table 5.17-2 compares results for solute species molalities. The results are within the 0.005% acceptance criterion.

Table 5.17-2. Test Case #16 (custbuf.3i) Calculated Solute Species Molalities, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
B(OH)3(aq)	4.4326E-02	4.4326E-02	0.000%
Na+	5.6662E-03	5.6662E-03	0.000%
BO2-	5.6492E-03	5.6492E-03	0.000%
O2(aq)	1.6414E-04	1.6414E-04	0.000%

NaB(OH)4(aq)	2.4353E-05	2.4353E-05	0.000%
OH-	1.6917E-05	1.6917E-05	0.000%
NaOH(aq)	1.4514E-08	1.4514E-08	0.000%
H+	1.0840E-08	1.0840E-08	0.000%
B2O(OH)5-	4.4168E-14	4.4168E-14	0.000%
HO2-	5.2248E-20	5.2248E-20	0.000%
H2(aq)	1.6229E-38	1.6229E-38	0.000%

Table 5.17-3 compares results for solute species activity coefficients. These results are largely complementary to the molality results. The comparison indicates that the acceptance criteria are met.

Table 5.17-3. Test Case #16 (custbuf.3i) Calculated Solute Species Activity Coefficients, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
B(OH)3(aq)	1.00000	1.00000	0.000%
Na+	0.91411	0.91411	0.000%
BO2-	0.91854	0.91854	0.000%
O2(aq)	1.00138	1.00138	0.000%
NaB(OH)4(aq)	1.00000	1.00000	0.000%
OH-	0.91770	0.91770	0.000%
NaOH(aq)	1.00000	1.00000	0.000%
H+	0.92257	0.92257	0.000%
B2O(OH)5-	0.91854	0.91854	0.000%
HO2-	0.91854	0.91854	0.000%
H2(aq)	1.00138	1.00138	0.000%

Table 5.17-4 compares results for saturation indices (log Q/K) for the relevant solid phases in the system. The acceptance criterion is met for both phases.

Table 5.17-4. Test Case #16 (custbuf.3i) Calculated Phase Saturation Indices, Version 8.0 vs. Version 8.0a.

Phase	Version 8.0	Version 8.0a	Δ
Boric_acid	-1.64512	-1.64512	0.0000
Ice	-0.33047	-0.33047	0.0000

5.18 Test Case #17 – Finding precipitates from multiply-saturated sea water

5.18.1 Test Overview

This test case verifies functional requirements R.1, R.3 and R.4 for comparison of Version 8.0 with Version 8.0a.

Test Files:

Thermodynamic data file:	data1.cmp
EQ6 input file:	pptmins.6i
EQ6 output files:	pptmins.6o, pptmins.6p

5.18.2 Acceptance Criteria

See 5.16.2.

5.18.3 Evaluation

Table 5-18-1 compares the results for the set of general parameter outputs. These results are within the acceptance criteria of 0.005% and 0.001 for linear and logarithmic parameters.

Table 5.18-1. Test Case #17 (pptmins.6i) General Parameter Outputs, Version 8.0 vs. Version 8.0a.

	Version 8.0	Version 8.0a	Δ
Ionic strength, m	0.622507	0.62251	0.000%
a_w	0.982307	0.98231	0.000%
x_w	0.980881	0.98088	0.000%
λ_w	1.00145	1.0015	0.005%
fO2, bars	0.183356	0.18336	0.002%
pH (NBS)	6.7553	6.7553	0.0000
pmH	6.6432	6.6432	0.0000
pHCl	7.2205	7.2205	0.0000

Table 5.18-2 compares results for solute species molalities. The results are within the 0.005% acceptance criterion.

Table 5.18-2. Test Case #17 (pptmins.6i) Calculated Solute Species Molalities, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
Cl-	5.2436E-01	5.2436E-01	0.000%
Na+	4.4497E-01	4.4497E-01	0.000%
Mg++	4.0618E-02	4.0618E-02	0.000%
NaCl(aq)	1.6485E-02	1.6485E-02	0.000%

SO4--	1.3229E-02	1.3229E-02	0.000%
K+	9.9809E-03	9.9809E-03	0.000%
Ca++	9.0859E-03	9.0859E-03	0.000%
MgSO4(aq)	7.5184E-03	7.5184E-03	0.000%
NaSO4-	6.6575E-03	6.6575E-03	0.000%
MgCl+	4.6269E-03	4.6269E-03	0.000%
HCO3-	9.1098E-04	9.1098E-04	0.000%
Br-	8.3529E-04	8.3529E-04	0.000%
CaSO4(aq)	6.5866E-04	6.5866E-04	0.000%
B(OH)3(aq)	4.2169E-04	4.2169E-04	0.000%
NaHCO3(aq)	2.6119E-04	2.6119E-04	0.000%
CaCl+	2.2270E-04	2.2270E-04	0.000%
CO2(aq)	2.1805E-04	2.1805E-04	0.000%
O2(aq)	2.0082E-04	2.0082E-04	0.000%
KSO4-	1.6028E-04	1.6028E-04	0.000%
MgHCO3+	1.2725E-04	1.2725E-04	0.000%
Sr++	8.0551E-05	8.0551E-05	0.000%
SiO2(aq)	7.0524E-05	7.0524E-05	0.000%
KCl(aq)	6.6290E-05	6.6290E-05	0.000%
CaCl2(aq)	5.5653E-05	5.5653E-05	0.000%
F-	5.5640E-05	5.5640E-05	0.000%
CaHCO3+	2.2845E-05	2.2845E-05	0.000%
MgF+	1.5623E-05	1.5623E-05	0.000%
SrSO4(aq)	7.6554E-06	7.6554E-06	0.000%
NaBr(aq)	6.9102E-06	6.9102E-06	0.000%
SrCl+	4.6907E-06	4.6907E-06	0.000%
BO2-	1.9910E-06	1.9910E-06	0.000%
MgB(OH)4+	1.9552E-06	1.9552E-06	0.000%
MgCO3(aq)	1.9288E-06	1.9288E-06	0.000%
NaF(aq)	1.0906E-06	1.0906E-06	0.000%
CO3--	8.2428E-07	8.2428E-07	0.000%
CaCO3(aq)	7.5269E-07	7.5269E-07	0.000%
NaB(OH)4(aq)	7.2078E-07	7.2078E-07	0.000%
CaF+	5.8372E-07	5.8372E-07	0.000%
NaHSiO3(aq)	5.6382E-07	5.6382E-07	0.000%
IO3-	4.8855E-07	4.8855E-07	0.000%
CaB(OH)4+	2.8763E-07	2.8763E-07	0.000%
NaCO3-	2.2891E-07	2.2891E-07	0.000%
H+	2.2738E-07	2.2738E-07	0.000%
OH-	8.3526E-08	8.3526E-08	0.000%
HSiO3-	6.2994E-08	6.2994E-08	0.000%
KBr(aq)	6.0402E-08	6.0402E-08	0.000%
HSO4-	5.8594E-08	5.8594E-08	0.000%
HCl(aq)	1.2869E-08	1.2869E-08	0.000%
HF(aq)	9.7457E-09	9.7457E-09	0.000%
MgHPO4(aq)	6.9493E-09	6.9493E-09	0.000%

HPO4--	3.8818E-09	3.8818E-09	0.000%
H2PO4-	2.8952E-09	2.8952E-09	0.000%
NaOH(aq)	2.5823E-09	2.5823E-09	0.000%
CaOH+	2.5471E-09	2.5471E-09	0.000%
NaHPO4-	2.4594E-09	2.4594E-09	0.000%
SrCO3(aq)	1.9554E-09	1.9554E-09	0.000%
AlO2-	1.5425E-09	1.5425E-09	0.000%
SrF+	1.2596E-09	1.2596E-09	0.000%
CaHPO4(aq)	8.2240E-10	8.2240E-10	0.000%
AlF2+	7.0959E-10	7.0959E-10	0.000%
HAlO2(aq)	5.3383E-10	5.3383E-10	0.000%
AlF3(aq)	2.1775E-10	2.1775E-10	0.000%
AlF++	1.7307E-10	1.7307E-10	0.000%
MgPO4-	1.2893E-10	1.2893E-10	0.000%
KOH(aq)	1.1716E-10	1.1716E-10	0.000%
Al(OH)2+	9.9901E-11	9.9901E-11	0.000%
NaAlO2(aq)	5.6009E-11	5.6009E-11	0.000%
KHPO4-	3.7393E-11	3.7393E-11	0.000%
AlOH++	2.8356E-11	2.8356E-11	0.000%
KHSO4(aq)	1.6891E-11	1.6891E-11	0.000%
CaPO4-	1.6768E-11	1.6768E-11	0.000%
SrOH+	6.9574E-12	6.9574E-12	0.000%
AlF4-	2.9504E-12	2.9504E-12	0.000%
SrHPO4(aq)	1.2927E-12	1.2927E-12	0.000%
Al+++	1.0546E-12	1.0546E-12	0.000%
BF2(OH)2-	6.3503E-13	6.3503E-13	0.000%
PO3F--	4.1381E-13	4.1381E-13	0.000%
AlSO4+	3.1413E-13	3.1413E-13	0.000%
Fe(OH)3(aq)	2.2257E-13	2.2257E-13	0.000%
HIO3(aq)	1.8587E-13	1.8587E-13	0.000%
Fe(OH)2+	1.3152E-13	1.3152E-13	0.000%
H2SiO4--	1.3086E-13	1.3086E-13	0.000%
HF2-	1.2692E-13	1.2692E-13	0.000%
PO4---	9.9090E-14	9.9090E-14	0.000%
Al(SO4)2-	5.5220E-14	5.5220E-14	0.000%
H3PO4(aq)	5.2500E-14	5.2500E-14	0.000%
HBrO(aq)	4.3299E-15	4.3299E-15	0.000%
AlHPO4+	2.2627E-15	2.2627E-15	0.000%
Fe(OH)4-	4.4764E-16	4.4764E-16	0.000%
FeOH++	2.5982E-16	2.5982E-16	0.000%
H2F2(aq)	2.5670E-16	2.5670E-16	0.000%
HPO3F-	2.4185E-16	2.4185E-16	0.000%
BrO-	1.4414E-16	1.4414E-16	0.000%
MgH2PO4+	1.0610E-16	1.0610E-16	0.000%
MgP2O7--	1.0033E-16	1.0033E-16	0.000%
H6(H2SiO4)4--	8.6159E-17	8.6159E-17	0.000%

Br2(aq)	6.8734E-17	6.8734E-17	0.000%
HClO(aq)	2.6902E-17	2.6902E-17	0.000%
BF3OH-	1.6020E-17	1.6020E-17	0.000%
CaH2PO4+	1.0206E-17	1.0206E-17	0.000%
H2SO4(aq)	7.1885E-18	7.1885E-18	0.000%
CaP2O7--	6.6922E-18	6.6922E-18	0.000%
ClO-	5.9128E-18	5.9128E-18	0.000%
Al2(OH)2++++	2.1170E-18	2.1170E-18	0.000%
Mg4(OH)4++++	1.7633E-18	1.7633E-18	0.000%
FeCO3+	1.7539E-18	1.7539E-18	0.000%
HP2O7---	1.3196E-18	1.3196E-18	0.000%
Br3-	1.3071E-18	1.3071E-18	0.000%
NaHP2O7--	1.0144E-18	1.0144E-18	0.000%
Na2P2O7--	6.5262E-19	6.5262E-19	0.000%
I-	3.0864E-19	3.0864E-19	0.000%
B2O(OH)5-	2.9930E-19	2.9930E-19	0.000%
NaP2O7---	2.6847E-19	2.6847E-19	0.000%
IO4-	1.4660E-19	1.4660E-19	0.000%
P2O7----	1.1199E-19	1.1199E-19	0.000%
H2P2O7--	1.0298E-19	1.0298E-19	0.000%
FeCl2+	3.1158E-20	3.1158E-20	0.000%
FeHPO4+	2.1358E-20	2.1358E-20	0.000%
Fe+++	1.6519E-20	1.6519E-20	0.000%
SrH2PO4+	1.6416E-20	1.6416E-20	0.000%
KP2O7---	6.0056E-21	6.0056E-21	0.000%
FeF++	3.7122E-21	3.7122E-21	0.000%
SrP2O7--	2.0044E-21	2.0044E-21	0.000%
NaI(aq)	1.6746E-21	1.6746E-21	0.000%
Fe++	8.2030E-22	8.2030E-22	0.000%
FeF2+	6.2478E-22	6.2478E-22	0.000%
IO-	5.4868E-22	5.4868E-22	0.000%
FeSO4+	4.0704E-22	4.0704E-22	0.000%
FeCl++	3.8120E-22	3.8120E-22	0.000%
H2PO3F(aq)	1.8977E-22	1.8977E-22	0.000%
FeHCO3+	9.7207E-23	9.7207E-23	0.000%
FeSO4(aq)	7.2974E-23	7.2974E-23	0.000%
Al3(OH)4(5+)	6.9609E-23	6.9609E-23	0.000%
FeCl+	6.8934E-23	6.8934E-23	0.000%
H4(H2SiO4)4----	3.0826E-23	3.0826E-23	0.000%
KI(aq)	3.0752E-23	3.0752E-23	0.000%
Fe(SO4)2-	1.7812E-23	1.7812E-23	0.000%
ClO3-	9.7915E-24	9.7915E-24	0.000%
BF4-	7.0344E-24	7.0344E-24	0.000%
HO2-	6.0815E-24	6.0815E-24	0.000%
ClO4-	5.3100E-24	5.3100E-24	0.000%
FeCl4-	4.0745E-24	4.0745E-24	0.000%

