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January 21, 1986
Contract No. NRC-02-85-008
Fin No. D-1020
Communication No. 21

Mr. Jeff Pohle
Division of Waste Management
Mail Stop SS-623
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

RE: NTS

Dear Jeff:

I have enclosed reviews of the following documents:

1. Kerrisk, J.F., 1983, Reaction-Path Calculations of Ground Water Chemistry and Mineral Formation at Rainer Mesa, Nevada: LA-9912-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 41 p.
2. Ogard, A.E., and Kerrisk, J.F., 1984, Ground Water Chemistry Along Flow Paths between a Proposed Repository Site in the Accessible Environment: LA-10188-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 48 p.
3. Travis, B.J., 1985, TRACR3D: A Model of Flow and Transport in Porous/Fractured Media: Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

If you have any questions concerning these reviews, please call.

Sincerely,

Roy Williams
Roy E. Williams

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REW:sl

enclosures

WM-Res
WM Record File
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WM Project 10, 11, 16
Docket No. _____

PDR
LPDR (B, N, S)

Distribution:

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(Return to WM, 623-SS)

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WMGT DOCUMENT REVIEW SHEET

FILE #:

DOCUMENT: Kerrisk, J.F., 1983, Reaction-Path Calculations of Ground Water Chemistry and Mineral Formation at Rainer Mesa, Nevada: LA-9912-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 41 p.

REVIEWER: Williams and Associates, Inc.

DATE REVIEW COMPLETED: January 21, 1986

BRIEF SUMMARY OF DOCUMENT:

DATE APPROVED:

The purpose of the paper under review is to describe reaction-path calculations of ground water chemistry and mineral formation based on the model proposed by Claassen and White (1978). The reaction-path calculations were performed to test whether equilibrium processes could be used to explain ground water chemistry and minerals found at Rainer Mesa, Yucca Mountain, and other NTS locations. The reaction-path calculations presented in the report under review represent a very simplified model of the complex geologic system. According to the report, only the major chemical components are included in the model, and only equilibrium processes are considered at each step in the reaction path. The reaction-path calculations were performed in an attempt to calculate and therefore predict ground water composition (major components) and mineral formation (major minerals) at Rainer Mesa. The physical model by Claassen and White (1978) was used to simulate the change in ground water quality along a flow path from recharge area to discharge area. Recharge water was modeled as being saturated with CO₂. The pH was assumed to be 4.5 as a consequence of aerobic biological activity in the soil zone. Reaction-path calculations were performed to identify the products formed as this water reacts with volcanic glass. According to the report, as dissolution of the volcanic glass proceeds, the aqueous phase becomes saturated with respect to various minerals. These minerals are allowed to precipitate, but it is assumed that they remain in contact with the aqueous phase. Thus, a mineral that precipitates early in the reaction path may redissolve later as conditions such as pH or cation concentrations change.

According to the report, the dissolution process consists of an ion exchange reaction in which H^+ from the aqueous phase is exchanged for cations from the volcanic glass to maintain electrical neutrality. The dissolution process was modeled by assuming that OH^- is one of the dissolution products. The OH^- dissolution rate was controlled by the requirement of maintaining electrical neutrality.

A major limitation of this technique is that the detailed mechanism of dissolution is ignored. However, the report notes that a better calculational model undoubtedly could be developed if mechanisms of glass hydration and dissolution were understood more quantitatively. Another limitation of the model is that if the aqueous phase becomes supersaturated with respect to a particular mineral during the reaction-path calculation, the mineral precipitates. The report under review notes, however, that in reality, many ground waters are supersaturated with respect to a number of minerals. Perhaps most importantly the assumed initial pH controls the supply of H^+ ions. In this model we think the assumed supply of H^+ ions is anomalously high (pH assumed to be anomalously low).

The reaction-path calculations were performed by the EQ3/6 chemical equilibrium computer program. The EQ3/6 program was modified to allow the dissolution rates of the various species from the volcanic glass to vary with the pH of the aqueous phase. Because of a lack of data, most of the solute solutions were treated as ideal solutions. Thermodynamic data were available for 223 minerals, 293 aqueous complexes, and 14 solute solutions.

The results of the reaction-path calculations consist of an aqueous-phase composition and a list of minerals that are in equilibrium with the aqueous phase. According to the report, the general trend of the results is the same for all of the cases modeled. The aqueous-phase composition is controlled by the dissolution process during the early stages of the reaction path; mineral precipitation is essentially non-existent in the early stages. During intermediate stages, various minerals begin to precipitate and the precipitation of the minerals begins to control the aqueous-phase composition. Later in the reaction path the aqueous-phase composition is controlled by a stable mineral assemblage. The results of the reaction-path calculations for various temperatures are presented in figures 4 through 20 of the report.

