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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

Analysis Plan for EQ3/6 Analytical Studies

Task 1.4.1.1

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Authored by:	_Thomas Wolery_	*for Thomas Wolery*	*May 15, 08*
	Print Name	Signature	Date
Reviewed by:	_Martin B. Nemer_		_5/15/08_
	Print Name	Signature	Date
	Technical Reviewer		
Reviewed by:	_Mario Chavez_		_5/15/08_
	Print Name	Signature	Date
	Quality Assurance Reviewer		
Approved by:	_Christi Leigh_		_5/15/08_
	Print Name	Signature	Date
	Department Manager		

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1.1   Introduction

The Waste Isolation Pilot Plant (WIPP) has used the Fracture-Matrix Transport (FMT) code (Novak, 1996, ERMS# 210790; see also Babb and Novak, 1995; Babb and Novak, 1997 and addenda; Wang, 1998) as its principal tool for modeling geochemical interactions in the WIPP repository. The geochemistry part of this software uses Pitzer's (1973, 1975, 1991) equations to represent the thermodynamic activity coefficients of aqueous species including both solutes and the solvent, water. The standard form of the Pitzer equations is based on molalities and requires data for interaction parameters for pairs and triplets of the solute species included in the model (interaction parameters explicitly involving the solvent, water, are not employed). The FMT model is based on the classic Pitzer model of Harvie et al. (1984) for the "sea-salt" system at 25°C and has been extended by adding data for organic complexants (e.g., oxalate, citrate, ethylenediaminetetraacetate [EDTA]) and actinides that are present in the WIPP repository. The most recent FMT model consists of the code FMT v. 2.4 (Wang, 1998) and the thermodynamic database fmt_050405.chemdat (Xiong, 2005). The database extensions have drawn on a number of papers and reports that are too numerous to mention here (complete references are documented in the database itself). Database extensions are all in the FMT Software Records Package under ERMS 210790.

Pitzer's equations have been incorporated into many other geochemistry, atmospheric chemistry, and chemical engineering codes. A complete review is beyond the scope of this analysis plan. These equations and the models based on them enjoy widespread acceptance and use. In geochemistry, Pitzer-based models have been incorporated into EQ3/6 (e.g., Wolery, 1992ab; Wolery and Daveler, 1992; Wolery and Jarek, 2003), the U.S. Geological Survey codes PHRQPITZ (Plummer et al., 1988) and its successor PHREEQC (as of v. 2.12, see http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), and Geochemist's Workbench (e.g., Bethke, 1996; see also http://www.rockware.com/product/overview.php?id=132). These are some of the better-known examples and are used by geochemists worldwide. They have been applied to a wide variety of problems in aqueous geochemistry including mineral-water interactions in many different settings, brine generation by evaporation, and deliquescence of salts. The Pitzer approach presently enjoys widespread credibility in the technical community, although alternative approaches such as Extended UNIQUAC (e.g., Thomsen, 2005) do exist and are drawing increasing interest.

The more widespread geochemistry codes are designed to work with any of several supporting thermodynamic databases, including user-modified and user-generated databases, with the understanding that the user is to pick the database that best suits the problem at hand. It is now common for one of these codes to permit the use of any of several different activity coefficient models (e.g., the Davies equation, the B-dot equation, Pitzer's equations; cf. Wolery 1992b, Section 3). A particular database generally exists for the combination of code and activity coefficient model. The geochemical "model" here thus consists of the code as a numerical engine and the particular database that is used to support it. The WIPP FMT geochemical model is basically unique only in regard to its thermodynamic database, which has been developed

especially for WIPP applications. A translation of the FMT database could be used with any of the other major codes acting as a numerical engine.

EQ3/6 (e.g., v. 8.0, Wolery and Jarek, 2003) is qualified software (Software Tracking Number: 10813-8.0-00) on the Yucca Mountain Project (YMP). On the YMP, EQ3/6 has been extensively used in applications with both a dilute-systems (non-Pitzer) database (data0.ymp) covering a very large number of chemical components and species, and a Pitzer database (data0.ypf) covering a smaller number of components and species. On the YMP, codes and supporting databases are qualified separately. Only the two databases noted above are qualified for YMP use, though over a dozen others exist, including two other databases (data0.hmw and data0.pit) that are based on Pitzer's equations. The database data0.hmw is the EQ3/6 rendition of the Harvie et al. (1984) "sea-salt" system model.

