

Attn: M Knapp J. Stamer MS 62355

SELECTION OF A BASELINE CODE FOR RADIONUCLIDE RETARDATION MODELING

(Letter Report on Milestone 1, Task 3)

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INTRODUCTION

A number of sophisticated computer codes have been written to model complex aqueous geochemical equilibria. They can be used to predict what will happen when aqueous fluids interact with geological media, i.e. how the pH, Eh or gas pressures will change when certain elements are added to the aqueous or solid phases or they might be used in understanding what will happen when the pH is altered by external means or what effect a change in oxygen or carbon dioxide pressure will make.

Just as importantly, they can provide valuable inferential insight while interpreting laboratory or field data. Using these codes to test models of the actual physical processes can help distinguish important from unimportant factors affecting the complex chemistry. Thereby they can help to develop a cohesive understanding of important mechanisms. For example, modeling can be used to test the hypothesis that chemical equilibrium has been attained, or conversely, determine which minerals are not in thermodynamic equilibrium. They can help to distinguish the relative importance of adsorption and precipitation and can, in the absence of some experimental data, identify the redox state of the system.

One of our tasks in the Radionuclide Retardation Modeling Program is to select from these existing geochemical codes the best one for application to radionuclide retardation problems at Hanford. Once this code has been chosen and its deficiencies noted, it will be our task to modify and update it to meet DOE needs and standards.

This report 1) provides a brief description of each code which has been examined, 2) outlines the methods and criteria we have used to select one of these codes, 3) presents our justification for choosing MINTEQA for the baseline code, and 4) identifies deficiencies in the code that must be corrected before DOE needs can be successfully met.

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BRIEF DESCRIPTION OF CANDIDATE CODES

The suite of codes chosen for detailed examination and testing are CHMTMP, EQ3NR/EQ6, GEOCHEM, MINTEQ, PHREEQE and REDEQL.UMD. Each code is capable of modeling very complex chemical behavior and represents a significant developmental investment. Figure 1 is a generalized schematic of the configurations that can be modeled by a combination of these codes. No single code can model

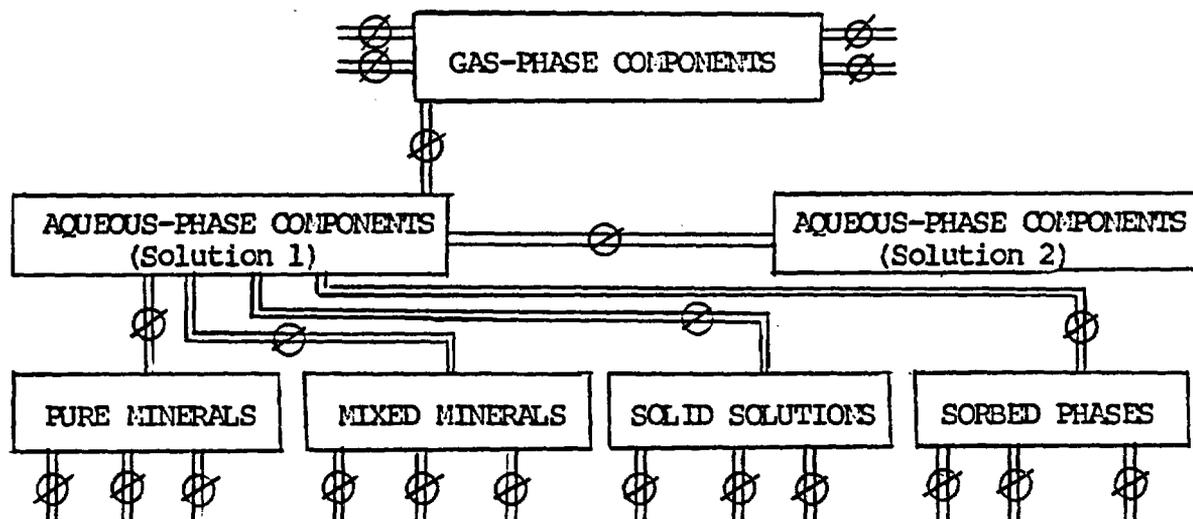


Figure 1: Schematic of Geochemical Modeling Capabilities Represented by Candidate codes