SIGNIFICANCE TO NRC WASTE MANAGEMENT PROGRAM:

The report under review presents reaction-path calculations of ground water chemistry and mineral formation at Rainer Mesa based on a model proposed by Claassen and White (1978). The report under review is significant with respect to understanding the precipitation of certain minerals along the reaction path. The information presented in the report is significant with respect to the geochemistry and mineralogy of the volcanic tuffs in the vicinity of the Nevada Test Site. The report also may be useful with respect to understanding the mechanisms that control radionuclide retardation along potential flow paths to the accessible environment. However, this would require a very detailed analysis of the ground water chemistry data that are available for the Nevada Test Site.

PROBLEMS, DEFICIENCIES, OR LIMITATIONS OF REPORT:

The reaction-path calculations presented in the report under review represent a very simplified model of the complex geologic system. Only major chemical components were included in the model. Limitations such as adding aqueous species to the aqueous phase to simulate glass dissolution, requiring precipitation as soon as the aqueous phase becomes supersaturated with respect to a particular mineral, and suppressing the precipitation of particular minerals to slow precipitation kinetics were necessary because of the limited data base and the limited capability of the model. These limitations appear to be inherent in the modeling technique used. However, we are not familiar with the degree of sophistication of the EQ3/6 chemical equilibrium program. In addition the assumed pH of the recharge water appears to us to be anomalously low. This assumption introduces an anomalously large supply of H^+ ions to the model.

SUGGESTED FOLLOW-UP ACTIVITY:

While ground water chemistry data are important with respect to supporting or disproving potential conceptual models of ground water flow, no specific follow-up activity is suggested for the report under review. The report under review deals primarily with mineral precipitation; therefore, any follow-up activity probably should be recommended by a geochemist.

REFERENCES CITED:

Claassen, H.C., and White, A.F., 1978, Application of Geochemical Kinetic Data to Ground Water Systems, A Tuffaceous-Rock System in Southern Nevada in Chemical Modeling in Aqueous Systems: E.A. Jenne, Ed., American Chemical Society Symposium Series 93, 771-793.

WMGT DOCUMENT REVIEW SHEET

FILE #:

DOCUMENT: Ogard, A.E., and Kerrisk, J.F., 1984, Ground Water Chemistry Along Flow Paths between a Proposed Repository Site in the Accessible Environment: LA-10188-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 48 p.

REVIEWER: Williams and Associates, Inc.

DATE REVIEW COMPLETED: January 21, 1986

BRIEF SUMMARY OF DOCUMENT:

DATE APPROVED:

The report under review discusses the chemical analyses of ground water from the saturated zone from several deep wells in the vicinity of Yucca Mountain. The report notes that pore water from the unsaturated zone has not been sampled as yet, but samples will be taken during construction of the exploratory shaft. The report notes that knowledge of the vertical and lateral variation of ground water composition at Yucca Mountain can aid in modeling local hydrology; however, no interpretation of the chemical data pertaining to ground water flow paths is presented in the report. The report is divided into four sections: 1) the experimental procedures for sampling and analyzing the water, 2) the water compositions determined, 3) the implications of the data for spatial and temporal variations in water chemistry, speciation and solubility, pH buffering capacity, and redox buffering capacity, and 4) conclusions and proposals for future work.

Three different methods were used to collect ground water samples. These methods are as follows:

- 1) Samples were taken aerobically and sometimes anaerobically during USGS pumping tests. These samples consisted of composite samples of ground water from all producing zones that contributed to the well during pumping.
- 2) Samples were collected from permeable zones that were isolated by inflatable packers. This sampling method was used to collect samples from well UE-25b#1 and well USW H-3. Values

of Eh were measured from the two wells to provide estimates of water Eh at depth.

- 3) These samples were collected from selected depths in static holes. The sampler consisted of an evacuated stainless steel bottle with an electronically activated valve. The report under review notes that it has not been established whether or not the results are representative of water that is in equilibrium with the particular zone sampled.

The ground water samples were analyzed for dissolved cations and anions, Eh, pH, sulfide, dissolved oxygen, alkalinity, and for detergent. According to the report under review, detergent was considered to be a good indicator or tracer of drilling fluids in the well.

The ground water chemistry data presented in the report indicate that sodium is the principal cation and that carbonate is the principal anion. According to the report under review, the molar distribution of anions in the water is relatively uniform for all wells: about 80% bicarbonate; the remainder is sulfate, chloride, and fluoride. The molar distribution of cations is more variable; sodium ranges from a high of over 95% to a low of about 65%. Calcium, potassium, and magnesium are the other cations present in significant concentrations. According to the report, the similarity of the relative cation and anion compositions of water from the tuffaceous aquifers at Yucca Mountain, Pahute Mesa and Rainer Mesa indicates a hydrologic connection or a similarity in reaction mechanism during recharge. While the relative cation and anion compositions of the water are similar, significant differences in the oxidation-reduction potential (Eh) were detected. For example, water from well USW H-3 and from the packed off Bullfrog zone of well UE-25b#1 are reducing. The report notes that the solubilities of many waste elements such as uranium, plutonium, neptunium, and technetium are greatly affected by the oxidation-reduction potential of the water. The report notes that there are no models describing water Eh at Yucca Mountain.