FeCO3(aq)	1.7184E-24	1.7184E-24	0.000%
H3P2O7-	1.0607E-24	1.0607E-24	0.000%
FeOH+	5.1481E-25	5.1481E-25	0.000%
FeF+	2.5125E-25	2.5125E-25	0.000%
FeCl4--	1.7690E-25	1.7690E-25	0.000%
FeCl2(aq)	7.7731E-26	7.7731E-26	0.000%
AlH2PO4++	7.2871E-26	7.2871E-26	0.000%
BrO3-	2.0396E-26	2.0396E-26	0.000%
ClO2-	8.8663E-28	8.8663E-28	0.000%
FeHPO4(aq)	5.3788E-28	5.3788E-28	0.000%
HSO5-	4.8384E-29	4.8384E-29	0.000%
FePO4-	4.4679E-29	4.4679E-29	0.000%
Fe2(OH)2++++	2.8560E-29	2.8560E-29	0.000%
Fe(OH)2(aq)	1.4795E-29	1.4795E-29	0.000%
H4P2O7(aq)	4.2089E-30	4.2089E-30	0.000%
SiF6--	2.0277E-31	2.0277E-31	0.000%
HClO2(aq)	1.6082E-31	1.6082E-31	0.000%
FeH2PO4++	1.3412E-32	1.3412E-32	0.000%
Fe(OH)3-	4.7161E-33	4.7161E-33	0.000%
FeH2PO4+	1.8385E-35	1.8385E-35	0.000%
Fe3(OH)4(5+)	1.0180E-38	1.0180E-38	0.000%
Fe(OH)4--	9.9677E-41	9.9677E-41	0.000%
S2O8--	4.8905E-43	4.8905E-43	0.000%
BrO4-	3.3025E-44	3.3025E-44	0.000%
Formate	9.6610E-45	9.6610E-45	0.000%
H2(aq)	4.3742E-45	4.3742E-45	0.000%
Mg(For)+	3.2442E-45	3.2442E-45	0.000%
Na(For)(aq)	2.1125E-45	2.1125E-45	0.000%
Al13O4(OH)24(7+)	7.5055E-46	7.5055E-46	0.000%
Ca(For)+	5.6786E-46	5.6786E-46	0.000%
K(For)(aq)	4.2361E-47	4.2361E-47	0.000%
I3-	3.0011E-47	3.0011E-47	0.000%
SO3--	1.8504E-47	1.8504E-47	0.000%
HSO3-	1.5392E-47	1.5392E-47	0.000%
Formic_acid(aq)	6.5065E-48	6.5065E-48	0.000%
Sr(For)+	3.8936E-48	3.8936E-48	0.000%
CO(aq)	1.4904E-50	1.4904E-50	0.000%
Oxalate	5.0255E-52	5.0255E-52	0.000%
H2SO3(aq)	1.9226E-52	1.9226E-52	0.000%
SO2(aq)	1.3933E-52	1.3933E-52	0.000%
H-Oxalate	4.2171E-55	4.2171E-55	0.000%
Oxalic_acid(aq)	9.6405E-61	9.6405E-61	0.000%
Fe(For)+	1.2798E-64	1.2798E-64	0.000%
S2O6--	2.5372E-68	2.5372E-68	0.000%
Mg(For)2(aq)	1.0181E-88	1.0181E-88	0.000%
Ca(For)2(aq)	1.7820E-89	1.7820E-89	0.000%

Na(For)2-	1.0382E-89	1.0382E-89	0.000%
K(For)2-	1.9894E-91	1.9894E-91	0.000%
Sr(For)2(aq)	1.1154E-91	1.1154E-91	0.000%
Formaldehyde(aq)	1.2908E-93	1.2908E-93	0.000%
S2O5--	9.6920E-99	9.6920E-99	0.000%

Table 5.18-3 compares results for solute species activity coefficients. These results are largely complementary to the molality results. The comparison indicates that the acceptance criteria are met.

Table 5.18-3. Test Case #17 (pptmins.6i) Calculated Solute Species Activity Coefficients, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
Cl-	0.65343	0.65343	0.000%
Na+	0.64699	0.64699	0.000%
Mg++	0.29343	0.29343	0.000%
NaCl(aq)	1.00000	1.00000	0.000%
SO4--	0.18476	0.18476	0.000%
K+	0.60534	0.60534	0.000%
Ca++	0.22961	0.22961	0.000%
MgSO4(aq)	1.00000	1.00000	0.000%
NaSO4-	0.69839	0.69839	0.000%
MgCl+	0.64699	0.64699	0.000%
HCO3-	0.69839	0.69839	0.000%
Br-	0.65343	0.65343	0.000%
CaSO4(aq)	1.00000	1.00000	0.000%
B(OH)3(aq)	1.00000	1.00000	0.000%
NaHCO3(aq)	1.00000	1.00000	0.000%
CaCl+	0.64699	0.64699	0.000%
CO2(aq)	1.15398	1.15398	0.000%
O2(aq)	1.15398	1.15398	0.000%
KSO4-	0.69839	0.69839	0.000%
MgHCO3+	0.64699	0.64699	0.000%
Sr++	0.19485	0.19485	0.000%
SiO2(aq)	1.00000	1.00000	0.000%
KCl(aq)	1.00000	1.00000	0.000%
CaCl2(aq)	1.00000	1.00000	0.000%
F-	0.67702	0.67702	0.000%
CaHCO3+	0.64699	0.64699	0.000%
MgF+	0.64699	0.64699	0.000%
SrSO4(aq)	1.00000	1.00000	0.000%
NaBr(aq)	1.00000	1.00000	0.000%

SrCl+	0.64699	0.64699	0.000%
BO2-	0.69839	0.69839	0.000%
MgB(OH)4+	0.64699	0.64699	0.000%
MgCO3(aq)	1.00000	1.00000	0.000%
NaF(aq)	1.00000	1.00000	0.000%
CO3--	0.20606	0.20606	0.000%
CaCO3(aq)	1.00000	1.00000	0.000%
NaB(OH)4(aq)	1.00000	1.00000	0.000%
CaF+	0.64699	0.64699	0.000%
NaHSiO3(aq)	1.00000	1.00000	0.000%
IO3-	0.69839	0.69839	0.000%
CaB(OH)4+	0.64699	0.64699	0.000%
NaCO3-	0.69839	0.69839	0.000%
H+	0.77250	0.77250	0.000%
OH-	0.67702	0.67702	0.000%
HSiO3-	0.69839	0.69839	0.000%
KBr(aq)	1.00000	1.00000	0.000%
HSO4-	0.69839	0.69839	0.000%
HCl(aq)	1.00000	1.00000	0.000%
HF(aq)	1.00000	1.00000	0.000%
MgHPO4(aq)	1.00000	1.00000	0.000%
HPO4--	0.18476	0.18476	0.000%
H2PO4-	0.69839	0.69839	0.000%
NaOH(aq)	1.00000	1.00000	0.000%
CaOH+	0.64699	0.64699	0.000%
NaHPO4-	0.69839	0.69839	0.000%
SrCO3(aq)	1.00000	1.00000	0.000%
AlO2-	0.69839	0.69839	0.000%
SrF+	0.64699	0.64699	0.000%
CaHPO4(aq)	1.00000	1.00000	0.000%
AlF2+	0.64699	0.64699	0.000%
HAlO2(aq)	1.00000	1.00000	0.000%
AlF3(aq)	1.00000	1.00000	0.000%
AlF++	0.17689	0.17689	0.000%
MgPO4-	0.69839	0.69839	0.000%
KOH(aq)	1.00000	1.00000	0.000%
Al(OH)2+	0.64699	0.64699	0.000%
NaAlO2(aq)	1.00000	1.00000	0.000%
KHPO4-	0.69839	0.69839	0.000%
AlOH++	0.17689	0.17689	0.000%
KHSO4(aq)	1.00000	1.00000	0.000%
CaPO4-	0.69839	0.69839	0.000%
SrOH+	0.64699	0.64699	0.000%
AlF4-	0.69839	0.69839	0.000%
SrHPO4(aq)	1.00000	1.00000	0.000%
Al+++	0.07705	0.07705	0.000%

BF2(OH)2-	0.69839	0.69839	0.000%
PO3F--	0.18476	0.18476	0.000%
AlSO4+	0.64699	0.64699	0.000%
Fe(OH)3(aq)	1.00000	1.00000	0.000%
HIO3(aq)	1.00000	1.00000	0.000%
Fe(OH)2+	0.64699	0.64699	0.000%
H2SiO4--	0.18476	0.18476	0.000%
HF2-	0.69839	0.69839	0.000%
PO4---	0.01964	0.01964	0.000%
Al(SO4)2-	0.69839	0.69839	0.000%
H3PO4(aq)	1.00000	1.00000	0.000%
HBrO(aq)	1.00000	1.00000	0.000%
AlHPO4+	0.64699	0.64699	0.000%
Fe(OH)4-	0.69839	0.69839	0.000%
FeOH++	0.17689	0.17689	0.000%
H2F2(aq)	1.00000	1.00000	0.000%
HPO3F-	0.69839	0.69839	0.000%
BrO-	0.69839	0.69839	0.000%
MgH2PO4+	0.64699	0.64699	0.000%
MgP2O7--	0.18476	0.18476	0.000%
H6(H2SiO4)4--	0.18476	0.18476	0.000%
Br2(aq)	1.00000	1.00000	0.000%
HClO(aq)	1.00000	1.00000	0.000%
BF3OH-	0.69839	0.69839	0.000%
CaH2PO4+	0.64699	0.64699	0.000%
H2SO4(aq)	1.00000	1.00000	0.000%
CaP2O7--	0.18476	0.18476	0.000%
ClO-	0.69839	0.69839	0.000%
Al2(OH)2++++	0.00199	0.00199	0.000%
Mg4(OH)4++++	0.00199	0.00199	0.000%
FeCO3+	0.64699	0.64699	0.000%
HP2O7---	0.01964	0.01964	0.000%
Br3-	0.69839	0.69839	0.000%
NaHP2O7--	0.18476	0.18476	0.000%
Na2P2O7--	0.18476	0.18476	0.000%
I-	0.65343	0.65343	0.000%
B2O(OH)5-	0.69839	0.69839	0.000%
NaP2O7---	0.01964	0.01964	0.000%
IO4-	0.67702	0.67702	0.000%
P2O7----	0.00084	0.00084	0.000%
H2P2O7--	0.18476	0.18476	0.000%
FeCl2+	0.64699	0.64699	0.000%
FeHPO4+	0.64699	0.64699	0.000%
Fe+++	0.07705	0.07705	0.000%
SrH2PO4+	0.64699	0.64699	0.000%
KP2O7---	0.01964	0.01964	0.000%