EQ3/6 (version 8.0 and some older versions) has also been qualified for use on the WIPP project. The WIPP qualification of v. 8.0 (using the data0.hmw database) is documented in the "Verification and Validation Plan/Validation Document" (Gilkey, A., 2006). That report examines the code performance on eighteen test cases from the EQ3/6 test case library (which is distributed with the software). To date, EQ3/6 has been used on WIPP mainly to supplement FMT calculations, as for the analysis of potential "excursions" in the repository system (localized or temporary variations vis-a-vis the geochemistry conceptual model). This has been done in part because FMT is not as numerically robust as EQ3/6. This does not mean that FMT results are incorrect; it means that FMT sometimes fails to complete calculations for certain problems. This is particularly true for reaction path problems, which simulate dynamic chemical reaction. The calculations made by FMT, EQ3/6, and similar geochemical software are often highly challenging from a numerical point of view, meaning that iterative calculations may not always converge (but results, when obtained, are generally correct).

It is desirable at this time to migrate the FMT-based WIPP geochemistry model to EQ3/6 in order to facilitate future analyses of the repository system. EQ3/6 is a good choice because it has credibility from its widespread usage and its role as a mainstay code on the Yucca Mountain Project, its strong numerical robustness (particularly for dynamic reaction-path calculations), and the fact that the existing FMT-based model can be migrated by porting the FMT thermodynamic database to an EQ3/6-compatible format. That model migration, consisting of the database port and necessary following activities, comprise the "EQ3/6 Analytical Studies" that are the subject of this Analysis Plan.

Thermodynamic models of aqueous electrolytes including natural brines are generally based on using the molality (moles/kg solvent water) as the "native" unit of concentration. This is true of model implementation in both EQ3/6 and FMT. FMT, however, also calculates concentrations in terms of molarity (moles/liter of solution) for input to WIPP performance assessment. Presently EQ3/6 only calculates concentrations in terms of molality. The EQ3NR code (Wolery, 1992b) that is part of the EQ3/6 package allows the use of molarity as input, but any such inputs are converted to molalities prior to making the main calculations. Output molalities can be converted to molarities external to EQ3/6 (as in a spreadsheet), using the same conversion formula utilized internally by FMT.

The molarity vs. molality issue extends to the pH, as WIPP uses three definitions, all of which are output by the FMT code. The first is $pcH = -\log(\text{molarity}(H^+))$. Experimentally, the pcH is

obtained from the standard "measured pH" by adding a brine-specific correction (Rai et al. 1995; see also discussion in Felmy et al. 2000) for the liquid-junction error that is encountered when the standard measurement practice is used on a concentrated salt solution. The second form of pH is pmH = - log(molality(H^+)). Experimentally, the pmH could be obtained in similar manner, using an analogous brine-specific correction (for any specific brine, this correction would be different from the one used to obtain the pcH). Alternatively, the pmH could be obtained from the pcH by employing a molarity to molality conversion. The FMT code provides a third form of pH (given simply as "pH") , defined as pH = - log(activity (H^+)), where the activity of the hydrogen ion is calculated as the product of the molality and the molal activity coefficient of the hydrogen ion, and this activity coefficient is evaluated using the common form of Pitzer's equations for single-ion activity coefficients (see for example Wolery, 1992b, Section 3.5). This "pH" is in effect the pH on an unsanctioned "Pitzer" pH scale. This pH has the advantage of consistency with the Debye-Huckel limiting law, and thus approaches pH on the standard NBS/NIST scale in dilute solutions (see Wolery, 1992b, Section 3).