The report suggests that three specific water compositions can be used to estimate the concentrations of waste elements along the flow paths from Yucca Mountain to the accessible environment. These water compositions are as follows:

- 1) The composition of ground water from well USW H-3 is indicative of water below the proposed repository site.
- 2) Ground water from well UE-25b#1 represents the carbonate aquifer underlying much of the area and is the most concentrated ground water possible along the flow path.

- 3) Ground water from well J-13 is typical of wells surrounding Yucca Mountain; the composition of such waters may be influenced greatly by juvenile recharge water.

Results of experiments on ground water from well J-13 indicate that the water alone or with minerals commonly found in Yucca Mountain has a relatively good pH buffering capacity. According to the report under review, this is particularly true for the water/mineral system that is subject to H⁺ addition. Ground water from wells UE-25b#1, USW H-1, H-4, H-5, H-6, and G-4 are expected to have buffering capacities similar to those of well J-13. Ground water from well USW H-3 has a higher pH and higher carbonate content than ground water from well J-13; therefore, it would have a higher buffering capacity for H⁺ addition. According to the report, insufficient data are available to determine the Eh buffering capacity of the system.

The report presents the following conclusions:

- 1) The water below the repository site at Yucca Mountain has the same relative chemical composition as the recharge water from Pahute Mesa; it is predominantly NaHCO₃ water.
- 2) There is a progressive increase in calcium and magnesium concentrations at the expense of sodium from Yucca Mountain to the Amargosa Desert.
- 3) The water below the repository site displays reducing conditions.
- 4) The natural organic content is very low in the ground water.
- 5) The chemical composition of the ground water can be modeled on the basis of the reaction of CO₂-saturated infiltration water with glassy and devitrified tuffs.
- 6) Sufficient data are available for the ground water compositions in the area between Yucca Mountain and discharge locations in the Amargosa Desert to adequately model the ground water composition along the flow path, once the flow path is totally defined. The only data that may need reinforcement are the negative oxidation-reduction potentials below the repository site.
- 7) The pH buffering capacity of the regional hydrology is determined by the CO₂ dissolved in the recharge water, the biota at the ground surface and zeolites in the saturated zone.

- 8) Four extremes or bounds of water composition for the area have been recognized from this work and the works of Claassen (1983) and White and others (1980).

SIGNIFICANCE TO NRC WASTE MANAGEMENT PROGRAM:

The report under review presents ground water chemistry data and interpretations of the data in the vicinity of Yucca Mountain. These data are important with respect to understanding the chemical factors that will control migration of wastes from the repository to the accessible environment. These data also are important with respect to the development of conceptual models of the ground water flow systems that exist in the vicinity of Yucca Mountain. The ground water chemistry data alone cannot be used to develop conceptual models of the ground water flow systems in the vicinity of Yucca Mountain; however, ground water chemistry data must support any conceptual models of the ground water flow systems that are developed.

PROBLEMS, DEFICIENCIES, OR LIMITATIONS OF REPORT:

The primary limitations of the report under review consist of unanswered questions concerning ground water composition along possible flow paths to the accessible environment. These limitations are listed in the report under review beginning on page 43. The report under review questions whether "thief" samples of ground water are representative of waters in equilibrium with the tuff strata from which the sample was taken. This is an important limitation of some of the water chemistry data because thief samplers yield mixed samples of the water contained in the borehole. Another significant limitation of the report is whether calculations and laboratory experiments on solubility, sorption, fracture transport, and filtration of particulates represent actual processes and conditions of the Yucca Mountain repository site. Despite these limitations, the report under review presents very valuable ground water chemistry data and interpretations.

SUGGESTED FOLLOW-UP ACTIVITIES:

The existing conceptual models should be evaluated to determine whether they are consistent with the ground water chemistry data presented in various reports.

REFERENCES CITED:

White, A.F., Claassen, H.C., and Benson, L.B., 1980, The Effect of Dissolution of Volcanic Glass on the Water Chemistry in a Tuffaceous Aquifer, Rainer Mesa, Nevada: USGS Water Supply Paper 1535-Q.

Claassen, H.C., 1983, Sources and Mechanisms of Recharge for Ground Water in the West Central Amargosa Desert, Nevada--A Geochemical Investigation: USGS-OFR-83-542.

