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Carlsbad Programs Group
4100 National Parks Highway
Carlsbad, NM 88220

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to: Record Center

from: Yongliang Xiong
Repository Performance Dept. 6212
MS-1395
Carlsbad Programs Group

Shannon Casey for Y. Xiong

subject: Summary Report for Migration of the WIPP Thermodynamic Code from FMT to EQ3/6
Version 8.0a

This memo is to summarize migration of the WIPP thermodynamic code from FMT to EQ3/6 version 8.0a.

INTRODUCTION

EQ3/6 version 8.0a is a minor revision of version 8.0, which was produced when the WIPP thermodynamic code migrated from FMT to EQ3/6. Version 8.0 has been a qualified software under WIPP (Gilkey, 2006), even though the scope of qualification did not include actinide chemistry. FMT (e.g., Babb and Novak, 1995, 1997; Novak, 1996; Wang, 1998) has been the principal geochemistry modeling code used on WIPP projects for many years, especially for calculations involving actinide chemistry. FMT Version 2.4 (Wang, 1998) has been stable for over ten years, although the supporting thermodynamic database continued to be improved (Xiong, 2005; 2009). The work accomplished under AP-140 extends the qualification of EQ3/6 into actinide chemistry so that it can be used in place of FMT in future WIPP applications (Wolery et al., 2010). The motivation for migration from FMT to EQ3/6 is that there are limitations in the FMT code as detailed in Wolery et al. (2010), and will be briefly described below. This work was performed as part of Analysis Plan AP-140 (Wolery, 2008) and the corresponding change control form (Wolery, 2009).

FMT AND EQ 3/6 FUNCTIONAL CAPABILITY

Both EQ3/6 and FMT contain options to use Pitzer's (1973, 1991) model to calculate the thermodynamic activity coefficients of aqueous species. Each code has a supporting thermodynamic data file largely based on the model of Harvie et al. (1984), which is a Pitzer-based model for the system Na—K—Mg—Ca—H—Cl—SO₄—OH—HCO₃—CO₃—CO₂—H₂O to high ionic strengths at 25 °C.

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There is a suite of supporting data files in EQ3/6, but only one of which can be used in a given calculation. Some support the use of Pitzer's model, and others support the use of other activity coefficient equations including the Davis and the B-dot equations. The "data0.hmw" data file is 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 been used in previous applications of EQ3/6 on WIPP. In contrast, FMT reads a single supporting thermodynamic data file (CHEMDAT) in each calculation. The CHEMDAT files have evolved by adding more species and data to the Harvie et al. (1984) original model. The FMT source code does contain provision for using the B-dot equation, but it seems that no data file has been developed to support this usage. As the B-dot equation is applicable only to dilute aqueous solutions (where Pitzer's equations can also be used) and WIPP applications must address concentrated brines, usage of the B-dot equation is not generally appropriate for WIPP cases. Therefore, the lack of an FMT data file supporting the usage of the B-dot equation is not important.

FMT LIMITATIONS AND ISSUES

As mentioned before, the motivation of migration from FMT to EQ3/6 is that there are some limitations in FMT. As detailed in Wolery et al. (2010), there are two principal functional limitations and one practical limitation in the FMT code. The first functional limitation 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. The second functional limitation of FMT is that it has a phase selection algorithm that is prone to divergence. A "reaction path" calculation in FMT is in fact a series of flash calculations for small increments of change in mass balance totals. Therefore, FMT is not very useful for reaction path calculations, since it has difficulty in adjusting to changes in the phase assemblage along the path and the user can specify only one assemblage for each run.

The practical limitation of FMT is related to the supporting data file. The data file is complex and difficult to safely modify in its present form. Addition of more species and data into the data file at this point would be very difficult.

There are also some additional issues with the FMT code. In the FMT code Pitzer's "eq. 47" approximation equation (Pitzer, 1975) is used for higher-order electrostatic terms. Harvie (1981, Appendix B) later proposed another approximation which is considered to be more accurate. This approximation was incorporated into the Harvie et al. (1984) model for the Na—K—Mg—Ca—H—Cl—SO₄—OH—HCO₃—CO₃—CO₂—H₂O system. As the WIPP geochemistry model is based on the Harvie et al. (1984) model, the FMT code should be using the Harvie (1981) approximation for consistency. In addition, FMT uses a value of 0.39 for the A^ϕ , the Debye-Hückel slope for osmotic coefficient at 25 °C, and a value of 0.2644 for the Pitzer coefficient $\beta^{(1)}_{\text{NaCl}}$. Although these values were given in the Harvie et al. (1984) paper, 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.