The treatment of pH in EQ3/6 is as follows. The pcH is not used, either as an input or as an output. That is because the usual thermodynamic framework for treating aqueous electrolyte solutions (including Pitzer's equations) is based on molalities, not molarities (cf. Garrels and Christ, 1965; Nordstrom and Munoz, 1985; Pitzer, 1973, 1991). Thermodynamic activities of aqueous solute species are defined on a molal basis, in which the activity is defined as the product of the molality and the molal activity coefficient ($a_i = m_i\gamma_i$, which in logarithmic form becomes $\log a_i = \log m_i + \log \gamma_i$). Various molality-based activity scales are possible, depending on how one chooses to deal with γ_i, which requires the assumption of an arbitrary convention (cf. Wolery 1992b, Section 3.4). Since an activity scale may affect pH through the usual definition of the pH in terms of activity of the hydrogen ion, an activity scale (affecting all ions in solution) is tied to, and can be defined as, a "pH scale." Since pcH does not directly fit into a molality-based framework, it must be converted to some molality-based form of pH before it can be used as a input. It can be calculated from a molality-based form if needed as the output of a calculation. EQ3/6 itself does not perform such calculations in regard to pcH. In EQ3/6 the pmH is known as pH on the "Mesmer" scale (Wolery, 1992b, Section 3.4). It is not normally an input, though it can be; it is a normal output. The pmH is a molality-based form of pH which is equivalent at least to defining $\log \gamma(H^+) = 0$ under all conditions (so that pH is then equal to -log molality(H^+)). Normally, the "pH" that is reported by (or input to) EQ3/6 is that on the standard NBS/NIST (National Bureau of Standards, now the National Institute of Standards and Technology) pH scale (see for example Wolery, 1992b, Section 3.4), which is another molality-based form of pH. This form is not directly used by WIPP, but is the scale pertinent to the modern standard "measured" pH. It uses the Bates-Guggenheim equation to define the activity coefficient of the chloride ion (cf. Wolery, 1992b, Section 3.4), and thus indirectly specifies the activity coefficient of the hydrogen ion. The WIPP methodology for experimental determination of pH (Rai et al., 1995) calls for measuring this in the presence of liquid junction error and making a brine-specific correction that yields pcH (thus correcting for the liquid junction error and converting to a molarity-based form of pH). In EQ3/6, the pH that is reported (or input) is the pH on the unsanctioned Pitzer scale noted above if Pitzer's equations are used and if the input file option for rescaling of single-ion activity coefficients is set to "no rescaling" (iopg(2) = -1). This appears to match the "pH" reported by FMT. The default rescaling option in EQ3/6 rescales single-ion activity coefficients to be consistent with the NBS/NIST pH scale. In EQ3/6, single-ion activities are tied to the scaling option chosen for single-ion activity coefficients. Thus,

rescaling the activity coefficients rescales the activities. For further information on the topic of pH, the reader is referred to Woleryn (1992b, Section 3) and sources cited therein.

1.2   Objectives

The overall objective is to migrate the current WIPP FMT-based model to EQ3/6, so that EQ3/6 can be used as the numerical engine in future analyses. A specific objective is to test EQ3/6 against FMT head-to-head in WIPP-relevant applications. This will serve the dual purpose of testing the WIPP FMT model migration to EQ3/6. It will also serve to alleviate any potential concerns about the original WIPP qualification of EQ3/6 v. 8.0 in that no test cases were run that involved either WIPP-relevant scenarios or head-to-head comparison with FMT. A second specific objective is to include this documentation in revisions of the relevant qualification documents. The understanding here is that the software, which is already qualified, is not being re-qualified. Rather, the documented basis of the qualification is being extended for confidence-building. A third specific objective is to ensure that EQ3/6 results can be used for input to performance assessment. This will require a means of converting molarities to molalities (including pcH to pmH), preferably using the same conversion formula that is used in FMT.

2   Approach

2.1   Database Conversion

The database conversion will be handled in the following manner. The EQ3/6 data file data0.hmw, which is the EQ3/6 rendition of the Harvie et al. (1984) "sea-salt" model will be used as the initial template for data0.fmt. It is noted that this datafile has previously been used as such a template for the addition of some WIPP-specific data to modified datafiles (in the following series: data0.hmp: Xiong, 2004; data0.hmy: Xiong 2006a; data0.hml: Xiong 2006b; data0.hmo, Xiong, 2007). These previously developed datafiles provide examples of some of the datablocks for specific species and associated reactions to be added to data0.fmt. However, they will not be used as direct sources of data to data0.fmt. The new datafile data0.fmt will instead be created directly from data0.hmw and the FMT datafile fmt_050405.chemdat (Xiong, 2005). The data0.hmo file (Xiong, 2007) may be used as a subsequent point of comparison for data0.fmt.