FeF++	0.17689	0.17689	0.000%
SrP2O7--	0.18476	0.18476	0.000%
NaI(aq)	1.00000	1.00000	0.000%
Fe++	0.22961	0.22961	0.000%
FeF2+	0.64699	0.64699	0.000%
IO-	0.69839	0.69839	0.000%
FeSO4+	0.64699	0.64699	0.000%
FeCl++	0.17689	0.17689	0.000%
H2PO3F(aq)	1.00000	1.00000	0.000%
FeHCO3+	0.64699	0.64699	0.000%
FeSO4(aq)	1.00000	1.00000	0.000%
Al3(OH)4(5+)	0.00010	0.00010	0.000%
FeCl+	0.64699	0.64699	0.000%
H4(H2SiO4)4----	0.00084	0.00084	0.000%
KI(aq)	1.00000	1.00000	0.000%
Fe(SO4)2-	0.69839	0.69839	0.000%
ClO3-	0.67702	0.67702	0.000%
BF4-	0.69839	0.69839	0.000%
HO2-	0.69839	0.69839	0.000%
ClO4-	0.67702	0.67702	0.000%
FeCl4-	0.69839	0.69839	0.000%
FeCO3(aq)	1.00000	1.00000	0.000%
H3P2O7-	0.69839	0.69839	0.000%
FeOH+	0.64699	0.64699	0.000%
FeF+	0.64699	0.64699	0.000%
FeCl4--	0.18476	0.18476	0.000%
FeCl2(aq)	1.00000	1.00000	0.000%
AlH2PO4++	0.17689	0.17689	0.000%
BrO3-	0.67702	0.67702	0.000%
ClO2-	0.69839	0.69839	0.000%
FeHPO4(aq)	1.00000	1.00000	0.000%
HSO5-	0.69839	0.69839	0.000%
FePO4-	0.69839	0.69839	0.000%
Fe2(OH)2++++	0.00199	0.00199	0.000%
Fe(OH)2(aq)	1.00000	1.00000	0.000%
H4P2O7(aq)	1.00000	1.00000	0.000%
SiF6--	0.18476	0.18476	0.000%
HClO2(aq)	1.00000	1.00000	0.000%
FeH2PO4++	0.17689	0.17689	0.000%
Fe(OH)3-	0.69839	0.69839	0.000%
FeH2PO4+	0.64699	0.64699	0.000%
Fe3(OH)4(5+)	0.00010	0.00010	0.000%
Fe(OH)4--	0.18476	0.18476	0.000%
S2O8--	0.18476	0.18476	0.000%
BrO4-	0.69839	0.69839	0.000%
Formate	0.67702	0.67702	0.000%

H2(aq)	1.15398	1.15398	0.000%
Mg(For)+	0.64699	0.64699	0.000%
Na(For)(aq)	1.00000	1.00000	0.000%
Al13O4(OH)24(7+)	0.00000	0.00000	0.000%
Ca(For)+	0.64699	0.64699	0.000%
K(For)(aq)	1.00000	1.00000	0.000%
I3-	0.69839	0.69839	0.000%
SO3--	0.20606	0.20606	0.000%
HSO3-	0.69839	0.69839	0.000%
Formic_acid(aq)	1.00000	1.00000	0.000%
Sr(For)+	0.64699	0.64699	0.000%
CO(aq)	1.00000	1.00000	0.000%
Oxalate	0.18476	0.18476	0.000%
H2SO3(aq)	1.00000	1.00000	0.000%
SO2(aq)	1.00000	1.00000	0.000%
H-Oxalate	0.69839	0.69839	0.000%
Oxalic_acid(aq)	1.00000	1.00000	0.000%
Fe(For)+	0.64699	0.64699	0.000%
S2O6--	0.18476	0.18476	0.000%
Mg(For)2(aq)	1.00000	1.00000	0.000%
Ca(For)2(aq)	1.00000	1.00000	0.000%
Na(For)2-	0.69839	0.69839	0.000%
K(For)2-	0.69839	0.69839	0.000%
Sr(For)2(aq)	1.00000	1.00000	0.000%
Formaldehyde(aq)	1.00000	1.00000	0.000%
S2O5--	0.18476	0.18476	0.000%

Table 5.18-4 compares results for saturation indices (log Q/K) for the relevant solid phases in the system. The acceptance criterion is met for all phases.

Table 5.18-4. Test Case #17 (pptmins.6i) Calculated Phase Saturation Indices, Version 8.0 vs. Version 8.0a.

Phase	Version 8.0	Version 8.0a	Δ
Albite	-1.84463	-1.84463	0.0000
Albite_high	-3.16333	-3.16333	0.0000
Albite_low	-1.84463	-1.84463	0.0000
Alunite	-5.87961	-5.87961	0.0000
Analcime	-1.77688	-1.77688	0.0000
Andalusite	-5.76781	-5.76781	0.0000
Anhydrite	-0.98604	-0.98604	0.0000
Aragonite	-1.11478	-1.11478	0.0000
Arcanite	-5.24863	-5.24863	0.0000
Artinite	-6.47270	-6.47270	0.0000

Bassanite	-1.63482	-1.63482	0.0000
Beidellite-Ca	-2.35755	-2.35755	0.0000
Beidellite-H	-3.18661	-3.18661	0.0000
Beidellite-K	-2.36486	-2.36486	0.0000
Beidellite-Mg	-2.19497	-2.19497	0.0000
Beidellite-Na	-2.14960	-2.14960	0.0000
Bischofite	-7.29287	-7.29287	0.0000
Bloedite	-5.78223	-5.78223	0.0000
Boehmite	-0.40390	-0.40390	0.0000
Boric_acid	-3.21670	-3.21670	0.0000
Brucite	-4.72662	-4.72662	0.0000
CaSO4:0.5H2O(beta)	-1.80292	-1.80292	0.0000
Calcite	-0.97038	-0.97038	0.0000
Celadonite	-0.79596	-0.79596	0.0000
Celestite	-1.73893	-1.73893	0.0000
Chalcedony	-0.42356	-0.42356	0.0000
Chrysotile	-4.70683	-4.70683	0.0000
Clinoptilolite-Na	-7.04655	-7.04655	0.0000
Clinoptilolite-hy-Na	-7.04410	-7.04410	0.0000
Coesite	-0.96236	-0.96236	0.0000
Corundum	-3.98375	-3.98375	0.0000
Cristobalite(alpha)	-0.70286	-0.70286	0.0000
Cristobalite(beta)	-1.14636	-1.14636	0.0000
Dawsonite	-0.92325	-0.92325	0.0000
Diaspore	0.00000	0.00000	0.0000
Diopside	-6.86623	-6.86623	0.0000
Dolomite	0.00000	0.00000	0.0000
Dolomite-dis	-1.54440	-1.54440	0.0000
Dolomite-ord	0.00000	0.00000	0.0000
Enstatite	-3.89943	-3.89943	0.0000
Epsomite	-2.62754	-2.62754	0.0000
Fe(OH)3	-6.30813	-6.30813	0.0000
Fluorapatite	0.00000	0.00000	0.0000
Fluorite	-1.49155	-1.49155	0.0000
Gibbsite	-0.60345	-0.60345	0.0000
Glauberite	-3.51679	-3.51679	0.0000
Goethite	-1.17928	-1.17928	0.0000
Gypsum	-0.82564	-0.82564	0.0000
Halite	-2.59141	-2.59141	0.0000
Hematite	-1.39040	-1.39040	0.0000
Hexahydrite	-2.85529	-2.85529	0.0000
Huntite	-4.51714	-4.51714	0.0000
Ice	-0.14645	-0.14645	0.0000
Illite	-1.47260	-1.47260	0.0000
Jadeite	-3.31727	-3.31727	0.0000
K-Feldspar	-0.48288	-0.48288	0.0000

KBr	-6.55085	-6.55085	0.0000
Kainite	-6.93139	-6.93139	0.0000
Kalicinite	-5.69889	-5.69889	0.0000
Kalsilite	-3.35355	-3.35355	0.0000
Kaolinite	-0.80058	-0.80058	0.0000
Kieserite	-4.27633	-4.27633	0.0000
Kyanite	-5.49731	-5.49731	0.0000
Lansfordite	-3.24448	-3.24448	0.0000
Laumontite	-5.15374	-5.15374	0.0000
Lawsonite	-5.38141	-5.38141	0.0000
Magnesite	-0.65842	-0.65842	0.0000
Maximum_Microcline	-0.48288	-0.48288	0.0000
Mesolite	-0.57077	-0.57077	0.0000
Mg1.25SO4(OH)0.5:0.5H2O	-6.90661	-6.90661	0.0000
Mirabilite	-2.63107	-2.63107	0.0000
Monohydrocalcite	-1.81183	-1.81183	0.0000
Montmor-Ca	-1.53864	-1.53864	0.0000
Montmor-K	-1.47565	-1.47565	0.0000
Montmor-Mg	-1.30646	-1.30646	0.0000
Montmor-Na	-1.26399	-1.26399	0.0000
Mordenite	-3.72797	-3.72797	0.0000
Muscovite	-0.02338	-0.02338	0.0000
Na4Ca(SO4)3:2H2O	-6.80084	-6.80084	0.0000
NaBr	-6.77761	-6.77761	0.0000
NaBr:2H2O	-5.92321	-5.92321	0.0000
Nahcolite	-3.62535	-3.62535	0.0000
Natrolite	-4.24118	-4.24118	0.0000
Natron	-7.21031	-7.21031	0.0000
Nepheline	-4.57741	-4.57741	0.0000
Nesquehonite	-3.38358	-3.38358	0.0000
Nontronite-Ca	-0.79410	-0.79410	0.0000
Nontronite-H	-1.62316	-1.62316	0.0000
Nontronite-K	-0.80141	-0.80141	0.0000
Nontronite-Mg	-0.63142	-0.63142	0.0000
Nontronite-Na	-0.58615	-0.58615	0.0000
Paragonite	-2.28153	-2.28153	0.0000
Pentahydrite	-3.18714	-3.18714	0.0000
Phlogopite	-3.46853	-3.46853	0.0000
Picromerite	-7.19193	-7.19193	0.0000
Pseudowollastonite	-7.32909	-7.32909	0.0000
Pyrophyllite	-2.72575	-2.72575	0.0000
Quartz	-0.15236	-0.15236	0.0000
Sanidine_high	-1.68208	-1.68208	0.0000
Saponite-Ca	-2.64711	-2.64711	0.0000
Saponite-H	-3.47616	-3.47616	0.0000
Saponite-K	-2.65451	-2.65451	0.0000

Saponite-Mg	-2.48453	-2.48453	0.0000
Saponite-Na	-2.43916	-2.43916	0.0000
Scolecite	-3.20433	-3.20433	0.0000
Sellaite	-1.38739	-1.38739	0.0000
SiO2(am)	-1.43806	-1.43806	0.0000
Sillimanite	-6.13131	-6.13131	0.0000
SrCl2:6H2O	-7.28482	-7.28482	0.0000
SrF2	-5.11214	-5.11214	0.0000
Starkeyite	-3.56669	-3.56669	0.0000
Stilbite	-1.90803	-1.90803	0.0000
Strontianite	-0.93157	-0.93157	0.0000
Sylvite	-3.52985	-3.52985	0.0000
Syngenite	-4.74953	-4.74953	0.0000
Talc	-3.01531	-3.01531	0.0000
Thenardite	-3.38425	-3.38425	0.0000
Tridymite	-0.32386	-0.32386	0.0000
Wollastonite	-7.08989	-7.08989	0.0000

5.19 Test Case #18 – Microcline dissolution in a fluid-centered flow-through open system

5.19.1 Test Overview

This test case verifies functional requirements R.1, R.3, and R.7 for comparison of Version 8.0 with Version 8.0a.

Test Files:

Thermodynamic data file:	data1.cmp
EQ6 input file:	microft.6i
EQ6 output files:	microft.6o, microft.6p

5.19.2 Acceptance Criteria

See 5.16.2.

5.19.3 Evaluation

Table 5-19-1 compares the results for the set of general parameter outputs. These results are within the acceptance criteria.

Table 5.19-1. Test Case #18 (microft.6i) General Parameter Outputs, Version 8.0 vs. Version 8.0a.

	Version 8.0	Version 8.0a	Δ
Ionic strength, m	1.02530E-04	1.0253E-04	0.000%
a_w	0.999992	0.99999	0.000%
x_w	0.999992	0.99999	0.000%
λ_w	1.00000	1.0000	0.000%
fO2, bars	0.199526	0.19953	0.002%
pH (NBS)	7.5351	7.5351	0.0000
pmH	7.5300	7.5300	0.0000
pHCl	11.5352	11.5352	0.0000

Table 5.19-2 compares results for solute species molalities. The results are within the 0.005% acceptance criterion.

