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P.O. Box X Oak Ridge, TN 37830		See JWBradbury for encl.

Dear Susan:

SUBJECT: QUARTERLY REPORT FOR B0290 (APRIL - JUNE, 1984)

I have reviewed the draft of the quarterly progress report entitled "Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-level Nuclear Waste Repository Site Projects: Volume 3, Report for April - June, 1984". In my opinion, this draft is well-written and needs little revision. I have enclosed a marked-up copy noting typos, imprecise terms and sections needing clarification.

In addition to the specific comments in the marked-up draft, I have the following general comments:

- The purpose of subtracting components from the synthetic groundwaters is not completely clear to me. What effects on ". . . removal from solution. . ." do you expect to see and how would you use the information? Groundwaters lacking silicate and/or carbonate component are not site-specific, so application of the information would require extrapolation. The Executive Summary discusses the effect of solution composition on sorption/precipitation reactions for GR-2 and GR-4. Shouldn't this information be included early in Section 3.3 to justify the expansion of the sensitivity analysis to include non site-specific groundwaters?
- Please consider expanding the discussion (page 6-1) on the kinetic conditions necessary for resolution of concentration peaks in chromatographic experiments involving multiple speciation. Reaction rates between species in solution and between these species and solid phases necessarily influence radionuclide migration. Have any chromatographic experiments from B0290 produced multiple concentration peaks? What is the range of retardation factors that can be resolved with your set up?
- * The discussion of increased peak broadening and asymmetry does not make sense to me. It appears to say that desorption reaction rates decrease with increasing temperature. This sounds backwards. The statement that

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peak asymmetry could be caused by different chemical reactions involving Np and basalt phase(s) appears to be the only viable alternative.

If any of the comments I made are incorrect or need clarification, please call me.

The action taken by this letter is considered to be within the scope of the current contract FIN B-0290. No change to costs or delivery of contract products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contract products.

Sincerely,

S

John W. Bradbury Geochemistry Section Geotechnical Branch Division of Waste Management Office of Nuclear Material Safety and Safeguards

Enclosure:

1. Marked-up draft of Quarterly Report for B0290 (April-June, 1984)

JFC	WMGT JUB			
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PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS: VOLUME 3, REPORT FOR APRIL-JUNE 1984

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Manuscript Completed: September 1984 Date of Issue:

Prepared for the U.S. Nuclear Regulatory Commission Office of Nuclear Materials Safety and Safeguards Washington, DC 20555 under Interagency Agreement DOE 40-549-75

NRC FIN No. B0290

Prepared by the OAK RIDGE NATIONAL LABORATORY Oak Ridge, Tennessee 37831 operated by MARTIN MARIETTA ENERGY SYSTEMS, INC. for the U.S. DEPARTMENT OF ENERGY under Contract No. DE-AC05-840R21400

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ABSTRACT

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Geochemical information relevant to the retention of radionuclides by candidate high-level waste repositories being developed by Department of Energy (DOE) projects is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). During this report period, the project has evaluated radionuclide sorption and solubility values applicable to the candidate repository site in the Columbia River basalt flows at the Hanford Reservation. The removal of technetium from pertechnetate-traced groundwater by McCoy Canyon basalt under anoxic redox conditions (air excluded) at 27°C was found to be sensitive to the groundwater composition. Sorption of uranium from groundwater by McCoy Canyon basalt under oxic redox conditions at 60°C showed low sorption ratios (1.8 to 2.4 L/kg) similar to those which we obtained previously at 27°C. The average sorption ratio for strontium in groundwater onto McCoy Canyon basalt at 27°C and oxic redox condition, was 225 L/kg. Column chromatographic experiments with neptunium in groundwater to measure retardation factors at temperatures from 25 to 80°C gave calculated sorption ratio values that were in good agreement with the values we previously obtained in batch contact tests.