every aspect of the schematic but together they have this capability. Given isolated compartments for aqueous, gaseous, and solid phases, they can calculate the final chemical equilibrium when the respective valves are opened. All of the codes perform aqueous speciation and some form of equilibration with solid phases. Some codes, however, can not model systems where finite quantities of minerals or gases are initially present (closed systems) and conversely some can not model systems where there is an infinite supply of specific gases or solids (open systems).

All of the codes mentioned above use ion-pair formation to calculate aqueous speciation. Since this is an attempt to describe solutions in microscopic detail, we designate it the "micro-descriptive approach." It is important to note, however, that an alternative thermodynamic approach is also possible. Instead of describing the detailed thermodynamics of aqueous species, one can deal with dissolved salts as components, ignoring the details of the structure of the aqueous phase. In this later case, one attempts to describe only the activity coefficients of dissolved salts and minimizes the total free energy of the system. We designate this formulation the "macrodescriptive approach." It has been developed largely by Pitzer⁽¹⁾, Weare⁽²⁾ and their associates who have fitted expanded virial coefficients to experimental measurements.

The advantages of the macro-descriptive approach are that fewer components are needed to calculate aqueous-solid equilibria and the parameters can be directly measured. This approach works best for systems where strong aqueous complexes are not formed; it has worked successfully for concentrated brines which could not be modeled reliably by micro-descriptive speciation models.

Thermodynamic properties and even identities of many aqueous species are often inferred from measurements of solution properties such as vapor pressure, conductivity and solubility. Nevertheless, there is ample evidence that a large number of spectroscopically verified species are important in aqueous systems because they preferentially respond to sorption and bio uptake

The reason micro-descriptive models have not been successful for solutions with ionic strengths much above 1 molal is that their algorithms universally compute activity coefficients on the assumption that they are dependent on only one solution-variant parameter, the ionic strength, I:

$$a_i = f(I)$$

whereas in concentrated solutions the activity is dependent on the interactions between individual neighboring ions and complexes:

$$a_i = f(c_i).$$

We believe that it would be unwise to disregard the preponderance of evidence and thermodynamic data already obtained for important aqueous species which often cause the activity coefficients of associated salts to vary widely but in a predictable fashion. Instead, it seems prudent to develop capabilities for modeling brines by extending the algorithms for activity coefficients of predominant species in much the same way as has been done by Pitzer and Weare in their pioneering efforts. That specific aqueous species selectively sorb and are bioactive are even more compelling reasons to restrict our choices to micro-descriptive codes.

We initially selected the codes briefly described below from a number of others by two criteria: (1) a selected code had to be a recent version of its respective family, and (2) it had to be capable of at least equilibrating with solid phases.

CHMTMP

CHMTMP is a modified version of EQUILIB, a code developed by J. R. Morrey of Pacific Northwest Laboratory for the Electric Power Research Institute⁽³⁾. Since EQUILIB is copywrited, DOE's use of either CHMTMP or EQUILIB would first require permission from EPRI. Our understanding is that permission for royalty free usage would be granted. Otherwise, it would have been excluded from the list of codes to be evaluated.

CHMTMP can model gaseous, liquid, and solid equilibria, as depicted by figure 1 if the solid solution, second liquid-phase and adsorbed-phase components are excluded.

CHMTMP is different from all of the other codes included in this study because it uses a ligand-projection method of convergence. The others all

employ Newton-Raphson iteration. Initially, CHMTMP was attractive because with it we experienced no convergence failures. Newton-Raphson techniques are not nearly as reliable. Furthermore, for complex problems the ligand-projection convergence algorithm proved to be much faster than the Newton-Raphson algorithm.