In the series data0.hmo, the organic ligand species (e.g., citrate, EDTA) were defined using fictive chemical elements such as "Citrate" instead of the actual chemical elements such as carbon, in order to preserve the desired mass balances for these ligands (e.g., as a method to prevent citrate from oxidizing to bicarbonate). In version 8.0 of EQ3/6, this is not necessary. Rather one species representing the ligand type (say citrate ion) can be defined on the datafile as an auxiliary basis species (see Wolery, 1992b, Section 5.2). The datablock for citrate ion as an auxiliary basis species would contain a reaction linking that species to the bicarbonate ion (the strict basis species representing elemental carbon; see Wolery, 1992b, Sections 5.1 and 5.2). The datablock for any other citrate species would contain a reaction linking that species to the citrate ion. The definition and preservation of a mass balance specific to citrate (whether or not citrate

can convert to other carbon-bearing species and vice versa) is then controlled entirely in software, following instructions given on the EQ3/6 input file (See Wolery 1992b, Section 6).

The FMT data file datafile fmt_050405.chemdat (Xiong, 2005) contains thermodynamic data in the form of standard Gibbs energies of formation at 25°C. This datafile does not contain chemical reactions. In EQ3/6, each species other than strict basis species is associated with a reaction in which that species is a reactant, and in which all other species are basis species of the strict or auxiliary type. Instead of a Gibbs energy for the species, an equilibrium constant (log K) for the reaction is provided. To accomplish the necessary data conversion, a set of requisite reactions will be constructed, and the corresponding log K values will be obtained from the fmt_050405.chemdat Gibbs energy values for the species appearing in the reactions. This will be accomplished using the standard thermodynamic relations (e.g., Garrels and Christ, 1965, p. 8; Nordstrom and Munoz, 1985, p. 210-217). A script or spreadsheet will be used to accomplish this translation, and the results will be put into the new data0.fmt file by hand-editing. Additional Pitzer coefficient data from fmt_050405.chemdat does not require conversion and will be added as-is.

2.2   Comparing Results: EQ3/6 vs. FMT

The data0.fmt file will be used in a head-to-head comparison of EQ3/6 v. 8.0 with FMT on a set of problems including ones that are directly WIPP-relevant. For this purpose, to ensure the highest degree of consistency, FMT runs will be repeated as necessary so that all FMT outputs are obtained from FMT 2.4 (Wang, 1998) using the database fmt_050405.chemdat (Xiong, 2005). A high degree of consistency is expected. Typically, consistency between results from different codes is limited by such factors as input/output precision, arithmetic precision in the calculations (e.g., single- vs. double-precision), precision in values assigned to constants, and convergence tolerance. For both EQ3/6 and FMT, these factors are not expected to be problematic. Most results should agree in the first four significant figures, if not better. However, this is a general expectation, not a requirement. In general, the values to be compared will consist of molalities and one or more relevant forms of pH, though in some test cases the output molalities will be unchanged from input values and attention will focus instead on activities and/or activity coefficients. In some cases, calculated values of oxygen fugacity or some other measure of the redox state may be compared.

For requirements planning purposes related to EQ3/6 qualification revision, molalities (or activities or activity coefficients, or oxygen fugacity) will be expected to agree within 1%. Alternatively, corresponding base-ten logarithmic values, if comparison is done in that form, will be expected to agree within 0.004 log unit (1% actually corresponds to a tolerance of 0.00432 log unit). The pH (as pmH or pcH or the "pH" on the unsanctioned Pitzer pH scale) will be expected to agree within 0.01 unit. In some problems, certain quantities may be fixed at input values; in such cases, comparison is not meaningful and will not be done. The revision to the EQ3/6 v. 8.0 requirements document will specify the actual quantities to be compared for each test problem. It is here noted that a key result of comparing results from the two pieces of software will be how well the calculations actually do agree, and that will be included in the documented results.

The above expectations and requirements presume that the codes are actually solving the same problem. Subtle differences in problem definition could cause different results. The test cases

will be carefully examined to eliminate or work around differences in problem definition. One notable difficulty is that in the FMT test cases, the pH (in any form) does not appear to be a normal input in defining the initial solution composition, whereas the EQ3NR code (generally required to initialize any EQ3/6 calculations) normally expects such an input. FMT does have an option for fixing the pH that might be used to work around that, but the efficacy of such an approach remains to be determined.