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PREFACE

This document is the third in a series of quarterly progress reports that are being issued by the Nuclear Regulatory Commission to describe the current status of an experimental program to evaluate the geochemical information developed by the high-level nuclear waste repository site projects of the Department of Energy. The preceding documents were:

Report Period

Report Number

2

October-December 1983 January-March 1984 NUREG/CR-3851 (Vol. 1) NUREG/CR-3851 (Vol. 2)

This project, supported by the Nuclear Regulatory Commission (NRC), is being conducted to evaluate radionuclide solubility and sorption information and data acquisition methodology that may be employed by Department of Energy (DOE) high-level waste repository site projects in performance assessment calculations to show reasonable assurance of expected compliance with regulatory requirements. This project is focused on parameters that are important to the mobility of radionuclides in geologic media (primarily, sorption behavior and apparent concentration limits) under the anticipated geochemical conditions of the repository. Initial emphasis is on information applicable to the candidate site on the DOE Hanford Reservation in the Columbia River basalts at Richland, Washington being developed by the Basalt Waste Isolation Project (BWIP).

Removal of technetium from groundwater by McCoy Canyon basalt under anoxic redox conditions (air excluded) was found to be sensitive to the composition of the solution employed in the experiments. (The phrase "removal from solution' is used to designate disappearance of technetium from the test solution since, at-this-time, we are not able to differentiate sorption and solubility effects.) Previous anoxic redox condition batch contact tests with pertechnetate-traced synthetic groundwater GR-2 and McCoy Canyon basalt had shown very little removal of technetium from solution in experiments lasting as long as 50 d, although recirculating column tests with a pertechnetate-traced dilute NaCl solution had given substantial technetium removal from solution by McCoy Canyon basalt. In parallel batch contact tests conducted during this report period with pertechnetatetraced synthetic groundwater GR-4 and McCoy Canyon basalt, considerable removal of technetium from solution was observed. Sensitivity tests demonstrated that the quantity of technetium removed from pertechnetatetrace<u>d solutions</u> of GR<u>-4_incre</u>ased when the carbonate and/or si<u>lica</u> components were eliminated from the initial solutions.) The results of this work clearly show that McCoy Canyon basalt has some ability to remove technetium from some groundwater compositions, but not from others.

A possible mechanism which could explain these observations is based on the assumption that Fe(II) atoms in a basalt phase such as the glass or that mesostasis acts as a reductant to remove Tc(VII) from solution by reduction to a lower-valence, less-soluble or more-readily adsorbed technetium species. It seems likely that this reduction reaction would be a heterogenous reaction between Fe(II) atoms in the basalt solid and the pertechnetate anions in the solution and, as such, the rate of reaction could be $J_0 \cup \Pi^S$ quite sensitive to basalt surface properties. (The groundwater formulations are meant to simulate the composition of groundwater which has been in contact with specific basalt flows for geologic periods and should represent steady state or near steady state conditions.) could this be moved, up. asshn

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Elimination of some of the groundwater components in tests, or use of groundwater compositions not representative of the basalt flow under investigation, could result in dissolution of some basalt phase(s) during the test and concomitant accelerated availability of Fe(II) for reaction

w/ the flow with pertechnetate. Experiments with GR-2, a groundwater formulation representative of the Umtanum flow underlying the McCoy Canyon flow resulted in little technetium removal from solution in batch tests. <u>Cohassett flow</u> overlies the McCoy Canyon flow, resulted in some technetium paragraph removal from solution. Experiments with solutions lacking some ground-water components resulted in the greater removal of technetium from solutions Conversely, experiments with <u>GR-4</u> groundwater, representative of the tion by McCoy Canyon basalt. The 0.1 M NaCl solution (all other groundwater components eliminated) gave the greatest removal of technetium.

To date the conclusions drawn from our experimental evaluation of the published information describing either the sorption behavior or apparent concentration limit for technetium relevant to the candidate repository site in the Columbia River basalts include:

1. If an oxic redox condition is utilized in the site performance assessment analysis of technetium retardation, then we are in agreement with the general conclusion that no significant sorption would be expected, i.e., the sorption ratio would be ~0 L/kg, and no solubility limit would be encountered since pertechnetate salts have high solubility. Thus, technetium released from emplaced waste would likely be modeled as being released at the rate of waste form dissolution and migrating at the dees the analysis same rate as the contaminated groundwater front.