CHMTMP was constructed for a particular purpose with compactness as a requirement, making modifications of the database difficult. This characteristic ultimately led us to exclude it from further consideration as a baseline code. Nevertheless, some of the techniques used by it probably will be used in the transport-coupled geochemical code.

EQ3NR/EQ6

The author of the EQ3NR/EQ6 suite of codes is T. J. Wolery, Lawrence Livermore National Laboratory⁽⁴⁾. Of all the codes tested, this code probably has the most extensive modeling capability. It will currently model all components illustrated in Figure 1 except the second liquid phase and adsorbed phases. Although the code has been structured to later include adsorption capability, it remains to be added. Part of its versatility is offset by difficulties in using the code and, in some cases, the awkwardness by which problems must be formulated.

Although EQ3NR/EQ6 was one of the two strongest candidates for the baseline code, it was not selected for two major reasons: 1) it did not include adsorption capabilities, and 2) its major strength, the capability to model paths to equilibrium, makes it slow and difficult to use in simple equilibrium or constrained equilibrium problems. Its capability to model paths is not needed in the baseline geochemical code. That capability must be developed instead as part of the transport-coupled code. Its size and complexity, excludes EQ6, the mass-transfer part of the code, from serious consideration as an element of the coupled code.

GEOCHEM

The authors of GEOCHEM are G. Sposito and S. V. Mattigod from the University of California at Riverside⁽⁵⁾. The code is a modification of an earlier code, REDEQL2, developed at the California Institute of Technology by F. M. M. Morel, R. E. McDuff and J. J. Morgan⁽⁶⁾. GEOCHEM differs from REDEQL2 principally in that it contains more than twice as many thermodynamic data (selected especially for soils), it incorporates an algorithm for cation exchange, and it uses a different algorithm for calculating activity coefficients. It models all of the functions of figure 1 except solid solutions and a second liquid phase. The adsorption capability, however, is limited. Furthermore, it can not model closed systems where finite quantities of mineral phases are initially present.

Three deficiencies finally caused us to exclude GEOCHEM from selection: 1) its incapability to model closed systems, 2) its lack of detailed documentation and 3) lack of documentation and temperature dependence of the database.

MINTEQ

MINTEQ was developed at PNL by A. R. Felmy and E. A. Jenne⁽⁷⁾ by combining the convergence algorithm of MINEQL, authored by J. C. Westall, J. L. Zachary, and F. M. M. Morel⁽⁸⁾, and the data base of WATEQ3, authored by J. W. Ball, D. K. Nordstrom and E. A. Jenne⁽⁹⁾. (WATEQ3 was formed by making a few corrections in the code and adding the uranium thermodynamic database.) MINTEQ now includes the most complete set of algorithms for adsorption of any of the codes being considered. It also has the most completely documented database for radionuclides and has been extended to model finite quantities of solids.

MINTEQ has demonstrated some limitations, the major one being its ability to solve a problem when the starting estimates are far from equilibrium. It also does not include capabilities for modeling solid solutions. Nevertheless, based on our assessment of its strengths in adsorption and database, along with its capability to at least partially successfully model closed solid systems, we have finally selected MINTEQ as the baseline code.

PHREEQE

D. L. Parkhurst, D. C. Thorstenson, and L. N. Plummer⁽¹⁰⁾ of the U.S. Geological Survey authored PHREEQE. It is one of a small family of programs capable of following one or more phase boundaries and calculating pH and redox potential as well as mass transfer and aqueous speciation as dependent variables. Its distinguishing characteristic is that it can simulate the combination two aqueous solutions (see figure 1). It, like EQ6, is designed to follow chemical reaction paths as solid phases are metered into the system. However, PHREEQE, unlike EQ6, requires the user to always choose the exact phases to be present during the simulation and often requires the user to supply his own thermodynamic database.

We finally excluded PHREEQE from further consideration, principally because its capability to model reaction paths was not needed for the baseline code. Furthermore, it does not have a fully developed data base, was not documented in sufficient detail for easy modification and was limited in modeling systems where it is desirable to have a large number of solids considered as part of the equilibrium.

