REVIEW OF THE DECEMBER 1, 2004 DRAFT RESEARCH REPORT ENTITLED "DOCUMENTATION AND APPLICATION OF THE REACTIVE GEOCHEMICAL TRANSPORT MODEL RATEQ"

Review Document:

Curtis, G.P., "Documentation and Application of the Reactive Geochemical Transport Model RATEQ". December 1, 2004.

I. Scope of Review

The Office of Nuclear Regulatory Research requested a review of the RATEQ manual [1] "especially with respect to the clarity of its descriptions of the use of RATEQ". Because the code was not supplied during the review period, this review includes only comments regarding the manual itself. This review does not include comments regarding the utility of the manual to a person using the code.

II. General Comments

1) Because of the complexity of the physical systems modeled by RATEQ, creation of appropriate models will require input from persons expert in developing hydrologic as well as chemical models. This requirement is inherent to the complex problems that RATEQ can be used to model and is not a flaw of the model or documentation. However, the high level of chemical and hydrologic expertise required to use the code effectively may limit its use if guidance is not provided with the code. Although outside the scope of the reviewed document [1], use of the code would be facilitated by additional documentation that describes the physical meaning of parameters and gives additional guidance on the use of the code.

2) RATEQ is capable of solving a variety of different types of problems, including 1-D, 2-D, and 3-D transport problems with and without rate controlled chemical reactions and with and without spatially varying chemical conditions. Because different sets of input files are required from the user to solve different types of problems, it would be helpful for the manual to include a table that lists types of problems that could be addressed and the input files that are necessary for each type of problem. For example, the manual describes how to define a reaction database file when batch and 1-D calculations are used [1, p. 28], and in a different location [1, p. 9] explains that an RDB file is used to define the reaction database when MODFLOW is used. A summary of the different input files used to solve different types of problems would help the user to create the necessary input files more efficiently. In addition it would be helpful if the table included the role of each file required to solve each type of problem. For example, it would be helpful to include a brief description of the role of the Reaction Data File and how it compares to the role of the Geochemical Reactions File.

3) It would be helpful for example problems to contain references to pages in the manual that explain the keyword or option being used. It was necessary to refer back to the text to understand the example problems, especially because the arguments of many of the options were not labeled in comments in the example problems.

4) The author should review the equations in Chapter 2. In some places, the equations do not seem to correspond to their descriptions in the text. For example, in Equations 2-3 and 2-5, it appears that the intent may have been to use the mobile porosity, θ_m, and the immobile porosity θ_{im}, but the total porosity, θ, was used instead. In addition, several of the symbols used in equations in Chapter 2 were not defined. For example, the symbol Ψ is used in Equations 2-12, 2-13, and 2-14, but the meaning of Ψ is not indicated. Furthermore, both an uppercase and lowercase Ψ are used in Equation 2-12, and it is not clear if there is meant to be a distinction between the meaning of Ψ and the meaning of ψ. This type of omission occurs in several places in the document and all occurrences are not listed here.

5) In general, the author of the RATEQ documentation presumes that the user will consult documentation for MODFLOW, MT3DMS, and PHREEQC before using RATEQ. This is a reasonable assumption and eliminates the duplication of work that would be required to reproduce existing documentation in the RATEQ manual. However, it would be helpful if the RATEQ manual could indicate which options are standard parts of MODFLOW, MT3DMS, or PHREEQC and which are unique to RATEQ. For example, Section 3.3.4 [1] describes options to be used in the geochemical input files but does not distinguish between options that are standard to PHREEQC and those that are unique to RATEQ. An indication of which options are unique to RATEQ could prevent the user from wasting time looking for documentation of those options in the PHREEQC manual.