2. If, on the other hand, the site performance assessment analysis elects to invoke a reducing redox condition, the available information may not be sufficient to permit a meaningful analysis of the technetium retardation to be expected after release from emplaced waste. The published sorption information obtained in the presence of hydrazine probably can not be considered conservative or defensible for performance assessment calculations (KELMERS 1984b). We have previously shown that the calculated values for technetium solubility appear to be too low (non-conservative) by possibly as much as seven to nine orders of magnitude (KELMERS 1984a, KELMERS 1984b). Our results under the anoxic redox condition, described in this report, suggest that some retardation of technetium migration by sorption and/or solubility effects could occur under repository redox conditions, but the present data seem too limited for this assumption to be defensible in performance assessment calculations.

Oxic redox condition batch contact tests with uranium(VI) in synthetic groundwater GR-2 in contact with McCoy Canyon basalt were conducted at 60°C during this report period. In tests at initial uranium concentrations of 10^{-7} to 10^{-5} mol/L, the sorption ratios ranged from 1.8 to 2.4 L/kg. These values are essentially identical to those we previously measured at 27°C. About 8 to 16% of the uranium was lost from solution in parallel blank experiments (no basalt present) and at the highest initial uranium concentration, 10^{-4} mol/L, a white precipitate was formed. This observation suggests that uranium(VI) may be less soluble in these groundwater solutions at 60°C than has been predicted (SCR 1982). We are continuing to explore the nature of this precipitate.

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It is possible that uranium sorption behavior may be specific for the basalt flow used in the test. In this situation, application of uranium sorption data obtained in tests with basalt from one flow may be of uncertain relevance for the description of expected behavior in different basalt flows. Our sorption ratio values are essentially the same as the value of 1.6 ± 0.3 L/kg reported (SALTER 1981b) for Flow E basalt (the same as McCoy Canyon basalt) and groundwater GR-2 under the same test conditions. The higher "conservative best estimate" sorption ratio of 6 L/kg given in the Site Characterization Report (SCR 1982) may have been established from information developed with Umtanum basalt and may not be applicable for the description of uranium sorption with McCoy Canyon basalt. The much higher value of 103 ± 12 L/kg for uranium sorption at 60°C (given in Table 6.18 of reference SRC 1982) does not seem comparable to our observations.

A limited effort has been initiated during this report period to evaluate published information on strontium sorption. Strontium migration is not expected to be solubility limited in basalt/groundwater systems, thus retardation would be primarily due to sorption. The results of our oxic redox condition tests at 27° C were generally in good agreement with published values. We obtained an average sorption ratio of 225 L/kg with McCoy Canyon basalt and synthetic groundwater GR-2; an average value of 182 L/kg was derived from published data for comparable materials and test conditions (SALTER 1981b).

The retardation factors for neptunium(V) in synthetic groundwater GR-4 were measured as a function of temperature with columns of McCoy Canyon basalt and the corresponding sorption ratios were calculated and compared with our Np(V) sorption ratio values previously obtained by batch contact methodology (KELMERS 1984c). The retardation factor increased from 10.5 at 25°C to 45.8 at 80°C. Excellent agreement existed between the sorption ratio values calculated from column runs and measured by batch contact; for example, values of 2.5 vs 1.7 L/kg at 25°C, and 6.1 vs 5.8 L/kg at 80°C. Considerable neptunium elution peak skewing and broadening was observed, especially at the higher temperatures. Such effects are often ascribed to sorption/desorption disequilibrium.

Both our column chromatographic and batch contact tests have shown a significant increase in neptunium(V) sorption by McCoy Canyon basalt as the temperature was increased. Our results are not in agreement with the reported absence of a temperature effect (SCR 1982), nor with the considerably higher sorption ratio values given (30 L/kg) for Umtanum basalt in that report. Again, our findings suggest that neptunium sorption behavior may be different with different basalt flows. In general, McCoy Canyon basalt seems to be giving significantly lower neptunium sorption than Umtanum basalt.

Geochemical modeling activities this quarter have concentrated on the acquisition and debugging of the EQ3/EQ6 software package.