REDEQL.UMD

This code was authored by D. K. Harriss and V. R. Magnuson of the University of Minnesota⁽¹¹⁾. Like GEOCHEM, it originates from REDEQL2. Some changes have been made to extend its capability over REDEQL2. Parameter storage has been placed in linear rather than rectangular arrays to reduce storage space requirements. This allows the formation of complexes with mixed ligands and metals and allows more than one precipitated form of a metal-ligand pair to be present at one time. Some new redox input options were added and the Magnuson equation for calculating activity coefficients has been added. Aside from these relatively minor changes, REDEQL.UMD and GEOCHEM are still very similar in their structure.

We finally excluded REDEQL.UMD from selection as the baseline code for the some of the same reasons that GEOCHEM was excluded. It is incapable of modeling closed solid phases, does not include adsorption capability and its database is not well documented though the code is.

SELECTION CRITERIA

In establishing criteria for the selection of the baseline geochemical code, we considered primary capabilities which the code must have or be modified to have and secondary capabilities which are desirable for efficient usage of the code. The secondary capabilities relate mostly to ease of use, input/output options, memory requirements, documentation, etc.

The primary criteria are listed below and are rated in Table 1. The secondary criteria, as we have evaluated them, appear in Table 2.

- o The code had to either be capable of modeling the chemical processes that come into play during radionuclide migration in aqueous media or it had to be structured so that these capabilities could be added without undue difficulty. The chemical processes currently believed to be important are 1) aqueous speciation; 2) generation or utilization of at least CO_2 , O_2 , N_2 , and H_2 , and preferably CH_4 ; 3) redox behavior; 4) mass-transfer to or from solid phase via precipitation/dissolution; mass transfer to or from solid phase via adsorption/desorption; and 5) formation of solid solutions.
- o The code had to be structured so that without extensive modification it could accept and use the internally consistent thermodynamic database which will be developed as part of this program. The database will include the reliable data for important radionuclides and will range over temperatures to 300°C .
- o The code had to be structured so that future advancements toward high ionic strengths could be incorporated.
- o The code had to have the flexibility to model both open and closed processes, i.e., it had to be able to equilibrate finite quantities of solid phases and it had to be capable of modeling constrained equilibria where solids or gases are present in infinite quantities.
- o The code had to perform reliably and efficiently, consistently converging to acceptable answers, or it had to be easily modifiable to accomplish this requirement.
- o The code had to be computationally efficient or easily modifiable to attain computational efficiency.
- o The code had to be publicly available.
- o The code must ultimately be able to model systems which contain organic compounds which can act as complexing ligands.

Tables I and II respectively summarize both the primary and secondary criteria to which points have been allocated, depending on our perceived importance of the criterion. Each code has been rated on each of these criteria.

Before the rating was made, each code was made operational on the VAX computer at PNL and exercised on a basalt groundwater problem. This exercise allowed us to become familiar with the operation of each code and to more objectively evaluate its performance.

To minimize the subjectivity of assigning a total number of points for each category, each technical member of our group has independently weighted the criteria. The weightings presented in Tables I and II are a consensus of their separate opinions. The normalized ranking at the bottom of Table II includes with it a variance which indicates that, in reality, all of the codes considered in the selection are valid candidates for selection, though EQ3NR/EQ6 and MINTEQ are the two highest ranked.