6) Reasons for and implications of differences between RATEQ and the standard implementations of MODFLOW-2000, MT3DMS, and PHREEQC should be explained in the RATEQ manual. For example, the report indicates [1, p. 22] that the "Log K must be 0.0 for primary master species for PHREEQC, but this in not necessary for RATEQ" but does not discuss the reasons for or the implications of this difference between PHREEQC and RATEQ. In this case, it would be helpful if the RATEQ manual discussed why the user may want to choose a non-zero Log K value for a primary master species when using RATEQ. In general, the reader can consult documentation for PHREEQC and MODFLOW for background information, but differences between RATEQ and these programs should be explained in the RATEQ manual.

7) There appears to be a great deal of opportunity for error caused by the use of incorrect units because the program does not read units from many types of input data. For example, in the example problem in Table 5.1, the duration of a timed event is specified as 4.17 (without units) and it is explained in the caption of Figure 5.1 that the duration of the timed event was 4.17 hours [1, p. 61]; however, in the same example problem the maximum time of the simulation is specified as 6.5 days. It is unclear where the units of the timed event are specified, and why they are different from the time units of the maximum time of the simulation. Because RATEQ does not convert units automatically, the use of different time units in the same simulation is potentially confusing to the user, especially when it is unclear where in the input file the units of the timed events are specified.

This type of error may be more difficult to detect when parameters that require compatible units are input in different files. For example, in the input file for the rate equations, it is assumed that the units are consistent with the time units in the flow model [1, p. 25]. Because the input for the flow model and rate equations are in different files, it appears that it will be easy for a user to use one unit for time in the rate equation in the geochemical input file and a different time

unit in the flow model, which will result in incorrect predictions. It would be helpful if there were a mechanism for specifying the time units of rate constants in the same record as the rate constants themselves. Ideally, the code would convert the rate constants into units compatible with the flow model. If that is not possible, it would be helpful if some type of warning could be given to the user if the units in the geochemical and flow models are not compatible.

III. Specific Technical Comments

1) The input for the SCONC record in the Basic Transport File requires additional explanation. The manual [1] indicates that the format of this record is modified with respect to the format used in MT3DMS [1, Table 3.3], but the input format for this record is not given in the discussion of SCONC in the RATEQ manual [1, p. 13]. The format also is difficult to infer from the example problems. For example, the manual indicates [1, p. 10] that a value of 170 as the first argument of the first record in an Array Reader Input Files indicates that the array reader should be invoked to read spatially varying values from an input file. However, in the example in Table 5.2, this parameter appears to be used as part of the Basic Transport File rather than as part of an Array Reader Input File. Furthermore, the example in Table 5.2 also uses the value 180 as the first argument of some of the chemical data records instead of 170, but no explanation is given of what this parameter value indicates. Because this issue is not discussed in the instructions for input to the Basic Transport File in the MT3DMS manual [3], it should be addressed in the RATEQ manual.

2) The option force_rate is included in Table 3.10 but is not discussed in the text. It is unclear why this option would be used because the default behavior described in the text [1, p. 23] is that a rate is always used if a rate controlled equation is included in the input file and the equilibrium relationship is used if a rate is not given.

3) The text states that only the diffuse layer model is supported [1, p. 29]. This statement is unexpected because RATEQ was used to perform transport calculations in NUREG/CR-6820, which it is stated that a non-electrostatic model was used. It is unclear how the user would specify the use of a non-electrostatic surface complexation model [1, p. 29].

4) The documentation of the timed events data block [1, p. 35] indicates that the data block is used only “when the LMT file is generated internally”. The meaning of this statement is unclear because the generation of the LMT file is not discussed in the RATEQ manual. It would be helpful to the user to include a discussion of when the LMT file is generated internally, what it means for the LMT file to be generated “internally”, and in what other ways the LMT file may be generated.

5) The arguments of the option “Boundary_Conditions” [1, p. 35] should be described. The reader can infer from the example problems that the arguments are location, ymin, ymax, and solution number [1, p. 49]. However, because this option is part of the geochemical reaction file that is unique to RATEQ (i.e., it is not a standard MT3DMS file) the option should be documented in the RATEQ manual. For example, the only value of “location” used in the example problems is “left”, and, because the arguments are not discussed in the text, the list of possible values of the argument is unclear.