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Oak Ridge National Laboratory is conducting an analysis and evaluation of selected geochemical information for DOE high-level waste repository candidate sites for the Nuclear Regulatory Commission. The project is a laboratory-oriented effort to evaluate data and acquisition methods for radionuclides likely to be major contributors to the release calculations employed by DOE in performance assessment calculations. ORNL is determining limiting radionuclide concentration values and radionuclide retardation parameters, such as radionuclide sorption isotherms, under site-specific conditions. ORNL also is evaluating experimental strategies, laboratory techniques, and geochemical modeling efforts undertaken by DOE. The results of this project will help the NRC staff to independently review and evaluate data employed by the DOE sites for performance assessment analyses, and the methods used to develop these values. The results will also help NRC evaluate the accuracy of or uncertainties in the DOE data and methods, and will aid in identifying technical areas that may require additional attention.

<u>Quantified knowledge</u> of radionuclide behavior will be necessary in order to show reasonable assurance of repository compliance with regulatory requirements. The draft EPA Standard (40 CFR 191) defines limits for the cumulative release of radionuclides to the accessible environment over a 10,000-year period. The NRC Regulation (10 CFR 60) requires that the release rate of radionuclides from the engineered barrier system be no greater than 10^{-5} per year of the inventory of each radionuclide calculated to be present 1,000 years after repository closure. The NRC rule

2-1

also requires that favorable and potentially adverse repository conditions be evaluated in providing reasonable assurance that the performance objectives will be met. Radionuclide solubility or limiting concentration values, as well as sorption data under site-specific conditions, will be important for the performance assessment calculations to demonstrate compliance with these regulatory requirements.

In the ORNL experimental work, attention is first being directed toward values produced to quantify the behavior of radionuclides in basalt/groundwater systems. This work is relevant to the Basalt Waste Isolation Project (BWIP) candidate site in the Columbia River basalts in eastern Washington in the DOE Hanford Reservation. In the future, work will include evaluation of radionuclide behavior in (1) tuff/groundwater systems relevant to the Nevada Nuclear Waste Storage Investigations (NNWSI) project candidate site in volcanic tuff beds at Yucca Mountain in the DOE Nevada Test Site (NTS), and (2) rock/groundwater systems relevant to several bedded and domal salt sites being developed by the Office of Nuclear Waste Isolation (ONWI). Other media (e.g., crystalline rock) may be added. Data and data-gathering techniques to be investigated will emphasize site- and media-specific problem aspects.

During the current report quarter (April through June 1984), all work involved basalt/synthetic groundwater systems. The sorption behavior and apparent concentration limit of the key radionuclides technetium, neptunium, and uranium were evaluated under site-relevant test conditions. Some work to evaluate strontium behavior also was carried out.

3. TECHNETIUM

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3.1 PUBLISHED SOLUBILITY AND SORPTION INFORMATION

The published information concerning radionuclide sorption behavior and limiting groundwater concentration relevant to the candidate repository site in the Columbia River basalts has been reviewed and assessed (BLENCOE 1984, KELMERS 1984d). Technetium-99 is considered to pose the greatest potential hazard to man during waste storage in a repository in a basalt flow (BARNEY 1980). Under oxic redox conditions (air present), technetium exists in the +7 oxidation state as the pertechnetate anion, TcO4. Pertechnetate salts are soluble in basalt/groundwater systems under oxic conditions and no solubility limit has been established for technetium. Also, under oxic conditions, no sorption [i.e., the sorption ratio (Rs) = 0 L/kg has been measured for the pertechnetate ion in synthetic groundwaters onto most Hanford site basalts or the secondary minerals present in these basalt flows. One exception seems to be Umtanum basalt which is reported (SALTER 1981b) to give low technetium sorption $(Rs = 1.3 \pm 0.4 L/kg)$ from synthetic groundwater GR-2. The chemistry of reduced technetium species has been recently reviewed (PAQUETTE 1980, JONES 1982, DAVISON 1982, RARD 1983, MEYER 1984b). Under a reducing redox condition (hydrazine added in laboratory tests), a "conservative best estimate" of 29 L/kg for the sorption ratio for technetium onto basalt has been reported (SCR 1982). This number apparently was obtained with deionized water containing hydrazine rather than a synthetic groundwater (SALTER 1981b). Sorption information for technetium measured in the presence of hydrazine is now believed to be of questionable relevance to in situ repository conditions (MEYER 1982, MEYER 1983, KELMERS 1984d).