TABLE I—PRIMARY CRITERIA FOR SELECTION

Criterion	Weight	Variance	C	E	G	M	R	P
Capability to model Primary Processes								
Aqueous speciation								
Sufficient Metals, ligands?	185	43	4	3	5	4	3	1
Vary or fix pH?	180	50	5	2	5	5	5	5
Vary or fix ionic strength?	118	80	3	5	5	5	5	0
B-dot activity coefficient?	101	96	5	5	0	0	0	0
Charge balance adjustable?	109	88	5	5	0	5	5	5
Equilibrate Solid Phases								
Pure Solids								
Open systems?	115	18	0	5	5	5	5	5
Closed systems?	115	18	5	5	0	5	0	5
Mixed Solids								
Open systems?	115	18	0	5	5	5	5	5
Closed systems?	115	18	5	5	0	5	0	5
Solid Solutions								
Open systems?	100	15	0	4	0	0	0	0
Closed systems?	100	15	0	4	0	0	0	0
Capability to select phases								
Suppress all?	130	26	5	5	5	5	5	0
Include all?	130	26	5	5	5	5	5	0
Suppress selected phases?	150	50	5	5	0	5	0	5
Control rates of dissolution?	106	54	0	5	0	0	0	5
Control rates of precipitation?	106	54	0	5	0	0	0	5
Adsorption Capability								
James-Healy?	450	150	0	1	2	5	0	0
Langmuir?					x			
Freundlich?						x		
Double Layer Model?						x		
Triple Layer Model?						x		
Capability to Model Organic Ligands								
50	20	0	2	5	3	5	2	
Capability to Control/Select Redox								
Selectively ignore equilib'n?	110	10	0	5	0	5	0	0
Ignore all redox?	75	40	0	5	5	5	5	0
Choice of redox couples?	74	40	0	5	0	5	5	5
Sufficient number of couples?	75	40	4	4	4	4	4	1
Capability to equilibrate gases								
Nitrogen								
Open system?	21	9	0	5	5	5	5	0
Closed system?	21	9	0	0	0	0	0	0
Oxygen								
Open system?	72	37	5	5	0	5	5	5
Closed system?	64	28	5	0	0	0	0	0

TABLE I—PRIMARY CRITERIA FOR SELECTION—CONTINUED

Criterion	Weight	variance	C	E	G	M	R	P
Hydrogen								
Open system?	55	43	5	5	0	5	0	0
Closed system?	45	28	5	0	0	0	0	0
Carbon Dioxide								
Open system?	90	52	5	5	5	5	5	5
Closed system?	90	52	5	0	0	0	0	0
Methane								
Open system?	50	46	0	0	0	5	0	0
Closed system?	42	31	0	0	0	0	0	0
Variable Gas Volume?	35	30	5	0	0	0	0	0
Adequacy of Thermodynamic Data Base								
Internally Consistent?	89	31	3	5	2	5	2	1
Well Documented?	167	84	3	4	2	5	2	1
Adaptable to other data bases?	288	210	1	3	3	3	3	3
Adequate radionuclide entries?	115	18	1	3	2	4	2	0
Easily expandable	123	80	1	3	3	3	3	3
Easily modified	141	60	5	5	5	5	5	5
Multi-temperature Capability								
van't Hoff?	375	223	2	5	0	2	1	0
Criss-Cobble Extrapolation?				x		x	x	
Sylvester-Pitzer Extrapolation?				x				
Polynomial coefficients?			x	x		x		
Mathematical Convergence Behavior								
Newton Raphson Method?	364	118	5	4	2	2	2	3
Pre-N-R conditioning?				x	x	x	x	x
Ligand Projection method?			x					