The above expectations and requirements also presume that the outputs being compared have values that are not indifferent to the problem definition. For example, values pertinent to the redox state will not be compared for test cases which are indifferent to the redox state. The above expectations and requirements further presume that the quantities to be compared are not themselves subtly different. The issue of different forms of pH has already been noted. Additional scaling issues may apply to reported activities and activity coefficients for single ions. A full accounting of these potential differences and means of accounting for them is beyond the scope of this document. Instead, the reader is referred to Section 3.4 of Wolery (1992b).

The set of problems to be used in this comparison will include existing test cases for both EQ3/6 and FMT, as well as some new test cases. Apart from revising the qualification documents for EQ3/6 v. 8.0, a principal purpose of the planned comparison is to provide confidence that the substitution of EQ3/6 for FMT does not cause unforeseen differences in the results. The overall set of test cases for this activity is designed with that in mind.

Sometimes a problem of the sort to be used in these comparisons permits the calculation to be made using more than one logical path. Consider the following illustration, which uses the codes in the EQ3/6 package. The solubility of a mineral (say, NaCl) in water can be found using the EQ6 program (e.g., Wolery and Daveler, 1992) by starting with a pure or "deionized" water and adding quantities of the mineral until saturation is reached. This is a titration or reaction-path approach. It may also be possible to find the same solubility using the EQ3NR program by specifying a solubility constraint on a constituent ion (say, Na^+) and an electrical balance constraint on another (say, Cl^-). This approach is less intuitive, but it leads to the same answer. It tends to be more challenging numerically, and it may not work for some extremely soluble minerals. For these comparisons, the same logical path will be followed in setting up a problem for both EQ3/6 and FMT, to the extent that it is feasible to do so. In some cases, it may not be feasible owing to differences between the two codes. Any instances involving the use of different logical paths will be documented in the revised validation report for EQ3/6 v. 8.0.

Existing EQ3/6 test cases will be altered as needed so that both codes can run them. In particular, EQ3/6 inputs generally specify the pH on the NBS/NIST pH scale. These NBS pH values will be replaced by pmH (Mesmer pH) values calculated by EQ3/6. For the purposes of this testing, the pmH results will be obtained using EQ3/6 running the original test case input file but with the data0.fmt data file. For the head-to-head comparison, the problem will be re-run with EQ3/6 using those pmH results. Inputting a Mesmer pH to EQ3/6 requires selection of a general rescaling of activity coefficients and activities of all aqueous ionic species for consistency with the Mesmer scale. This is by design (see Wolery, 1992b, Section 3 for discussion of activity coefficients, scaling issues, and equations used in scale conversion). Thus, the EQ3/6 values of these quantities may not directly match those reported by FMT (which may treat these scaling issues in a different way). In such instances, any comparisons of single ion property values must be made using combinations that correspond to electrical neutrality [e.g., log a(Na^+) + log a(Cl^-);

pHCl = -log a(H$^+$) - log a(Cl$^-$)]. The reported values for the activity of water (which is electrically neutral) should be comparable, as should the molalities of the solute species. In general, it will be sufficient to focus the comparisons to be made on molalities and the pH (as one or more of pcH, pmH, and pH on the unsanctioned Pitzer pH scale), although attention should be shifted to activities in certain problems in which the final molalities are unchanged from input values (an example is the sea water test case discussed below).

2.3 WIPP-Relevant Test Cases

The test cases to be used will be drawn from the EQ3/6 test case library (Wolery, 1992b, Wolery and Daveler, 1992), the test cases used in the qualification of FMT v. 2.4 (Wang, 1998), and recent WIPP calculations (Brush 2005; Brush et al. 2008). The actual set of test cases to be used will be selected in the revised requirements document for the qualification of EQ3/6 v. 8.0. At least eleven test cases will be used for the head-to-head comparison to be included in the revised qualification documents. The head-to-head comparison work will be segregated in these documents. The previous test case work will be left as-is. Each of the three EQ3/6 test cases that were included in the original EQ3/6 v. 8.0 qualification and which will also be used in the head-to-head comparison with FMT will be treated as two separate test cases (one in the original set, one in the head-to-head set). This will be necessary because a different thermodynamic database will be used in the head-to-head calculations.