Table 5.19-2. Test Case #18 (microft.6i) Calculated Solute Species Molalities, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
SiO2(aq)	2.6172E-04	2.6172E-04	0.000%
K+	1.0250E-04	1.0250E-04	0.000%
Cl-	1.0116E-04	1.0116E-04	0.000%
HSiO3-	1.0127E-06	1.0127E-06	0.000%
OH-	3.5081E-07	3.5080E-07	-0.003%
H+	2.9510E-08	2.9510E-08	0.000%
AlO2-	3.8673E-09	3.8673E-09	0.000%
KCl(aq)	3.2427E-10	3.2427E-10	0.000%
HAlO2(aq)	3.1452E-10	3.1452E-10	0.000%
KOH(aq)	1.2041E-11	1.2041E-11	0.000%
Al(OH)2+	6.3988E-12	6.3989E-12	0.002%
H2SiO4--	3.5348E-12	3.5348E-12	0.000%
HCl(aq)	6.2351E-13	6.2351E-13	0.000%
H6(H2SiO4)4--	1.3239E-13	1.3239E-13	0.000%
AlOH++	8.3897E-14	8.3898E-14	0.001%
Al+++	2.3477E-16	2.3477E-16	0.000%
H4(H2SiO4)4----	8.9799E-21	8.9799E-21	0.000%
Al2(OH)2++++	1.2943E-24	1.2943E-24	0.000%
Al3(OH)4(5+)	2.3067E-31	2.3068E-31	0.004%
Al13O4(OH)24(7+)	7.4220E-62	7.4222E-62	0.003%

Table 5.19-3 compares results for solute species activity coefficients. These results are largely complementary to the molality results. The comparison indicates that the acceptance criteria are met for all species.

Table 5.19-3. Test Case #18 (microft.6i) Calculated Solute Species Activity Coefficients, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
SiO2(aq)	1.00000	1.00000	0.000%
K+	0.98833	0.98833	0.000%
Cl-	0.98833	0.98833	0.000%
HSiO3-	0.98833	0.98833	0.000%
OH-	0.98833	0.98833	0.000%
H+	0.98855	0.98855	0.000%
AlO2-	0.98833	0.98833	0.000%
KCl(aq)	1.00000	1.00000	0.000%
HAlO2(aq)	1.00000	1.00000	0.000%
KOH(aq)	1.00000	1.00000	0.000%
Al(OH)2+	0.98833	0.98833	0.000%
H2SiO4--	0.95411	0.95411	0.000%
HCl(aq)	1.00000	1.00000	0.000%
H6(H2SiO4)4--	0.95411	0.95411	0.000%
AlOH++	0.95411	0.95411	0.000%
Al+++	0.90095	0.90095	0.000%
H4(H2SiO4)4----	0.82851	0.82851	0.000%
Al2(OH)2++++	0.82909	0.82909	0.000%
Al3(OH)4(5+)	0.74645	0.74645	0.000%
Al13O4(OH)24(7+)	0.56377	0.56377	0.000%

Table 5.19-4 compares results for saturation indices (log Q/K) for the relevant solid phases in the system. The acceptance criterion is met for all phases.

Table 5.19-4. Test Case #18 (microft.6i) Calculated Phase Saturation Indices, Version 8.0 vs. Version 8.0a.

Phase	Version 8.0	Version 8.0a	Δ
Andalusite	-5.66557E+00	-5.66557E+00	0.0000
Beidellite-H	-1.63188E+00	-1.63188E+00	0.0000
Beidellite-K	-1.13876E+00	-1.13876E+00	0.0000
Boehmite	-6.33650E-01	-6.33650E-01	0.0000
Chalcedony	1.45930E-01	1.45930E-01	0.0000
Coesite	-3.92870E-01	-3.92870E-01	0.0000
Corundum	-4.45100E+00	-4.45100E+00	0.0000
Cristobalite(alpha)	-1.33370E-01	-1.33370E-01	0.0000
Cristobalite(beta)	-5.76870E-01	-5.76870E-01	0.0000

Diaspore	-2.29750E-01	-2.29750E-01	0.0000
Gibbsite	-8.25450E-01	-8.25450E-01	0.0000
Ice	-1.38700E-01	-1.38700E-01	0.0000
K-Feldspar	0.00000E+00	0.00000E+00	0.0000
Kalsilite	-4.00966E+00	-4.00966E+00	0.0000
Kaolinite	-1.13340E-01	-1.13340E-01	0.0000
Kyanite	-5.39507E+00	-5.39507E+00	0.0000
Maximum_Microcline	0.00000E+00	0.00000E+00	0.0000
Muscovite	0.00000E+00	0.00000E+00	0.0000
Pyrophyllite	-9.07280E-01	-9.07280E-01	0.0000
Quartz	4.17130E-01	4.17130E-01	0.0000
Sanidine_high	-1.19920E+00	-1.19920E+00	0.0000
SiO2(am)	-8.68570E-01	-8.68570E-01	0.0000
Sillimanite	-6.02907E+00	-6.02907E+00	0.0000
Tridymite	2.45630E-01	2.45630E-01	0.0000

5.20 Test Case #19 – Kinetics of quartz precipitation

5.20.1 Test Overview

This test case verifies functional requirements R.1 and R.6 for comparison of Version 8.0 with Version 8.0a.

Test Files:

Thermodynamic data file:	data1.cmp
EQ6 input file:	pptqtz.6i
EQ6 output files:	pptqtz.6o, pptqtz.6p

5.20.2 Acceptance Criteria

See 5.16.2.

5.20.3 Evaluation

Table 5-20-1 compares the results for the set of general parameter outputs. These results are within the acceptance criteria.

Table 5.20-1. Test Case #19 (pptqtz.6i) General Parameter Outputs, Version 8.0 vs. Version 8.0a.

	Version 8.0	Version 8.0a	Δ
Ionic strength, m	2.43909E-06	2.4391E-06	0.000%

a_w	0.999980	0.99998	0.000%
x_w	0.999980	0.99998	0.000%
λ_w	1.000000	1.00000	0.000%
fO2, bars	1.000000	1.00000	0.000%
pH (NBS)	5.6137	5.6137	0.0000
pmH	5.6128	5.6128	0.0000

Table 5.20-2 compares results for solute species molalities. The results are within the 0.005% acceptance criterion.

Table 5.20-2. Test Case #19 (pptqtz.6i) Calculated Solute Species Molalities, Version 8.0 vs. Version 8.0a.

Species	*Version 8.0*	*Version 8.0a*	Δ
SiO2(aq)	1.0775E-03	1.0775E-03	0.000%
CO2(aq)	1.1138E-05	1.1138E-05	0.000%
H+	2.4390E-06	2.4390E-06	0.000%
HCO3-	1.7690E-06	1.7690E-06	0.000%
HSiO3-	3.9638E-07	3.9638E-07	0.000%
OH-	2.7358E-07	2.7358E-07	0.000%
CO3--	5.9830E-11	5.9830E-11	0.000%

Table 5.20-3 compares results for solute species activity coefficients. These results are largely complementary to the molality results. The comparison indicates that the acceptance criteria are met for all species.

Table 5.20-3. Test Case #19 (pptqtz.6i) Calculated Solute Species Activity Coefficients, Version 8.0 vs. Version 8.0a.

Species	Version 8.0	Version 8.0a	Δ
SiO2(aq)	1.00000	1.00000	0.000%
CO2(aq)	1.00000	1.00000	0.000%
H+	0.99793	0.99793	0.000%
HCO3-	0.99793	0.99793	0.000%
HSiO3-	0.99793	0.99793	0.000%
OH-	0.99793	0.99793	0.000%
CO3--	0.99129	0.99129	0.000%

Table 5.20-4 compares results for saturation indices (log Q/K) for the relevant solid phases in the system. The acceptance criterion is met for all phases.

Table 5.20-4. Test Case #19 (pptqtz.6i) Calculated Phase Saturation Indices, Version 8.0 vs. Version 8.0a.

Phase	Version 8.0	Version 8.0a	Δ
Chalcedony	-1.43900E-01	-1.43900E-01	0.0000
Coesite	-5.80580E-01	-5.80580E-01	0.0000
Cristobalite(alpha)	-3.40720E-01	-3.40720E-01	0.0000
Cristobalite(beta)	-6.36440E-01	-6.36440E-01	0.0000
Ice	-4.90450E-01	-4.90450E-01	0.0000
Quartz	6.99400E-02	6.99400E-02	0.0000
SiO2(am)	-8.06270E-01	-8.06270E-01	0.0000
Tridymite	-1.05710E-01	-1.05710E-01	0.0000

Table 5.20-5 compares results for dissolved Si molalities on a logarithmic scale as a function of reaction progress (time). It should be noted that in Version 8.0, dissolved Si molalities as a function of reaction progress are reported in the pptqtz.6t file on a logarithmic scale. In Version 8.0a, dissolved Si molalities as a function of reaction progress are reported in the pptqtz.csv file on a linear scale. Therefore, dissolved Si molalities are compared on a logarithmic scale. The acceptance criterion of 0.001 is met for all points of reaction progress.

Table 5.20-5. Test Case #19 (pptqtz.6i) Calculated Dissolved Si Molalities on a Logarithmic Scale as a Function of Reaction Progress, Version 8.0 vs. Version 8.0a.

Reaction Progress, Xi	time (days)	Version 8.0	Version 8.0a	Δ
0	0.000E+00	-2.7744	-2.7744	0.0000
1.00E-09	6.723E-06	-2.7744	-2.7744	0.0000
5.00E-05	3.477E-01	-2.7876	-2.7875	0.0001
1.00E-04	7.206E-01	-2.8011	-2.8011	0.0000
1.50E-04	1.123E+00	-2.8150	-2.8150	0.0000
2.00E-04	1.559E+00	-2.8295	-2.8294	0.0001
2.50E-04	2.036E+00	-2.8444	-2.8444	0.0000
3.00E-04	2.562E+00	-2.8598	-2.8598	0.0000
3.50E-04	3.148E+00	-2.8758	-2.8758	0.0000
4.00E-04	3.810E+00	-2.8925	-2.8925	0.0000
4.50E-04	4.569E+00	-2.9098	-2.9097	0.0001
5.00E-04	5.462E+00	-2.9278	-2.9278	0.0000
5.50E-04	6.542E+00	-2.9465	-2.9465	0.0000
6.00E-04	7.913E+00	-2.9662	-2.9662	0.0000
6.03E-04	8.009E+00	-2.9674	-2.9674	0.0000

6.0 CONCLUSIONS

EQ3/6 v. 8.0a has been tested against FMT v. 2.4 using a suite of WIPP-related and WIPP-specific problems. The EQ3/6 runs were made using the data0.fmt data file, which is a translation of the FMT_050405.CHEMDAT file used with the FMT runs. Differences in the results obtained from the two codes are mainly attributed to two factors. The first is the "front end" problem which results from the two codes requiring different kinds of inputs for the initial aqueous solution composition. EQ3/6 has a front end in the EQ3NR code which accepts the usual kinds of inputs describing an aqueous solution, such as solute component molalities and pH. FMT does not have a proper front end. The code takes as input value for the number of moles of chemical elements (and pseudo-elements). These must be calculated a priori from solution data. Generally pH is ignored. The actual pH which results is largely a function of how certain components are represented in calculating the moles of the elements. For example, the carbonate component can be represented as HCO_3^-, CO_3^{2-}, CO_2 (aq), or some mixture thereof. In the past, the details of such calculations seem to be somewhat obscure, though attention has been paid to the reasonableness of the resulting pH values (generally as represented by the "Pitzer pH"). Closely tied to the front end problem is how the codes address charge balance. FMT adjusts the number of moles of oxygen. EQ3/6 offers two options (calculate and fix the imbalance, or adjust one of the ionic components for to achieve charge balance). What the two codes do is necessarily non-equivalent. The second major factor in differences between results of the two codes is the fact that FMT uses the Pitzer (1975, eq. 47) approximation for the J(x) function used in the calculation of higher-order electrical interaction terms in the activity coefficients. EQ3/6 uses the later Harvie (1981) approximation, which is the one used in essentially all modern work involving Pitzer's equations (including the Harvie et al. 1984 model for the sea-salt system that forms the core of the FMT CHEMDAT database). A lesser factor is how the two codes treat the special (and fictive) species NegIon and PosIon. EQ3/6 includes these in calculating the ionic strength. FMT does not. These appear to have been not much used in FMT calculations. NegIon does appear in two of the test cases addressed in the previous section (Test Case #4 and Test Case #10).