Code: C=CHIMP; E=EQ3NR/EQ6; G=GEOCHEM; M=MINTEQ; R=REDEQL.UFD;
P=PHREEQE

TABLE II—SECONDARY SELECTION CRITERIA

Criterion	Weight	variance	C	E	G	M	R	P
Ease of Usage								
Formulation of Problems								
Interactive Capability?	92	53	5	0	0	3	0	0
Ease of coding species?								
Aqueous?	63	12	5	4	2	2	2	2
Solids?	63	12	2	4	2	2	2	2
Adequacy of documentation?	183	96	4	1	1	2	5	2
Problem stacking capability?	73	17	5	0	5	5	5	0
Safety cross checks?	47	20	5	4	2	2	2	1
Adequate input print options?	62	12	4	3	1	2	1	1
Optional concentration units?	62	12	0	5	0	5	5	5
Optional redox units?	49	24	5	5	2	2	2	2
PO ₂		x	x		x			
eH			x	x		x	x	x
pe			x	x	x	x	x	
Modification of thermo data base								
Change at run time?	121	98	0	5	0	5	0	5
T correction at run time?	82	32	5	5	0	5	0	5
Optional carbon input?	62	12	2	5	2	5	5	2
Iteration control?	82	32	5	0	5	5	0	5
Adequate Diagnostics	328	265	5	5	2	5	2	2
Adequate Output								
Output Options for levels of detail?	62	12	0	5	5	5	5	5
Ease of Interpretation?	124	94	5	5	2	5	2	5
Labeling of chemical species?	82	32	5	5	2	5	2	5
Thermodata output options?	59	17	3	5	0	5	4	4
Mineral Saturation Indices	119	51	5	5	0	5	5	5
Normalized Ranking			70	100	73	95	84	92
Variance			36	41	28	37	36	38

Code: C=CHMTP; E=EQ3NR/EQ6; G=GEOCHEM; M=MINTEQ; R=REDEQLJMD;
P=PHREEQE

SELECTION OF CODE

As observed from Tables I and II, each code has its strong points. However, none of them is acceptable in its present state of development. Substantial modifications would be required of any of them.

On the basis of the above analysis, we first narrowed the choice to either EQ3NR/EQ6 or MINTEQ. Between these two, we have chosen MINTEQ as the baseline code for further development at PNL. The major reasons for this choice are itemized below:

- o EQ3NR/EQ6 is still being developed at another DOE site and will provide an excellent independent code for verification studies. We believe that at least two independent codes ought to be developed for this reason. There is great value in being able to compare results from different complex codes which have comparable capabilities.
- o MINTEQ ranks well with EQ3NR/EQ6 and the needed modifications can be made more efficiently on it because PNL staff members are more intimately familiar with its structure.

PROJECTED MODIFICATIONS OF MINTEQA2 AS A BASELINE CODE

Before MINTEQA2 will be completely acceptable as a baseline DOE code, several modifications will be required, as briefly outlined below:

- o More work must be done to improve the convergence reliability. The Newton-Raphson technique should be supplemented by other alternative methods when divergence is detected. Although a ligand projection algorithm has been included, it is not yet performing well. One simple addition would be the inclusion of the Marquardt scaling parameter to insure that the change vectors do not allow changes in the hyperspace that will allow divergent behavior.
- o More work must be done to make defining problems as efficient and error-free as possible. Our experience with all of the codes has shown that large amounts of time are lost in aborted runs caused by errors in defining problems. A large fraction could be avoided by constructing a problem-defining preprocessor or interactive subroutine.
- o The algorithm used to calculate activity coefficients from ionic strength should be extended to include the B-dot formulation of Helgeson because our experience dictates that it is better behaved at high ionic strengths. The current version is ill-behaved at high ionic strengths, consequently frequently causing the code to fail to converge.
We note that the B-dot formulation will not be acceptable for brines. This requirement is addressed below.
- o High temperature competency must be added. As the code now stands, it only has van't Hoff extrapolation capability to 100°C. Other options should also be added.
- o Modifications must be made to allow the code to model closed solid systems with finite quantities of soluble materials. In some cases, the code fails to give answers because it artificially dissolves enough soluble salt to saturate the aqueous phase with respect to that salt. If the ionic strength becomes too high in the process, the code will fail. Part of this deficiency will be remedied by the inclusion of the B-dot activity-coefficient algorithm.
- o Solid-solution competency should be added.
- o A longer range addition should be high ionic strength competency. This projected improvement is different than the B-dot addition listed above. Instead, it refers to the inclusion of methods developed by Pitzer and Weare for brine solutions. This addition is expected to be the most challenging of all because it requires a fundamental development for aqueous species and likely will be reliant on additional experimental measurements which remain to be made by the scientific

community.

- o Conservation of water should be built into the code.
- o An adequate database must be developed for MINTEQ to use in calculating the aqueous speciation and solubility equilibria for actinides, other radionuclides and constituents important to the disposal of nuclear waste. This development is part of task II.

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