WMGT DOCUMENT REVIEW SHEET

FILE #:

DOCUMENT: TRACR3D: A Model of Flow and Transport in Porous/Fractured Media by B.J. Travis, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

REVIEWER: Williams and Associates, Inc.

DATE REVIEW COMPLETED: January 21, 1986

BRIEF SUMMARY OF DOCUMENT:

DATE APPROVED:

This report describes the TRACR3D computer code which solves the equations of transient two-phase flow and multi-component transport in deformable, heterogeneous, reactive, porous/fractured media. The application of this program is in areas of transport of fluids (water, air and a variety of reactive chemical species) through porous/fractured materials such as soils and rock.

An implicit finite-difference scheme is used for flow; a semi implicit scheme is used for transport. The equations used in the model are introduced, the numerical solution procedure is described, some partial verification and validation is presented. A users guide also is given. The program will consider the air-water system as well as hydrocarbon reservoir problems as examples of two phase flow systems.

COMMENTS:

The Model:

On page 3 the author states that the program was written with flexibility in mind. This is partly true because it will handle a great variety of problems. However, units used in the model must be in the CGS system. It would have been preferable to formulate the code such that any consistent system of units could be used. In this section there are also several equations introduced that have undefined symbols. The author does not define symbols immediately after the equation is presented and

some of the symbols are not even defined in the table at the beginning of the report. For this reason, it is somewhat difficult to follow his derivations. In this same section on page 6 the Forchheimer equation is introduced in an unfamiliar form and the source is not given. The actual formulation of the flow process involves satisfying the continuity equation in an element of the finite difference mesh and satisfying the Darcy equation for flow across all faces. This is basically the process used in the integrated finite difference formulation.

On page 25 the author discusses the formulation for fracture flow. The program will allow flow into the matrix from fractures but it does not appear to allow flow across a fracture when the fracture is only partially saturated.

Boundary Conditions:

The program allows several boundary conditions: 1) constant flux, 2) constant potential or concentration, 3) continuative outflow, 4) band release of radionuclides, and 5) time dependent. It does not appear to handle such conditions as atmospherically controlled evaporation or infiltration.

Time Step Control:

The time step limit is calculated from an equation relating the time increment to the square of the spatial increment. It is necessary to input a value of maximum time step which appears to be a very arbitrary value. The program uses a different time step for tracer transport than for flow transport. The steps involved in the numerical procedure are given below:

- 1) Set initial values of dependent variables, set time and material properties.
- 2) Sweep through the mesh at each cell, solve the non-linear algebraic set of finite difference equations. After each sweep, test pressure in the gas and pressure in the liquid for convergence; if not converged make another sweep through the mesh. In each cell, latest values are used for neighboring cell dependent variables.
- 3) After cell centered variables have been up-dated in Step 2, cell air and liquid interface velocities are calculated.
- 4) Up-dating of tracer movement is accomplished next. If tracers have been specified, they can move with one phase or the other but not both simultaneously.

- 5) Boundary conditions and time are up-dated.
- 6) Printouts and plotting dumps are checked.
- 7) Problem and time is checked. If the calculation has not reached the end time, return to Step 2 for the next time level.

Verification of Flow:

The report lists three tests of the flow model:

- 1) Comparison with the solution for water infiltration into partly saturated soil.
- 2) Comparison with the solution for two-dimensional steady potential flow with a sink and a source.
- 3) Steady flow with pressure dependent permeability.

These are all compared with analytical solutions and appear to give good verification.

Verification of Transport:

Five comparisons of the computer code with analytical solutions are given. These comparisons all appear to be very good.

Validation:

Three experiments are used for validation of the code. These are: 1) water pulse in a partially saturated column of crushed tuff, 2) diffusion of adsorbing tracer into a thin wafer of tuff from a thoroughly stirred solution, and 3) migration of radioactive tracers from an underground nuclear test to a nearby well as a result of pumping in the well. The validation in the first two of these is very good. In the last it does not appear to be very good except that the author states that the difference between calculated and observed breakthrough curves is approximately equal to the margin of error in the observations. The users guide in Appendix A appears to be satisfactory although if one was to attempt to run the program from the information given here, there undoubtedly would be many questions. The author does give several sample problems which include the data input as well as the output. As in all large programs, the data input appears to involve a large amount of work and the output

from even a small program consists of many, many pages of data. In the case of the example problem run here there are over 100 pages of output.

SIGNIFICANCE TO NRC WASTE MANAGEMENT PROGRAM:

The report under review is one of many computer models that are being developed to simulate multiphase flow in porous media.

PROBLEMS, DEFICIENCIES OR LIMITATIONS OF REPORT:

There are no major problems or deficiencies in the report. However, the program is large and it is questionable whether field, data collection methodologies are sophisticated enough to provide the data necessary for optimal use of the program.

SUGGESTED FOLLOW-UP ACTIVITY:

No follow-up activity is suggested.