Three numerical acceptance criteria were used in evaluating the differences: 1% for "linear" quantities, 0.01 for pH (which is intrinsically logarithmic), and 0.004 for other "logarithmic" quantities. In practice, the 0.004 criterion only applied to saturation indices (log Q/K). In general, the limited precision with which FMT reports saturation indices meant that even in the best of cases this criterion was often exceeded. Put more succinctly, this criterion was of limited usefulness.

Three kinds of test problems have been defined. Type 1 problems start with "pure" water, to which various minerals are added. Because the initial solution is necessarily well-balanced with respect to electric charge and dissociation of pure water produces very little H^+ and OH^-, these problems greatly minimize differences resulting from the front end factor. In all test cases of this type (Test Cases #3 and Test Cases #6-9), the results reported by the two codes are excellent, within numerical criteria discussed above, with the usual exception of the criterion applied to saturation indices owing to limited FMT reporting precision. These results were excellent despite the fact that the two codes were using different approximations for the J(x) function. When Test Case #3 was re-run having EQ3/6 use the same approximation used by FMT, the results were even closer. Similar recalculations were not attempted for the other test cases in this category.

Type 2 problems start with an aqueous solution composition that is typically relatively simply and well-charge balanced, thus minimizing front end problems associated with how the two codes treat charge imbalance. The test cases of this type were Test Cases #1-2 and Test Cases #5A and 5B. Excellent results (within the usual numerical criteria) were obtained for Test Cases #1 and #2. Substantially larger discrepancies were obtained in the case of Test Cases #5A, and #5B. Discrepancies were especially notable for highly charged species. These test cases were re-run using EQ3/6, with the code set to use the same J(x) approximation. The results were much improved, and become excellent for Test Case #5B. Agreement was not quite so good for Test Case #5A, apparently due to the presence of extra water in the FMT run. This appears to be somehow associated with the fact that on the FMT side, Test Cases #5A and 5B were obtained as parts of a titration simulation (but Test Case #5B did not seem to be much affected).

Type 3 problems start with an aqueous solution that is more complex and usually not well charge-balanced (or at least seemingly so to at least one of the codes). These problems include Test Case #4, Test Case #10, and Test Cases #11-14. These problems are the most strongly affected by the front end issue. Also, they typically include some very highly charged species and thus are sensitive as well to the issue of different J(x) approximations. Test Cases #4 and #10 in addition make use of the NegIon species. Agreement between the two codes for Test Cases #4 and #10 (SPC brine and SPC brine with actinides, respectively) was not very good. This is attributed to a combination of front end effects, the use of different J(x) approximations, and different treatment of the NegIon input. No further attempt was made to improve the results for these test cases, principally because there was no way to compensate for the NegIon effect without changing one or both codes. Because of a general similarity of Test Case #10 with Test Cases #11-14, which do not involve the use of NegIon, it was decided to move on and do further analyses only with of those test cases. Test Case #11 (add minerals and actinides to GWB brine) typifies the last four test cases. Initial agreement between the two codes was fair at best (poor for the molalities and activity coefficients of highly charged species). By re-running the problem with EQ3/6 using the same J(x) approximation as FMT, the results were improved noticeably but agreement was still only fair at best. By going one step farther redefining the EQ3/6 input to be consistent with the FMT model for the initial solution (taking results from the FMT .INGUESS file), the front end problem was overcome as well and excellent results (within the numerical acceptance criteria, allowing for the low precision with which FMT reports saturation indices) were obtained. This was similarly shown for Test Case #13 (in which the EDTA level was increased tenfold. The same factors are considered to apply to Test Cases #12 and #14, although additional runs to demonstrate this were not made. It is believed that excellent results could also be obtained for Test Cases #4 and #10 if the problems were redefined as for Test Cases #11 and #13 (eliminate NegIon in the process, as by charge-balancing on chloride) and running EQ3/6 with the same J(x) approximation as FMT.

For future work, it is recommended that only the Harvie (1981) approximation should be used. This is the default approximation in EQ3/6 (but which is not available in FMT). Also, the value of the A^{φ} Debye-Hückel parameter should be changed from 0.39 to 0.392 and that of the Pitzer coefficient $\beta^{(1)}_{NaCl}$ should be changed from 0.2644 to 0.2664 as noted in Section 1.0. The slightly incorrect values were used for the code comparison. The A^{φ} parameter value is hard-coded into FMT. The $\beta^{(1)}_{NaCl}$ value was contained on the FMT_050405.CHEMDAT file. These values have been used in past FMT applications, including the problems used here as test cases. It is recommended that the key brine compositions used by WIPP be modified as in Test Case #11 by using as EQ3NR inputs the molalities and pmH implied on the .FOR88 or .INGUESS file produced by FMT. The charge imbalance may be off slightly due to the change to the Harvie (1981) approximation for J(x) and the use of the corrected values for A^{φ} and $\beta^{(1)}_{NaCl}$. To deal with this, EQ3NR should be instructed to charge-balance on chloride (the most abundant anion). An example of this for GWB brine is presented in Appendix B.

Verification tests are also performed for migration from Version 8.0 to Version 8.0a. The acceptance criteria are $\leq 0.005\%$ and ≤ 0.001 for linear and logarithmic quantities, respectively. All test results are within the established acceptance criteria.

7.0 REFERENCES

Babb, S.C., and C.F. Novak. 1995. "WIPP PA User's Manual for FMT, Version 2.0." Albuquerque, NM: Sandia National Laboratories. ERMS 228119.

Babb, S.C., and C.F. Novak. 1997 and addenda. "User's Manual for FMT Version 2.3: A Computer Code Employing the Pitzer Activity Coefficient Formalism for Calculating Thermodynamic Equilibrium in Geochemical Systems to High Electrolyte Concentrations." Albuquerque, NM: Sandia National Laboratories. ERMS 243037.

Brush, L.H. 2005. "Results of Calculations of Actinide Solubilities for the WIPP Performance Assessment Baseline Calculations." Analysis report, May 18, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539800.

Brush, L.H. 2009. Software Problem Report (SPR) 2009-03 for EQ3/6, Version 8.0. Carlsbad, NM: Sandia National Laboratories. ERMS 551949.

Brush, L.H., Y. Xiong, J.W. Garner, T.B. Kirchner, and J.J. Long. 2008. "Sensitivity of the Long-Term Performance of the WIPP to ETDA." Unpublished analysis report, May 8, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 529131.

Gilkey, A. 2006. "Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0." Document Version 8.01. Carlsbad, NM: Sandia National Laboratories. ERMS #544574.

Harvie, C.E. 1981. Theoretical Investigations in Geochemistry and Atom Surface Scattering. Ph.D. thesis, University of California, San Diego. 8203026, University Microfilms International, #00 N. Zeeb Road, Ann Arbor, MI.

Harvie, C.E., and Weare, J.H. 1980. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O system from zero to high concentration at 25°C: Geochimica et Cosmochimica Acta, v. 44, p. 981-997.

Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The prediction of mineral solubilities in natural waters. The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C." Geochim. Cosmochim. Acta, vol. 48, p. 723-751.

Helgeson, H. C. 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, v. 267, p. 729-804

Ismail, A.E., Deng, H.-R., Jang, J.-H., Wolery, T.J., 2008. "Verification of FMT Database and Conversion to EQ3/6 Format." Memorandum to Record Center. Carlsbad, NM: Sandia National Laboratories. ERMS 550689.

Novak, C., 1996, FMT Software Packages, SNL WIPP. ERMS# 210790.

Pitzer, K.S. 1973. "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations." *J. Phys. Chem.* Vol. 77, no. 2, 268.

Pitzer, K.S., 1975. Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms. Journal of Solution Chemistry, 4:249–265.

Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions*, 2nd ed. Boca Raton, FL: CRC Press.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., and Dunkle, S.A. 1988. A Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines. U.S. Geological Survey Water-Resources Investigations Report 88-4153, U.S. Department of the Interior, Reston, Virginia. 310. p.

Wang, Y. 1998. "WIPP PA Validation Document for FMT (Version 2.4)." Document Version 2.4. Carlsbad, NM: Sandia National Laboratories. ERMS 251587.

WIPP. 1996. WIPP PA User's Manual for NONLIN, Version 2.0. Document Version 1.0, WPO #30740, January 31, 1996

WIPP. 2006. Requirements Document for EQ3/6 Version 8.0. Sandia National Laboratories. Sandia WIPP Central Files ERMS #543602.

Wolery, T.J. 1990. On the thermodynamic framework of solutions (with special reference to aqueous electrolyte solutions. American Journal of Science, v. 290, p. 296-320.

Wolery, T.J. 1992. EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0): UCRL-MA-110662-PT-III, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T.J. 2008. Analysis Plan for EQ3/6 Analytical Studies. Analysis Plan AP-140. Carlsbad, NM: Sandia National Laboratories. ERMS 548930.

Wolery, T.J. 2009. Change Control for EQ3/6, Version 8.0 [Proposed 8.0a]. Carlsbad, NM: Sandia National Laboratories. ERMS 551823.

Wolery, T. J., and Daveler, S. A. 1992. EQ6, A Computer Code for Reaction-Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0): UCRL-MA-110662-PT-IV, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T.J. and Jarek, R.L. 2003. Software User's Manual for EQ3/6, Version 8.0. U.S. Department of Energy, Office of Civilian Radioactive Waste Management. Las Vegas, Nevada. Software Document Number 10813-UM-8.0-00.

Xiong, Y.-L. 2004. "Incorporation of Six Solid Phases Including Hydromagnesite (5424) and Hydromagnesite (4323) into EQ3/6 HMW Database and Its Modified Version HMP." Memorandum to L.H. Brush, August 4, 2004. Carlsbad, NM: Sandia National Laboratories. ERMS 536321.

Xiong, Y.-L. 2005. "Release of FMT_050405.CHEMDAT." E-mail to J.F. Kanney and J.J. Long, April 5, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539304.

Xiong, Y.-L., and Lord, A.C.S., 2008. Experimental investigations of the reaction path in the MgO–CO_2–H_2O system in solutions with various ionic strengths, and their applications to nuclear waste isolation. *Applied Geochemistry*, 23:1634–1659.

APPENDIX A. APPROXIMATIONS TO THE FUNCTION J(X)

Pitzer (1975) proposed a treatment of higher-order electrical interactions in the calculation of activity coefficients of aqueous species. Central to this treatment is a function called J(x) and its derivative J'(x). These functions are defined by integral equations and exact closed-form solutions are unknown. The independent variable x has the following meaning: for ions i and j, $x_{ij} = 6z_iz_jA^{\varphi}\sqrt{I}$, where z_i is the charge number of ion i, z_j is the charge number of ion j, A^{φ} is the Debye-Hückel "A-phi" parameter used in Pitzer's equations, and I is the ionic strength. Discussion here of the J(x) function (including its derivative) is partly based on the spreadsheet Pitzer_HOET_analysis.xls, which is part of the spreadsheet package associated with the present document.

Table A-1 presents numerical results from Table II of Pitzer (1975). These values are based on numerical integration. They form a point of comparison with the results of closed-form approximations. The source does not note the accuracy of these results.

Table A-1.Table II from Pitzer (1975). These values are based on numerical integration.

x	J(x)	J'(x)
0.01	0.0000706	0.0127
0.02	0.0002387	0.0207
0.03	0.0004806	0.0275
0.04	0.0007850	0.0333
0.05	0.0011443	0.0385
0.06	0.0015529	0.0432
0.07	0.0020063	0.0475
0.08	0.0025010	0.0514
0.09	0.0030340	0.0551
0.10	0.0036028	0.0586
0.12	0.0048393	0.0649
0.14	0.0061961	0.0706
0.16	0.0076615	0.0758
0.18	0.0092260	0.0806
0.20	0.010882	0.0850
0.24	0.014441	0.0928
0.28	0.018295	0.0997
0.32	0.022409	0.1059
0.36	0.026755	0.1114
0.40	0.031313	0.1164
0.44	0.036061	0.1210
0.48	0.040985	0.1252
0.52	0.046070	0.1291
0.56	0.051306	0.1327
0.60	0.056680	0.1360
0.80	0.085346	0.1499
1.00	0.11644	0.1605

1.20	0.14941	0.1689
1.40	0.18390	0.1758
1.60	0.21965	0.1815
1.80	0.25645	0.1864
2.00	0.29416	0.1906
3.00	0.49283	0.2053
4.00	0.70293	0.2142
5.00	0.92035	0.2202
6.00	1.14288	0.2246
7.00	1.36918	0.2279
8.00	1.59839	0.2304
9.00	1.82990	0.2325
10.00	2.06328	0.2342
12.00	2.53446	0.2368
16.00	3.48916	0.2402
20.00	4.45453	0.2423
24.00	5.57865*	0.2374*
28.00	6.40378	0.2447
32.00	7.38429**	0.2455
36.00	8.36745	0.2461
40.00	9.35270	0.2465
50.00	11.82248	0.2474
60.00	14.29890	0.2479
70.00	16.77979	0.2483
80.00	19.26387	0.2485
90.00	21.75033	0.2487
100.00	24.23861	0.2489
200.00	49.17099	0.2496
400.00	99.11907	0.2498
600.00	149.09520	0.2499
800.00	199.08083	0.2499
1000.00	249.07101	0.2500
2000.00	499.04682	0.2500
4000.00	999.03028	0.2500
6000.00	1499.02328	0.2500
8000.00	1999.01925	0.2500
10000.00	2499.01659	0.2500

*The values for J(24) and J'(24) appear to be slightly erroneous as they plot off their respective trends (see spreadsheet Pitzer_HOET_analysis.xls). The value for J'(24) is also inconsistent with the monotonically increasing nature of the J'(x) function.
**An obvious typographical error in J(32) has been corrected here.