6) Based on the description of the timed events data block [1, p. 35], it is unclear how to specify the point in the simulation at which the change in flow velocity specified in Records 4 and 5 is applied.

7) The distinction between the terms "fixed" and "total" should be clarified. The meaning of the term "fixed" is not included in the description of the other chemical input types [1, p.30]. The distinction is difficult to determine from the example problems. For example, in some examples [1, p. 69] water is listed as a "fixed" type, and in other examples it is has a type of "total" [1, 30]. Furthermore, in the example problem in Table 5.1 Alkalinity is listed as a "fixed" species with a concentration of 1.51 E-3 M, but the initial guess is 2.0 E-3 M. It is unclear why the initial guess of the concentration of a fixed species would be different than the concentration of the fixed species, if "fixed" implies that the concentration is not changing with time.

8) The meaning of the "guess" parameter in the geochemical input file should be further clarified. The manual states only that "guess is an optional value that is used as an initial guess in computing the speciation" [1, p. 30] but does not indicate what the value represents. The meaning is difficult to infer from the example problems. For instance, the example in Table 6.1 lists UO_2^{+2} as an aqueous species with a concentration of 4.0 E-6 M and an initial guess of 1 E-24 M. This entry appears to indicate that the concentration of dissolved uranium is 4.0 E-6 M, of which 1.0 E-24 M is in the UO_2^{+2} form. However, in the same example, Br^- is listed as an aqueous species with a concentration of 1.0 E-5 M, and an initial guess of 2.0 E-3 M. One might assume, by analogy with the entry for uranium, that the aqueous concentration of Br is 1.0 E-5 M, of which 2.0 E-3 M is in the Br^- form. However, because the value of the "guess" parameter is two orders of magnitude greater than the aqueous concentration of Br , it appears that the initial guess also includes sorbed or precipitated species.

9) In the example in Table 5.1, species to be ignored are listed both in Reaction Set 1 [1, p.58] and in the Calculation Block [1, p. 59]. Because the Calculation Block specifies that Reaction Set 1 is to be used in the transport equations, it is unclear why the species to be ignored must be listed again in the Calculation block. An explanation of this requirement would be helpful to the user.

IV. Clarifying Comments

x) Readability would be improved by using one consistent font for superscripts and subscripts. On page 4 [1], for example, the superscripts and subscripts of C_m^k are a different size than the subscripts for R_r^k, which are a different size than the subscripts on D_{ij}. Similarly, readability would be improved if subscripts were used consistently. On page 4 [1], for example, letters I and j appended to x were expected to be subscripts but were not written as subscripts. Additional instances of this type of issue occur in the document.

x) The documentation of the timed events data block [1, p. 35] indicates that Record 7 specifies the velocity in the column. However, it also is indicated that Record 5 specifies the velocity in the column [1, p. 35]. The expected meaning of Record 7 relates to the duration of the experiment.

X) The meaning of the value 1.e19 as the xmax parameter of the Initial Conditions data block in the examples in Table 6.1 [1, p. 70] and Table 6.2 [1, p.73] is unclear. A value of 1 E 19 m also does not seem to be a reasonable value for the maximum x domain of the problem.

V. References

[1] Curtis, G.P., "Documentation and Application of the Reactive Geochemical Transport Model RATEQ". December 1, 2004.

[2] Harbaugh, A.W., Banta, E.R., Hill, M.C., McDonald, M.G. (2000) MODFLOW-2000, The U.S. Geological Survey Modular Ground-Water Model - User guide to Modularization Concepts and the Ground-Water Flow Process. Open-File Report 00-92. U.S. Geological Survey, Restin, Virginia.

[3] Zheng, C., Wang, P.P., (1999) MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide. U.S. Army Corps of Engineers, Engineer Research and Development Center. Contract Report SERDP-99-1.