CHANGES MADE TO EQ 3/6

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The changes described below were implemented for Sandia National Laboratories WIPP programs (SNL-WIPP) by Tom Wolery as part of the SNL-WIPP Software Agreement TS03197 with Lawrence Livermore National Laboratory (LLNL). Since EQ3/6 is considered to be an 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 discovered 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 supporting the Pitzer model. The FMT data file requires that a value be explicitly assigned to every parameter within the scope of the software. In creating the data0.fmt data file, most of the Pitzer coefficients with zero values were omitted, allowing for a smaller data file. It was found out 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, EQPT, 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. However, the relation between a ψ and its corresponding μ does involve other Pitzer parameters. For instance, $\mu_{cc'a}$ is a function of $\psi_{cc'a}$, C^ϕ_{ca} and $C^\phi_{c'a}$, where c denotes a cation, c' a different cation, and a an anion. This problem was fixed in EQ3/6 version 8.0a by redesigning how the Pitzer C^ϕ , ψ , and ζ coefficients are handled and how the equations are evaluated. These coefficients are all “third order” coefficients. There was no issue with the C^ϕ and ζ coefficients, but the treatment of them was also 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). These two software problem reports and related activities can be found in the Licensing Support Network (LSN) (<http://www.lsnnet.gov>) by first typing SPR001420060309 or SPR001520060309 in the field of Document Content and then by clicking Search. This network supports the license application of Yucca Mountain, and is still accessible as of 12/02/2010. In addition, a small problem in the EQPT database preprocessor was corrected. 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. Some changes were also 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 complexes 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.

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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: The WIPP brine density model in FMT is based on densities of NaCl solutions to output various concentration units. 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 EQ3/6 version 8.0a. 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.

TEST CASE COMPARISON AND ACCEPTANCE CRITERIA

Nineteen test cases were chosen for verification tests. Five test cases were chosen for regression tests for migration from version 8.0 to version 8.0a. These are summarized in Table 1. All of the test cases for verification tests 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).

Table 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	EQ3NR	f24vc3s1	fmt_test3	ThO ₂ (am) solubility in NaCl solutions up to 6 m at pmH 3.8
5B	EQ3NR	f24vc3s2	fmt_test3	ThO ₂ (am) solubility in NaCl solutions up to 6 m at pmH 5.5

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6	EQ6	f24vc7m	fmt_test7a	Invariant point of aphthitite/glaserite–picromerite/schoenite–halite–sylvite in Na-K-Mg-Cl-SO ₄ system
7	EQ6	f24vc7b3	fmt_test7b	Invariant point of borax–teepelite–halite in Na-Cl-B ₄ O 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	EQ3NR	oxcalhem	N/A	Using mineral solubility constraints
16	EQ3NR	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

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 cases have been defined. Type 1 test cases 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

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approximation used by FMT, the results were even closer. Similar recalculations were not attempted for the other test cases in this category.

Type 2 test cases start with an aqueous solution composition that is typically relatively simple 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 test cases 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 test cases include Test Case #4, Test Case #10, and Test Cases #11-14. These calculations 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 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 , the Debye-Hückel slope for osmotic coefficient at 25 °C, should be changed from 0.39 to 0.392 and that of the Pitzer coefficient $\beta^{(1)}_{\text{NaCl}}$ should be changed from 0.2644 to 0.2664 as noted above. The slightly incorrect values were used for the code comparison. The A^ϕ parameter value is hard-coded into FMT. The $\beta^{(1)}_{\text{NaCl}}$ 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 $\beta^{(1)}_{\text{NaCl}}$. To deal with this, EQ3NR should be instructed to charge-balance on chloride (the most abundant anion).

Verification tests (Test Cases #15 through #19) 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.

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Casey, Shannon Leigh

Shannon Casey

From: Xiong, Yongliang
Sent: Wednesday, December 08, 2010 11:13 AM
To: Casey, Shannon Leigh
Subject: Signature Authority

Shannon,

I hereby authorize you to sign for me for the following document (both DRC and authentication) while I am out of my office in December 2010.

Summary Report for Migration of the WIPP Thermodynamic Code from FMT to EQ3/6 Version
8.0a.

Thanks!

Yongliang Xiong

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