2.3.1 Test Cases from the EQ3/6 Test Case Library

The test cases previously used for EQ3/6 are documented in the original qualification activity for version 8.0 (cf. Gilkey, 2006, "Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0." Document Version 8.01. ERMS #544574. July 18, 2006). The test cases that will be taken and modified from this set are:

- Test #2 (modified), Sea water test case, using Pitzer's equations. Only the major components of sea water are included here. This test calculates the molalities, activity coefficients, and activities of the aqueous species. The original problem specifies an NBS pH of 8.22. This will be replaced by the corresponding pmH obtained as described above. In the EQ3/6 context, this is an EQ3NR speciation-solubility calculation. In the FMT context, it is a "batch" calculation. Although not WIPP-specific (it does not use data specific to WIPP) and not directly WIPP-relevant, this is a classic code-to-code test case (e.g., Nordstrom et al., 1978). Sea water is a relatively dilute brine. It has essentially the same major "sea salt" components as WIPP brines.

- Test #7 (modified as needed), Dead Sea brine test case. This test case addresses a concentrated surface brine. This test calculates the molalities, activity coefficients, and activities of the aqueous species. No pH value is input. Instead, the pH is calculated from other concentration inputs along with the constraint of a log CO_2 fugacity of -3.5 (approximately the atmospheric value). The scaling of activity coefficients and activities of ionic solute species may be redefined to allow easier comparison with the results obtained from FMT (EQ3/.6 has a no-scaling option; by default, it scales for consistency with the NBS pH scale). Mode-wise, this is the same

type of calculation as in Test #2 above. This test case is also not WIPP-specific and not directly WIPP-relevant, but addresses a concentrated surface brine of considerable interest. It has essentially the same major components as WIPP brines.

- Test #13 (modified as needed), Gypsum solubility in NaCl solutions. This test case calculates the solubility of gypsum ($CaSO_4.2H_2O$) as a function of NaCl molality from zero molal to halite saturation (just over 6 molal). This is accomplished by adding NaCl to an initially gypsum-saturated water, with excess gypsum present. The scaling of activity coefficients and activities of ionic solute species in this problem may be redefined to allow easier comparison with the results obtained from FMT. In the EQ3/6 context, this is an EQ6 titration or reaction-path calculation which must be initialized by an EQ3NR calculation (but the same results could be obtained from a series of EQ3NR runs in which the NaCl molality is varied over the desired range). In the FMT context, this is a "titration" calculation. This test case addresses (in a simplified chemical system) the two brine-mineral equilibria (sodium chloride, calcium sulfate) that strongly exemplify WIPP brines. This test case is WIPP-relevant, but it is not WIPP-specific (it does not use data exclusive to WIPP, such as an actual WIPP brine composition).

2.3.2   Test Cases Used to Validate FMT v. 2.4

The test cases used for the validation of FMT v. 2.4 are documented in Wang (1998, "WIPP PA Validation Document for FMT (Version 2.4)"). The eight cases are:

- Test Case #1. Speciation in WIIPP SPC (Salado Primary Constituent) Brine. This test case is similar in form to EQ3/6 Test #2, in that the objective is limited to calculating species concentrations and activities in an aqueous solution comprised of "sea salt" components. In this case, the solution is a WIPP brine.

- Test Case #2. Solubility of Hydrated $NaNpO_2CO_3$ in NaCl Solution.

- Test Case #3. ThO_2 (am) Solubility in 6 m NaCl Solution.

- Test Case #4. Solubility of $NaAm(CO_3)_2 \cdot 6H_2O$ in Na_2CO_3 and $NaHCO_3$ Solutions.

- Test Case #5. Solubility of $AmPO_4$ in Na_2SO_4 Solutions.

- Test Case #6. Fixing CO_2 Fugacity or pH and Disabling Chemical Species as Needed.

- Test Case #7. Calculation of Chemical Invariant Points.

- Test Case #8. Speciation of Am(III), Th(IV), and Np(V) in WIPP SPC Brine.

At least four of these test cases, or slight modifications thereof, will be used in the head-to-head comparison of EQ3/6 with FMT (the final selection will be made in the revision to the EQ3/6 v. 8.0 requirements document).