Pitzer (1975) discusses several possible practical approximations for J(x) and J'(x). The one used in FMT (v. 2.4 and older versions) is that associated with his equation 47. At one time, this formulation was also available as an option in EQ3/6. Later versions of EQ3/6 (up to and including version 8.0) use only the later approximation recommended by Harvie (1981). Harvie's approximation was used in the classic sea-salt system model of Harvie et al. (1984). His approximation is also used in almost all subsequent work involving Pitzer's equations (see discussion in Section 1.0 of the present document). The older eq. 47 formulation was put back into EQ3/6 in version 8.0a as an option (using the input file title option string USEOLDPITZER75) to allow better comparison with FMT results. By default, EQ3/6 v. 8.0a uses the Harvie (1981) approximation. All future practical work should be using the Harvie approximation, as it is generally the one which has been used in data regression, as of the Pitzer interaction coefficients.

Table A-2 presents the results of evaluating the Pitzer (1975, eq. 47) approximation in Microsoft Excel 2007.

Table A-2.Excel Evaluation of the Pitzer (1975, eq. 47) Approximation (spreadsheet Pitzer_HOET_analysis.xls).

x	J(x)	J'(x)
0.01	0.0000756	0.0128766
0.02	0.0002451	0.0206992
0.03	0.0004851	0.0271304
0.04	0.0007850	0.0327329
0.05	0.0011378	0.0377534
0.06	0.0015386	0.0423302
0.07	0.0019833	0.0465516
0.08	0.0024686	0.0504784
0.09	0.0029920	0.0541551
0.10	0.0035510	0.0576157
0.12	0.0047682	0.0639896
0.14	0.0061066	0.0697582
0.16	0.0075552	0.0750308
0.18	0.0091050	0.0798873
0.20	0.0107483	0.0843881
0.24	0.0142898	0.0925032
0.28	0.0181358	0.0996562
0.32	0.0222520	0.1060384
0.36	0.0266105	0.1117879
0.40	0.0311880	0.1170080
0.44	0.0359651	0.1217784
0.48	0.0409251	0.1261620
0.52	0.0460536	0.1302094
0.56	0.0513379	0.1339621
0.60	0.0567671	0.1374544
0.80	0.0857748	0.1518794
1.00	0.1172834	0.1627368
1.20	0.1507152	0.1712622

1.40	0.1856805	0.1781629
1.60	0.2219017	0.1838788
1.80	0.2591726	0.1887003
2.00	0.2973357	0.1928281
3.00	0.4979507	0.2069839
4.00	0.7094240	0.2153311
5.00	0.9276931	0.2208697
6.00	1.1506424	0.2248267
7.00	1.3770220	0.2278018
8.00	1.6060297	0.2301240
9.00	1.8371185	0.2319894
10.00	2.0698980	0.2335223
12.00	2.5394450	0.2358961
16.00	3.4897900	0.2390077
20.00	4.4500043	0.2409668
24.00	5.4167279	0.2423197
28.00	6.3880876	0.2433132
32.00	7.3629278	0.2440756
36.00	8.3404832	0.2446802
40.00	9.3202198	0.2451721
50.00	11.7767881	0.2460791
60.00	14.2408689	0.2467019
70.00	16.7102755	0.2471576
80.00	19.1836670	0.2475063
90.00	21.6601592	0.2477821
100.00	24.1391367	0.2480060
200.00	49.0037117	0.2490592
400.00	98.8840445	0.2496201
600.00	148.8295716	0.2498093
800.00	198.8015800	0.2499014
1000.00	248.7875645	0.2499541
2000.00	498.7990428	0.2500430
4000.00	998.9139558	0.2500619
6000.00	1499.0329763	0.2500562
8000.00	1999.1378835	0.2500487
10000.00	2499.2283299	0.2500419
Parameter values:		
	C1 =	4.581
	C2 =	0.7237
	C3 =	0.0120
	C4 =	0.528

Table A-3 compares the results of evaluating the Pitzer (1975, eq. 47) approximation in Microsoft Excel 2007 against the results given by Pitzer (1975) in his Table II. One can see that agreement is excellent for both J(x) and J'(x) in the lower range of x values considered here.

However, above x = 32, the differences in J(x) are significantly more pronounced, though agreement for J'(x) is still fairly good.

Table A-3.Difference Between the Excel Evaluation of the Pitzer (1975, eq. 47) Approximation and Pitzer's (1975) Table II (spreadsheet Pitzer_HOET_analysis.xls).

x	Δ(J(x))	Δ(J'(x))
0.01	0.0000050	0.0002
0.02	0.0000064	0.0000
0.03	0.0000045	-0.0004
0.04	0.0000000	-0.0006
0.05	-0.0000065	-0.0007
0.06	-0.0000143	-0.0009
0.07	-0.0000230	-0.0009
0.08	-0.0000324	-0.0009
0.09	-0.0000420	-0.0009
0.10	-0.0000518	-0.0010
0.12	-0.0000711	-0.0009
0.14	-0.0000895	-0.0008
0.16	-0.0001063	-0.0008
0.18	-0.0001210	-0.0007
0.20	-0.000134	-0.0006
0.24	-0.000151	-0.0003
0.28	-0.000159	0.0000
0.32	-0.000157	0.0001
0.36	-0.000145	0.0004
0.40	-0.000125	0.0006
0.44	-0.000096	0.0008
0.48	-0.000060	0.0010
0.52	-0.000016	0.0011
0.56	0.000032	0.0013
0.60	0.000087	0.0015
0.80	0.000429	0.0020
1.00	0.00084	0.0022
1.20	0.00131	0.0024
1.40	0.00178	0.0024
1.60	0.00225	0.0024
1.80	0.00272	0.0023
2.00	0.00318	0.0022
3.00	0.00512	0.0017
4.00	0.00649	0.0011
5.00	0.00734	0.0007
6.00	0.00776	0.0002
7.00	0.00784	-0.0001
8.00	0.00764	-0.0003
9.00	0.00722	-0.0005
10.00	0.00662	-0.0007

12.00	0.00498	-0.0009
16.00	0.00063	-0.0012
20.00	-0.00453	-0.0013
24.00	-0.16192	0.0049
28.00	-0.01569	-0.0014
32.00	-0.02136	-0.0014
36.00	-0.02697	-0.0014
40.00	-0.03248	-0.0013
50.00	-0.04569	-0.0013
60.00	-0.05803	-0.0012
70.00	-0.06951	-0.0011
80.00	-0.08020	-0.0010
90.00	-0.09017	-0.0009
100.00	-0.09947	-0.0009
200.00	-0.16728	-0.0005
400.00	-0.23503	-0.0002
600.00	-0.26563	-0.0001
800.00	-0.27925	0.0000
1000.00	-0.28345	0.0000
2000.00	-0.24778	0.0000
4000.00	-0.11632	0.0001
6000.00	0.00970	0.0001
8000.00	0.11863	0.0000
10000.00	0.21174	0.0000
Max |Δ|	0.28345	0.0049
Mean |Δ|	0.05593	0.0009

Table A-4 presents the results of EQ3/6 evaluation (from subroutine cwrpjt.f). This table was generated using the input file option string WRITEPITZERJTABLES.

Table A-4. EQ3/6-Calculated Evaluation of the Pitzer (1975, eq. 47) Approximation (spreadsheet Pitzer_HOET_analysis.xls).

x	J(x)	J'(x)
0.01	0.0000756	0.0129
0.02	0.0002451	0.0207
0.03	0.0004851	0.0271
0.04	0.0007850	0.0327
0.05	0.0011378	0.0378
0.06	0.0015386	0.0423
0.07	0.0019833	0.0466
0.08	0.0024686	0.0505
0.09	0.0029920	0.0542
0.10	0.0035510	0.0576
0.12	0.0047682	0.0640
0.14	0.0061066	0.0698

0.16	0.0075552	0.0750
0.18	0.0091050	0.0799
0.20	0.010748	0.0844
0.24	0.014290	0.0925
0.28	0.018136	0.0997
0.32	0.022252	0.1060
0.36	0.026610	0.1118
0.40	0.031188	0.1170
0.44	0.035965	0.1218
0.48	0.040925	0.1262
0.52	0.046054	0.1302
0.56	0.051338	0.1340
0.60	0.056767	0.1375
0.80	0.085775	0.1519
1.00	0.11728	0.1627
1.20	0.15072	0.1713
1.40	0.18568	0.1782
1.60	0.22190	0.1839
1.80	0.25917	0.1887
2.00	0.29734	0.1928
3.00	0.49795	0.2070
4.00	0.70942	0.2153
5.00	0.92769	0.2209
6.00	1.15064	0.2248
7.00	1.37702	0.2278
8.00	1.60603	0.2301
9.00	1.83712	0.2320
10.00	2.06990	0.2335
12.00	2.53944	0.2359
16.00	3.48979	0.2390
20.00	4.45000	0.2410
24.00	5.41673	0.2423
28.00	6.38809	0.2433
32.00	7.36293	0.2441
36.00	8.34048	0.2447
40.00	9.32022	0.2452
50.00	11.77679	0.2461
60.00	14.24087	0.2467
70.00	16.71028	0.2472
80.00	19.18367	0.2475
90.00	21.66016	0.2478
100.00	24.13914	0.2480
200.00	49.00371	0.2491
400.00	98.88404	0.2496
600.00	148.82957	0.2498
800.00	198.80158	0.2499

1000.00	248.78756	0.2500
2000.00	498.79904	0.2500
4000.00	998.91396	0.2501
6000.00	1499.03298	0.2501
8000.00	1999.13788	0.2500
10000.00	2499.22833	0.2500

Table A-5 shows the difference between the EQ3/6-calculated evaluation of the Pitzer (1975, eq. 47) approximation and the evaluation of the same approximation obtained using Microsoft Excel 2007. The results are nearly identical to within the precision used here. These results validate the reincorporation of the Pitzer (1975, eq. 47) approximation into EQ3/6.