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Calculated solubility limits for technetium in repository groundwater compositions under a reducing redox condition were reported to be $>10^{-14}$ mol/L (EARLY 1982) and 10^{-12} mol/L (SALTER 1981a).

3.2 EXPERIMENTAL METHODS AND MATERIALS

We are exploring a laboratory method of establishing an experimental redox condition which will be representative of the in situ basalt/groundwater systems and have identified this methodology as "anoxic redox condition" tests. Air is excluded as thoroughly as possible from the basalt, the groundwater, and all apparatus used in the experiments. The purpose is to allow the basalt and the radionuclide species in the synthetic groundwater to react without interference from oxygen introduced from air or from The exclusion of air (oxygen) by from added chemical reagents such as hydrazine. Abconce of oxygen does not produce constitute a reducing redox condition, but it yould permits the basalt to act as a reductant if it is capable of doing so. If technetium(VII) is reduced to a lower valence(s) by basalt in experimental time periods of months or less, then these anoxic redox condition tests should show some technetium reduction and concomitant technetium removal from solution by sorption and/or precipitation processes involving the reduced species.

Our anoxic redox condition tests have been carried out in a controlledatmosphere glove box containing an argon atmosphere. Oxygen levels of about 0.3 to 0.4 ppm were maintained in the argon by continuous circulation of the argon through an oxygen getter which was periodically renewed by reduction with hydrogen. The oxygen level in the argon was monitored by a gas phase oxygen meter. As discussed previously (KELMERS 1984c), this level of oxygen in the argon would correspond to an oxygen

3-2

concentration level of about $5 \ge 10^{-10}$ mol/L in the groundwater solution at equilibrium. The basalt sample used in the anoxic redox condition tests was crushed, screened to the desired particle size, and stored under argon in the glove box. The technetium-traced synthetic groundwater was prepared outside the controlled atmosphere box by diluting concentrates of the groundwater components with freshly boiled distilled water. The groundwater was sparged with argon, placed into the box, and traced with 99Tc and/or 95mTc solutions.

Recently, we have also found it necessary to evacuate the plastic test tubes prior to their use in the batch contact experiments. To varying degrees, plastics are permeable to oxygen and therefore contain small amounts of oxygen from air. Removal of this oxygen probably involves a diffusion process and could take considerable time, depending on the thickness of the plastic and the diffusion coefficient of oxygen in the plastic. In experiments done under NRC/RESEARCH Project FIN #B0462 (MEYER 1984b), we determined that the polypropylene tubes which we use in the batch contact experiments must be evacuated for at least three days prior evacuate to use in order to observe reduction of technetium(VII) by basalt. of the observe reduction of technetium(VII) by basalt.

In our experiments, the extent of technetium removal from solution was $(f)^{form}$ determined by analysis of the 95mTc concentration in solution by gamma counting techniques. The technetium in solution after contact with the basalt, or subsequently leached from the basalt surface, was determined to be either Tc(VII) or reduced technetium by a solvent extraction method (TRIBALAT 1953). Other details of the batch contact experimental methodo-logy for anoxic redox condition experiments have been given previously (KELMERS 1984b, KELMERS 1984c.)

3.3 RESULTS

The sensitivity of technetium removal from solution by basalt to the solution composition was explored during this report period. Anoxic redox condition tests at 27°C were completed with McCoy Canyon basalt and technetium-traced synthetic groundwater GR-4. Compared to GR-2, used in our previous experiments, the GR-4 formulation has a slightly lower con-AR THE AVERIA centration of dissolved silica, about 18 times less sulfate ion, and no magnesion (compared to 0.07 mg/L for GR-2). Carbonate and chloride compositions of the two formulations are roughly the same. Groundwaters GR-2 and GR-4 may be considered to be approxidenately equivalent to 0.01 M NaCl containing dissolved silica, carbonate ions, and small amounts of K^+ , Ca^{2+} , F⁻, and SO_4^{2-} . (A discussion of the various BWIP groundwater formulations was given in KELMERS 1984c.) In addition to tests using GR-4, we carried out parallel tests in which various components of GR-4 were Can the discussion of this be expanded somewhat? The purpose? what doyou expect to what would you do with the information? removed, as shown in Table 3.1.