The first FMT test case on the above list is similar mode-wise to EQ3/6 Test #2. It substitutes a WIPP brine for seawater. The last case (#8) is also similar mode-wise to Test #2. It substitutes a WIPP brine containing some dissolved actinides. The remaining test cases are similar mode-wise to EQ3/6 Test #13. In regard to test case #6, EQ3/6 does not permit directly fixing the pH in titration or reaction-path mode, although a series of EQ3NR runs or even a series of EQ6 runs could be used to make equivalent calculations. Generally calculations involving fixed pH are only of interest when making Eh-pH diagrams or modeling an experiment using a pH-stat. EQ3/6 does permit fixing CO_2 fugacity in both EQ3NR and EQ6. Hence, this case will likely be modified to remove the fixed pH element or it will probably not be used.

2.3.3   Test Cases Drawn from Recent WIPP Calculations

The above test cases do not include examples in which actinides and organic ligands such as citrate or EDTA are present. At least four additional test cases including organic ligands will be drawn from recent WIPP calculations that utilized FMT. Brush (2005, Table 4) summarizes 12 runs, of which 6 include organic ligands. Two runs (#7 and #11) were used to provide actinide solubilities used for PABC (Performance Assessment Baseline Calculations). Both include organic ligands and brucite-hydromagnesite assemblages. Run #7 includes GWB brine (Generic Weep Brine, a synthetic brine representative of intergranular Salado brines). Run #11 includes ERDA-6 brine (Energy Research and Development Administration [WIPP Well] 6, a synthetic brine representative of fluids in Castile brine reservoirs). Test cases based on Runs #7 and #11 will be included in the test cases used for the head-to-head comparison of EQ3/6 and FMT. Brush et al. (2008) have made recent FMT runs to examine the sensitivity of calculated actinide solubilities in WIPP brines to the assumed concentration of EDTA. Test cases based on the two "10x" EDTA runs for the GWB and ERDA-6 brines will also be used in the head-to-head comparison. Thus, the minimal set of four test cases including the effect of organic ligands has been defined.

2.4   Molarity vs. Molality

For the purposes of head-to-head comparison of EQ3/6 and FMT results, concentrations in molality units will suffice. For subsequent usage of EQ3/6, a means will be necessary to convert EQ3/6 molality outputs to molarities for subsequent usage in performance assessment. The equations for interconverting molality and molarity are discussed in various sources (see for example, Garrels and Christ, 1965, p. 3-5; Wolery, 1992b, Section 2.2). Required are the solution density (mass per unit volume) and the total dissolved salt content (mass per unit volume of solution or mass per unit mass of solution). If all solute molalities are known, it is straightforward to calculate the total dissolved salt content. The density, however, must be known, calculated from the solution composition using a volumetric properties model, or approximated by using the volumetric properties of a model dissolved salt, such as sodium chloride. FMT uses the latter approach (sodium chloride proxy), which is embedded in function "density" (fmt_density.for). The proxy correlation function is fit to NaCl density data at 20°C that are given on p. E-227-228 and D-261-262 of Weast and Astle (1979, "CRC Handbook of Chemistry and Physics, 60th edition). The same proxy correlation and conversion equation will be used in a spreadsheet to convert EQ3/6 molality outputs to molarities. A template spreadsheet

will be created for this purpose. The template spreadsheet will be designed to facilitate copying and pasting EQ3/6 results in molality units from EQ3/6 output (.3o., .6o, .6t) files.

3   Software List

The WIPP codes to be used for this analysis are listed in Table 3-1. These codes will be used for comparative calculations of WIPP-relevant geochemistry scenarios to enhance the qualification of EQ3/6 as described above in Section 2. These codes will be executed on the machines listed in Table 3-2. Commercial off-the-shelf (COTS) software such as MATHEMATICA®, MATLAB®, MathCAD®, Excel®, Visio®, CorelDRAW®, Corel Paint Shop Pro X®, or Origin®, running on MS Windows XP®-based PC workstations may also be utilized. The use of any COTS application for routine calculations will be justified per NP 9-1, Appendix C and NP 19-1 as appropriate.

Table 3-1 Codes to be used for the EQ3/6 Analytical Studies Analysis.

Code	Version	Use
EQ3/6*	8.0	Software comparison
FMT*	2.4	Software comparison

* - Qualified

Table 3-2. Platforms to be used for the EQ3/6 Analytical Studies Analysis.