Table A-5. Difference between the EQ3/6-Calculated Evaluation of the Pitzer (1975, eq. 47) Approximation and the Evaluation Obtained Using Microsoft Excel 2007 (spreadsheet Pitzer_HOET_analysis.xls).

x	Δ(J(x))	Δ(J'(x))
0.01	0.0000000	0.0000
0.02	0.0000000	0.0000
0.03	0.0000000	0.0000
0.04	0.0000000	0.0000
0.05	0.0000000	0.0000
0.06	0.0000000	0.0000
0.07	0.0000000	0.0000
0.08	0.0000000	0.0000
0.09	0.0000000	0.0000
0.10	0.0000000	0.0000
0.12	0.0000000	0.0000
0.14	0.0000000	0.0000
0.16	0.0000000	0.0000
0.18	0.0000000	0.0000
0.20	0.0000000	0.0000
0.24	0.0000000	0.0000
0.28	0.0000000	0.0000
0.32	0.0000000	0.0000
0.36	0.0000000	0.0000
0.40	0.0000000	0.0000
0.44	0.0000000	0.0000
0.48	0.0000000	0.0000
0.52	0.0000000	0.0000
0.56	0.0000000	0.0000
0.60	0.0000000	0.0000
0.80	0.0000000	0.0000
1.00	0.0000000	0.0000
1.20	0.0000000	0.0000
1.40	0.0000000	0.0000
1.60	0.0000000	0.0000

1.80	0.0000000	0.0000
2.00	0.0000000	0.0000
3.00	0.0000000	0.0000
4.00	0.0000000	0.0000
5.00	0.0000000	0.0000
6.00	0.0000000	0.0000
7.00	0.0000000	0.0000
8.00	0.0000000	0.0000
9.00	0.0000000	0.0000
10.00	0.0000000	0.0000
12.00	0.0000000	0.0000
16.00	0.0000000	0.0000
20.00	0.0000000	0.0000
24.00	0.0000000	0.0000
28.00	0.0000000	0.0000
32.00	0.0000000	0.0000
36.00	0.0000000	0.0000
40.00	0.0000000	0.0000
50.00	0.0000000	0.0000
60.00	0.0000000	0.0000
70.00	0.0000000	0.0000
80.00	0.0000000	0.0000
90.00	0.0000000	0.0000
100.00	0.0000000	0.0000
200.00	0.0000000	0.0000
400.00	-0.0000001	0.0000
600.00	-0.0000001	0.0000
800.00	-0.0000001	0.0000
1000.00	-0.0000001	0.0000
2000.00	-0.0000001	0.0000
4000.00	-0.0000001	0.0000
6000.00	-0.0000001	0.0000
8000.00	-0.0000001	0.0000
10000.00	-0.0000001	0.0000
Max |Δ|	0.0000001	0.0000
Mean Δ	0.0000000	0.0000

The spreadsheet Pitzer_HOET_analysis.xls contains other evaluations and comparisons that will not be presented here.

APPENDIX B. TEST CASE #11: FINISHING THE STORY

Appendix B of this document presents some results in how the WIPP geochemistry model results have changed once EQ3/6 is used in conjunction with the Harvie (1981) approximation and the corrected values of A^{φ} (0.392 in place of 0.39) and $\beta^{(1)}_{NaCl}$ (0.2664 in place of 0.2644). Only the case of the c4pgwb problem will be addressed here. The c4pgwbx, c4per6, and c4per6x problems could be treated in similar manner. The results shown here are taken from the spreadsheet c4pgwb_FMX.xls. Note that the formal acceptance criteria pertinent to the comparisons in the main body of this document are not relevant here. The present comparisons merely show the effect of corrections to the model for the one problem so examined.

The approach taken here was to begin with the c4pgwb_P75_Mfix EQ3/6 inputs for the starting GWB brine (Table 5-12-12). These are repeated below in Table B-1. These inputs were based on the FMT .INGUESS file, which gives speciation information for the starting brine after FMT does charge-balancing on oxygen, thus avoiding inconsistencies due to the "front end" problem.

Table B-1. Test Case #11 Two-Off (c4pgwb_P75_Mfix) Revised EQ3NR Inputs Calculated from the FMT .INGUESS File.

Basis Species	Molality
Na+	3.9080347
K+	0.5143333
Ca++	8.04470E-04
Mg++	1.1229985
pmH	2.4791652
Cl-	6.1877216
SO4=	0.1965247
B(OH)4-	0.1740648
Br-	2.91980E-02
Oxalate-	3.61789E-02
Acetate-	1.19038E-02
EDTA----	9.14121E-06
Citrate---	9.05137E-04
HCO3-	1.0E-18
Am+++	1.0E-18
Th++++	1.0E-18
NpO2+	1.0E-18
pmH	2.4791652

Because of the changes in the J(x) approximation and in the two model parameters (A^{φ} and $\beta^{(1)}_{NaCl}$), there must now be some small difference in the calculated results. To evaluate this difference, we tried three different approaches. The first was to use the EQ3NR code to calculate the resulting charge imbalance. This turned out to have a value of -7.225998×10^{-5} eq/kg.H_2O. The second approach was to charge-balance on pH instead. This changed the pmH from 2.4792 to 2.4767, an adjustment of -0.0024 units. Although this might have been considered acceptable, it was decided to follow a third approach, which was to charge-balance instead on chloride, which is present in relatively high concentration. This yielded a change from 6.1877218 molal to 6.1876496 molal, an adjustment of -0.0000722 molal. This is an essentially negligible change. Subsequent calculations with EQ6 reacting this solution with the requisite minerals were based on this. Comparison of the results with the original FMT results was made in the spreadsheet c4pgwb_FMX.xls, from which the following tables were derived.

Table B-2 compares the results for general parameter outputs obtained from EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^φ and $\beta^{(1)}_{NaCl}$) and FMT (using the Pitzer, 1975, eq. 47 approximation and uncorrected values of A^φ and $\beta^{(1)}_{NaCl}$). There are no notable differences here.

Table B-2. Test Case #13 (c4pgwb_FMX) General Parameter Outputs, EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^φ and $\beta^{(1)}_{NaCl}$) vs. FMT.

	FMT	EQ3/6	Δ
Solution mass, g	1293.458658	1296.8962	0.266%
H2O mass, g	914.2900833	916.20852	0.210%
Ionic strength, m	7.663835	7.6981	0.447%
density, g/L	1232.10	1232.5	0.032%
TDS, g/L	361.1827591	361.78	0.165%
a_w	0.732297	0.73146	-0.114%
x_w	0.812688	0.81239	-0.037%
λ_w	0.9011	0.90038	-0.080%
fCO2, bars	0.000003135	3.13527E-06	0.009%
pH (Pitzer)	8.6887	8.6897	0.0010
pmH	9.3347	9.3348	0.0001
pcH	9.3947	9.3949	0.0002

Table B-3 compares the corresponding results for solute species molalities. Here there are some large discrepancies, the largest being one of 122.698% for the species $Th(CO_3)_5^{6-}$ (which is of little quantitative significance as its molality is less than 1×10^{-14}). However, the discrepancy is 6.064% for Ca^{2+}, which is minor but still relatively abundant in concentration. There are many other potentially notable discrepancies as well.

Table B-3. Test Case #13 (c4pgwb_FMX) Solute Species Molalities, EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^φ and $\beta^{(1)}_{NaCl}$) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	6.17604	6.1954	0.313%
Na+	4.99121	4.9841	-0.142%
Mg++	0.576993	0.59074	2.383%
K+	0.562550	0.56137	-0.210%
SO4--	0.262347	0.26243	0.032%
MgB(OH)4+	0.0753902	0.075004	-0.512%
B(OH)4-	0.0549134	0.055113	0.363%
Br-	0.0319351	0.031868	-0.210%
B(OH)3(aq)	0.0254070	0.025084	-1.271%

Ca++	0.00849908	0.0090145	6.064%
Acetate-	0.00654112	0.0066197	1.201%
MgAcetate+	0.00642842	0.0063218	-1.659%
B4O5(OH)4--	0.00575374	0.0058139	1.046%
B3O3(OH)4-	0.00331851	0.0032585	-1.808%
MgOH+	0.00182005	0.0018408	1.140%
CaB(OH)4+	0.00170130	0.0017508	2.910%
MgOxalate(aq)	0.00153978	0.0014915	-3.136%
MgCitrate-	0.000962646	0.00095778	-0.505%
MgCO3(aq)	0.000323947	0.00032433	0.118%
CaAcetate+	4.96558E-05	0.000050435	1.569%
HCO3-	4.84103E-05	0.000048836	0.879%
CO3--	2.48257E-05	2.6118E-05	5.205%
Citrate---	1.99049E-05	2.2497E-05	13.022%
Oxalate--	1.38711E-05	1.4017E-05	1.052%
CaOxalate(aq)	1.18939E-05	1.1899E-05	0.043%
MgEDTA--	9.72185E-06	9.7079E-06	-0.143%
OH-	8.12100E-06	8.2347E-06	1.400%
CaCitrate-	7.43588E-06	7.6411E-06	2.760%
CaCO3(aq)	4.17958E-06	4.3219E-06	3.405%
HAcetate(aq)	4.26585E-07	4.2446E-07	-0.498%
Am(OH)2+	2.37430E-07	2.4211E-07	1.971%
AmEDTA-	2.01094E-07	1.9171E-07	-4.666%
NpO2+	1.45815E-07	1.4786E-07	1.402%
NpO2CO3-	1.19968E-07	1.2343E-07	2.886%
NpO2Acetate(aq)	8.44036E-08	8.5308E-08	1.072%
CaEDTA--	7.50956E-08	7.7449E-08	3.134%
Th(OH)4(aq)	5.19575E-08	5.1842E-08	-0.222%
NpO2Oxalate-	5.03499E-08	4.9132E-08	-2.419%
CO2(aq)	2.93478E-08	2.9245E-08	-0.350%
Th(OH)3(CO3)-	1.27974E-08	1.2903E-08	0.825%
NpO2OH(aq)	4.97922E-09	5.0680E-09	1.783%
AmOH++	2.82968E-09	2.9133E-09	2.955%
HSO4-	1.33874E-09	1.2894E-09	-3.686%
AmAcetate++	1.28786E-09	1.3460E-09	4.514%
NpO2(CO3)2---	1.33679E-09	1.5461E-09	15.658%
Am(OH)3(aq)	6.87418E-10	6.9040E-10	0.434%
HCitrate--	6.54933E-10	6.7083E-10	2.427%
AmCitrate(aq)	5.10997E-10	5.0788E-10	-0.610%
H+	4.62711E-10	4.6258E-10	-0.028%
AmCO3+	4.32475E-10	4.3387E-10	0.323%
NpO2Citrate--	1.71501E-10	1.7598E-10	2.612%
Am(CO3)2-	1.53197E-10	1.5426E-10	0.694%
AmSO4+	1.43332E-10	1.3873E-10	-3.211%
EDTA----	9.60883E-11	1.2595E-10	31.077%
HOxalate-	4.08059E-11	3.9621E-11	-2.904%

Am(CO3)3---	3.82087E-11	4.4306E-11	15.958%
AmOxalate+	2.91986E-11	2.7809E-11	-4.759%
Am(SO4)2-	2.21879E-11	2.0841E-11	-6.070%
NpO2(CO3)3(5-)	1.47730E-11	2.4103E-11	63.156%
Am+++	1.26375E-11	1.3720E-11	8.566%
Am(CO3)4(5-)	1.09972E-11	1.9791E-11	79.964%
HEDTA---	8.88268E-12	9.8106E-12	10.446%
NpO2(OH)2-	7.28398E-12	7.4958E-12	2.908%
AmCl++	2.11486E-12	2.1587E-12	2.073%
NpO2EDTA---	5.07797E-13	5.6940E-13	12.131%
AmCl2+	1.09730E-13	1.1005E-13	0.292%
H2EDTA--	1.10656E-14	1.0946E-14	-1.081%
H2Citrate-	4.80754E-15	4.7279E-15	-1.657%
NpO2HEDTA--	9.81711E-16	9.8119E-16	-0.053%
Th(CO3)5(6-)	4.55775E-16	1.0150E-15	122.698%
Th(SO4)3--	1.83058E-17	1.7366E-17	-5.134%
ThEDTA(aq)	8.65338E-18	8.1432E-18	-5.896%
H2Oxalate(aq)	5.87859E-19	5.6859E-19	-3.278%
Th(SO4)2(aq)	3.41990E-19	3.1633E-19	-7.503%
NpO2H2EDTA-	1.50741E-19	1.4147E-19	-6.150%
ThCitrate+	6.39131E-20	5.9752E-20	-6.511%
Th(Acetate)2++	8.70115E-21	8.5495E-21	-1.743%
H3Citrate(aq)	2.21771E-21	2.1624E-21	-2.494%
H3EDTA-	1.22934E-21	1.1644E-21	-5.283%
ThAcetate+++	1.10948E-21	1.1565E-21	4.238%
ThOxalate++	1.55293E-22	1.4422E-22	-7.130%
Th++++	-----	1.4335E-24	-----
H4EDTA(aq)	-----	1.7094E-28	-----

Table B-4 compares the corresponding results for solute species activity coefficients. Here again there are some large discrepancies, the largest being one of -54.627% for the species $Th(CO_3)_5^{6-}$. These discrepancies tend to somewhat mirror those for the molalities.

Table B-4. Test Case #13 (c4pgwb_FMX) Solute Species Activity Coefficients, EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^{Φ} and $\beta^{(1)}_{NaCl}$) vs. FMT.