Platform Description	ID Number	Operating System	Location	User(s)
Dell Precision Workstation 650	DOE# 8594134	Windows XP®	LLNL (B543, R2210)	Wolery
Dell Precision Workstation 340	S838019	Windows XP®	SNL, Carlsbad	Xiong
Dell Precision Workstation 360	S85186	Windows XP®	SNL, Carlsbad	Xiong
Dell Optiplex 745	S891823	Windows XP®	SNL, Carlsbad	Deng
Seals		Unix/Linux	SNL, Carlsbad	Ismail

4   Tasks

Table 4-1 Summary of Tasks.

Task	Description	Approximate Completion Date	Responsible Individual(s)
1	Convert FMT database "fmt_050405.chemdat" to EQ3/6 format ("data0.fmt"), using a spreadsheet or script to make the necessary numerical conversions	5/31/2008	Wolery, Ismail

Task	Description	Approximate Completion Date	Responsible Individual(s)
2	Check converted database for possible errors, including check against original data sources	6/15/2008	Deng, Xiong
3	Resolve any potential database issues arising from checking, and complete any changes to both the FMT and EQ3/6 databases	6/30/2008	Wolery, Deng, Xiong
4	Select and describe test cases for head-to-head comparison of EQ3/6 with FMT for WIPP-relevant geochemistry scenarios	6/30/2008	Wolery, Xiong, Deng
4a	Complete the NP 19-1 Change Control Form for EQ 3/6	6/10/2008	Wolery, Xiong, Deng
4b	Revise the EQ3/6 v. 8.0 requirements document and the verification and validation plan section of the verification and validation plan/validation document to include this information.	6/30/2008	Wolery, Xiong, Deng
4b	Technical and management QA review		
5	Create and test template spreadsheet for converting EQ3/6 concentration output from molalities to molarities (including pmH to pcH).	7/15/2008	Wolery, Xiong
6	Exercise the new test cases	7/31/2005	Wolery, Xiong, Deng
6a	Create/gather EQ3/6 and FMT input files for the selected test cases	6/30/2005	Wolery, Xiong, Deng
6b	Run the selected test cases	7/15/2005	Wolery, Xiong, Deng
6c	Complete comparisons	7/31/2005	Wolery, Xiong, Deng
7	Revise the validation section of the EQ3/6 v. 8.0 "verification and validation plan/validation document"	9/28/2008	Wolery, Xiong, Deng
7a	Complete revised draft	(8/31/2008)	
7b	Technical and management QA review		
8	Complete Summary Report Deliverable (regarding NP 19-1)	9/28/2008	Wolery, Xiong

5 Special Considerations

No special considerations have been identified.

6   Applicable Procedures

All applicable WIPP AQ procedures will be followed when conducting these analyses.

- Training of personnel will be conducted in accordance with the requirements of NP 2-1, *Qualification and Training.*
- Analyses will be conducted and documented in accordance with the requirements of NP 9-1, *Analyses.*
- All software used will meet the requirements laid out in NP 19-1, *Software Requirements* and NP 19-1, as applicable.
- The analyses will be reviewed following NP 6-1, *Document Review Process.*
- All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records.*
- New and revised parameters will be created as discussed in NP 9-2, *Parameters.*

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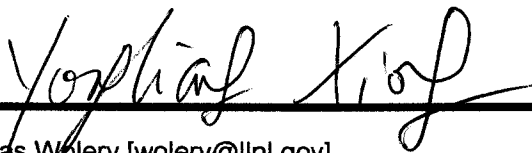
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Chavez, Mario Joseph

From:	Thomas Wolery [wolery@llnl.gov]
Sent:	Thursday, May 08, 2008 10:40 AM
To:	Xiong, Yongliang
Cc:	Chavez, Mario Joseph; Leigh, Christi D
Subject:	Signature authority for me for AP-140

Yongliang,

   I hereby authorize you to sign AP-140 on my behalf. Please push folks as needed to get this AP signed off on asap, so we can get started on the work next week.

     Thanks, Tom

Thomas J. Wolery
Deputy Associate Program Leader
Yucca Mountain & Repository Science Program L-645, LLNL, PO Box 808 Livermore, CA 94550
E-mail: wolery@llnl.gov
Voice: 925-422-5789
Fax: 925-422-2105

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