Species	FMT	EQ3/6	Δ
Cl-	1.305	1.30858	0.274%
Na+	0.9246	0.92045	-0.449%
Mg++	1.742	1.69746	-2.557%
K+	0.4298	0.42530	-1.046%
SO4--	0.021331	0.020692	-2.996%
MgB(OH)4+	1.873	1.86595	-0.376%
B(OH)4-	0.1020	0.10097	-1.008%
Br-	0.2683	0.26620	-0.785%
B(OH)3(aq)	1.069	1.07448	0.513%
Ca++	0.9135	0.88756	-2.839%

Acetate-	0.5575	0.54941	-1.450%
MgAcetate+	7.398	7.48514	1.178%
B4O5(OH)4--	0.0042179	0.0040804	-3.261%
B3O3(OH)4-	0.1631	0.16304	-0.035%
MgOH+	0.3065	0.30269	-1.243%
CaB(OH)4+	1.143	1.13684	-0.539%
MgOxalate(aq)	1.263	1.26386	0.068%
MgCitrate-	0.1662	0.16364	-1.538%
MgCO3(aq)	1.000	1.00000	0.000%
CaAcetate+	7.398	7.48514	1.178%
HCO3-	0.3511	0.34842	-0.764%
CO3--	0.015308	0.014602	-4.615%
Citrate---	0.000040119	0.000034842	-13.154%
Oxalate--	0.02246	0.021592	-3.863%
CaOxalate(aq)	1.263	1.26386	0.068%
MgEDTA--	0.1302	0.12371	-4.986%
OH-	0.4438	0.43803	-1.301%
CaCitrate-	0.1662	0.16364	-1.538%
CaCO3(aq)	1.000	1.00000	0.000%
HAcetate(aq)	1.000	1.00000	0.000%
Am(OH)2+	0.00074059	0.00072544	-2.046%
AmEDTA-	0.029535	0.029376	-0.537%
NpO2+	1.858	1.84969	-0.447%
NpO2CO3-	0.089249	0.087842	-1.577%
NpO2Acetate(aq)	0.2768	0.27561	-0.429%
CaEDTA--	0.1302	0.12371	-4.986%
Th(OH)4(aq)	1.000	1.00000	0.000%
NpO2Oxalate-	0.029135	0.029275	0.481%
CO2(aq)	3.522	3.53427	0.348%
Th(OH)3(CO3)-	0.2683	0.26620	-0.785%
NpO2OH(aq)	0.095666	0.094973	-0.724%
AmOH++	0.023758	0.023025	-3.085%
HSO4-	0.8149	0.81903	0.507%
AmAcetate++	0.010578	0.010060	-4.897%
NpO2(CO3)2---	0.000081462	0.000071581	-12.129%
Am(OH)3(aq)	0.009169	0.0091285	-0.442%
HCitrate--	0.006616	0.0063256	-4.390%
AmCitrate(aq)	0.006638	0.0065343	-1.562%
H+	4.426	4.41672	-0.210%
AmCO3+	0.7483	0.74593	-0.316%
NpO2Citrate--	0.0039615	0.0038247	-3.453%
Am(CO3)2-	0.063985	0.063768	-0.340%
AmSO4+	0.4676	0.46720	-0.086%
EDTA----	9.8019E-07	7.1138E-07	-27.425%
HOxalate-	0.2842	0.28379	-0.144%
Am(CO3)3---	0.000015457	1.3425E-05	-13.149%

AmOxalate+	0.1034	0.10512	1.667%
Am(SO4)2-	0.048011	0.047962	-0.101%
NpO2(CO3)3(5-)	2.1613E-10	1.3508E-10	-37.499%
Am+++	0.5347	0.49091	-8.190%
Am(CO3)4(5-)	1.2771E-13	7.1697E-14	-43.860%
HEDTA---	0.00080805	0.00069438	-14.067%
NpO2(OH)2-	0.013842	0.013605	-1.712%
AmCl++	44.67	43.8834	-1.761%
NpO2EDTA---	0.017233	0.014757	-14.367%
AmCl2+	727.7	731.81	0.565%
H2EDTA--	0.010058	0.0096316	-4.239%
H2Citrate-	0.1276	0.12682	-0.608%
NpO2HEDTA--	0.1873	0.17956	-4.135%
Th(CO3)5(6-)	2.2699E-14	1.0299E-14	-54.627%
Th(SO4)3--	0.025738	0.024621	-4.341%
ThEDTA(aq)	3.944	3.96187	0.453%
H2Oxalate(aq)	1.000	1.00000	0.000%
Th(SO4)2(aq)	35.95	36.358	1.135%
NpO2H2EDTA-	0.5200	0.52966	1.858%
ThCitrate+	21.60	22.527	4.291%
Th(Acetate)2++	266.4	267.92	0.569%
H3Citrate(aq)	1.000	1.00000	0.000%
H3EDTA-	0.2267	0.22620	-0.219%
ThAcetate+++	75.98	72.210	-4.961%
ThOxalate++	490.8	510.04	3.919%
Th++++	0.8146	0.69647	-14.502%
H4EDTA(aq)	1.000	1.00000	0.000%

Table B-5 compares the results for mineral saturation indices. The differences are roughly of the same magnitude as those seen previously. In many instances the differences may be explained by the relatively low reporting precision used by FMT. However, some additional difference would be expected owing to the change in approximation for the J(x) function and the used of the corrected values of the two thermodynamic parameters.

Table B-5. Test Case #13 (c4pgwb_FMX) Mineral Saturation Indices (log Q/K), EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^{φ} and $\beta^{(1)}_{NaCl}$) vs. FMT.

Mineral	FMT	EQ3/6	Δ
Dolomite	2.13	2.14946	0.01946
Magnesite	1.42	1.41638	-0.00362
Am(OH)3(s)	0.00000	0.00000	0.00000
ThO2(am)	0.00000	0.00000	0.00000
KNpO2CO3	0.00000	0.00000	0.00000
Anhydrite	0.00000	0.00000	0.00000
Whewellite	0.00000	0.00000	0.00000
Brucite	0.00000	0.00000	0.00000
Halite	0.00000	0.00000	0.00000

Mg2Cl(OH)3.4H2O	0.00000	0.00000	0.00000
Hydromagnesite5424	0.00000	0.00000	0.00000
Glauberite	-0.0413	-0.05966	-0.01836
Gypsum	-0.0522	-0.05322	-0.00102
Calcite	-0.124	-0.10933	0.01467
Aragonite	-0.311	-0.29613	0.01487
AmOHCO3(c)	-0.334	-0.33382	0.00018
Hydromagnesite4323	-0.344	-0.34347	0.00053
Syngenite	-0.534	-0.55885	-0.02485
Sylvite	-0.610	-0.61314	-0.00314
Thenardite	-0.636	-0.65456	-0.01856
Borax	-0.699	-0.71839	-0.01939
Labile_Salt	-0.808	-0.84553	-0.03753
Polyhalite	-0.986	-1.02505	-0.03905
Mirabilite	-1.05	-1.07234	-0.02234
Epsomite	-1.32	-1.33355	-0.01355
Bloedite	-1.37	-1.40238	-0.03238
Hexahydrite	-1.43	-1.44374	-0.01374
B(OH)3	-1.54	-1.53902	0.00098
Teepleite(20C)	-1.62	-1.62376	-0.00376
Nesquehonite	-1.66	-1.65784	0.00216
Arcanite	-1.71	-1.73304	-0.02304
Aphthitalite/Glaserite	-1.89	-1.93234	-0.04234
Kainite	-2.17	-2.19206	-0.02206
Na_Metaborate	-2.19	-2.19377	-0.00377
Picromerite/Schoenite	-2.22	-2.26048	-0.04048
Kieserite	-2.26	-2.27710	-0.01710
Leonite	-2.30	-2.33757	-0.03757
NpO2OH(aged)	-2.53	-2.52561	0.00439
Na2Oxalate	-2.77	-2.79075	-0.02075
NaAm(CO3)2.6H2O(c)	-2.77	-2.77071	-0.00071
Carnallite	-3.04	-3.03963	0.00037
NpO2OH(am)	-3.23	-3.22571	0.00429
Na3NpO2(CO3)2	-3.23	-3.23554	-0.00554
2[NaNpO2CO3.7/2H2O]	-3.41	-3.41097	-0.00097
Bischofite	-3.45	-3.45138	-0.00138
Nahcolite	-3.70	-3.70456	-0.00456
K-Tetraborate(30C)	-3.89	-3.91312	-0.02312
K-Pentaborate(30C)	-4.02	-4.04376	-0.02376
Na_Pentaborate	-4.10	-4.11953	-0.01953
Pirssonite	-4.65	-4.63962	0.01038
Gaylussite	-4.88	-4.86925	0.01075
K3NpO2(CO3)2	-5.33	-5.33587	-0.00587
Na2CO3.7H2O	-5.58	-5.58604	-0.00604
Natron	-5.62	-5.62886	-0.00886
Kalicinite	-5.67	-5.6726	-0.00260

Thermonatrite	-5.71	-5.71319	-0.00319
Burkeite	-6.17	-6.20749	-0.03749
CaCl2.4H2O	-6.56	-6.53958	0.02042
KNaCO3.6H2O	-7.07	-7.07807	-0.00807

Table B-6 compares the corresponding results for moles of precipitated and remaining (undissolved reactant) solids. There is a small but notable discrepancy in the amount of $Mg_2Cl(OH)_3.4H_2O$. The much larger whewellite discrepancy traces back to the addition of extra whewellite in the FMT run (which has been previously addressed in conjunction with this particular problem).

Table B-6. Test Case #13 (c4pgwb_FMX) Moles of Precipitated and Remaining Solids, EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^{φ} and $\beta^{(1)}_{NaCl}$) vs. FMT.

Mineral	FMT	EQ3/6	Δ
Anhydrite	9.95666	9.9561	-0.006%
Halite	9.34462	9.3416	-0.032%
Brucite	8.12404	8.1639	0.491%
Mg2Cl(OH)3.4H2O	1.19641	1.1698	-2.224%
Am(OH)3(s)	1.00000	1.0000	0.000%
ThO2(am)	1.00000	1.0000	0.000%
KNpO2CO3	1.00000	1.0000	0.000%
Hydromagnesite5424	0.999908	0.99991	0.000%
Whewellite	0.049665	0.034789	-29.953%

Table B-7 compares the corresponding results for actinide species distributions, which are the results of perhaps greatest interest. The discrepancies here for total molalities are within 2%. The differences for some individual species are larger, mostly prominently the -4.67% for $AmEDTA^-$.

Table B-7. Test Case #13 (c4pgwb_FMX) Actinide Species Distributions, EQ3/6 (using the Harvie, 1981 approximation and corrected values of A^{φ} and $\beta^{(1)}_{NaCl}$) vs. FMT.

	FMT		EQ3/6		
	Molality	Percentage	Molality	Percentage	Δ(molality)%
Total Am+++	4.44684E-07	100.00%	4.4013E-07	100.00%	-1.02%
Am(OH)2+	2.37430E-07	53.39%	2.4211E-07	55.01%	1.97%
AmEDTA-	2.01094E-07	45.22%	1.9171E-07	43.56%	-4.67%
AmOH++	2.82968E-09	0.64%	2.9133E-09	0.66%	2.96%
Subtotal	4.41354E-07	99.25%	4.3673E-07	99.23%	-1.05%
Total NpO2+	4.07047E-07	100.00%	4.1255E-07	100.00%	1.35%
NpO2+	1.45815E-07	35.82%	1.4786E-07	35.84%	1.40%
NpO2CO3-	1.19968E-07	29.47%	1.2343E-07	29.92%	2.89%
NpO2Acetate(aq)	8.44036E-08	20.74%	8.5308E-08	20.68%	1.07%
NpO2Oxalate-	5.03499E-08	12.37%	4.9132E-08	11.91%	-2.42%
NpO2OH(aq)	4.97922E-09	1.22%	5.0680E-09	1.23%	1.78%
Subtotal	4.05516E-07	99.62%	4.1080E-07	99.57%	1.30%
Total Th++++	6.47549E-08	100.00%	6.4745E-08	100.00%	-0.02%
Th(OH)4(aq)	5.19575E-08	80.24%	5.1842E-08	80.07%	-0.22%
Th(OH)3(CO3)-	1.27974E-08	19.76%	1.2903E-08	19.93%	0.83%
Subtotal	6.47549E-08	100.00%	6.4745E-08	100.00%	-0.02%

The corrected EQ3/6 model results for the c4pgwb problem are fairly similar to the uncorrected FMT results in regard to what matters most (gross system composition and actinide total concentrations). There are some notable discrepancies in the details. Similar results would be expected for the c4pgwbx, c4per6, and c4per6x problems. Those problems could be re-worked using the approach illustrated here.