Significant removal of technetium from solution was observed in all of these experiments (Table 3.1). (Since at this time we are not able to differentiate sorption effects from apparent concentration limit effects, the term "removal from solution" is employed.) This is the first time that we have seen removal of technetium from a synthetic groundwater to this extent by McCoy Canyon basalt. Previous anoxic redox condition tests using GR-2 (KELMERS 1984c) showed essentially no technetium reduction or removal from solution. We have previously seen removal from solution of technetium by McCoy Canyon basalt from an 0.1 M NaCl solution (KELMERS 1984c).

There appears (Table 3.1) to be a correlation between the final solution pH and the extent of removal from solution. Comparing the four samples which were initially at pH 9.7, the extent of removal increased a factor of over 5 with a corresponding total pH change of 1.1 (pH 9.7 to 8.6). In each of these experiments, a small but significant amount of reduced technetium remained in solution. At this time, we do not know whether this removal-from-solution vs pH trend was due to the final contact pH or solution composition, or to the absence of some of the initial components of the GR-4 formulation. Since these groundwater formulations are representative of groundwater compositions present in the basalt formations after | egus libe geologic times, elimination of some component(s) could yield a groundwater MINTEQ Is this forminalogy OK? significantly out of steady state with the phases found in the basalt. (A HREERE change of pH after contact thus could indicate attack of the solution on a an auti basalt phase and the correlation of removal from solution with final pH long se could actually be the result of the dissolution of some basalt phase containing ferrous iron which, in turn, released ferrous iron into the solution or made ferrous iron accessible at the surface of the basalt for reaction with the dissolved pertechnetate ion. / [The assumption in this reasoning is that Fe(II) is the active reductant in these systems.]

3.4 DISCUSSION AND CONCLUSIONS

The degree of removal from solution of technetium by basalt seems to be dependent upon a number of the experimental parameters. Under an oxic redox condition, there is general agreement among all investigators that little or no sorption of technetium (present as TcO_4^-) is observed on

GR-4	pH		Rs ^C	Reduced Tc in solution after contact	
formulation ^b	Initial	Final	(L/kg)	% of total	(mo1/L)
Complete	9.7	9.3	10.9 ± 1.0	7.8	6.9 x 10 ⁻¹⁴
No silicate	10.2	9.3	13.4 ± 2.2	9.6	7.1×10^{-14}
*1	9.7	9.0	27.5 ± 3.5	21.3	9.6 x 10^{-14}
No carbonates	10.8	9.9	9.9 ± 1.5	13.7	12.2×10^{-14}
	9.7	9.1	22.2 ± 2.0	11.4	6.2×10^{-14}
No silicate or carbonates	9.7	8.6	53.1 ± 8.9	30.9	6.8×10^{-14}

Table 3.1. Technetium Sorption from Synthetic Groundwater onto McCoy Canyon Basalt Under an Anoxic Redox Condition^a

^aThe experimental conditions were: anoxic environment, -70/+325 McCoy Canyon basalt crushed and stored under argon, TcO_4 - concentration initially 10^{-8} M, contacted for 14 d at 27°C, and the solution recovered after contact by centrifugation for 30 min at 5000 rcf under argon. About 0.4 g of basalt was contacted with 4 mL of groundwater. The results were adjusted for a small loss (2-10%) of technetium onto the test tubes as determined in parallel control experiments (no basalt present).

^bSynthetic groundwater composition as given in SALTER 1984, with deletions as indicated.

^CTechnetium removal from solution calculated as sorption ratios; values are mean ± 1 standard deviation for three replicate samples.

basalt and that TcO4 is highly soluble. In our anoxic redox condition experiments, the oxygen (from air) had to be eliminated with great care from the experimental apparatus and constituents for technetium removal from solution to be observed at all. Even when the oxygen had been carefully eliminated from the test, technetium removal from solution by McCoy Canyon basalt still was not necessarily observed. We have only obtained significant technetium removal from solution when either a NaCl solution or the synthetic groundwater formulation GR-4 was used with McCoy Canyon basalt, but not with the synthetic groundwater formulation GR-2. The principal difference between the GR-2 and GR-4 formulations is that GR-4 contains a significantly higher amount of sulfate ion (72 mg/L compared to 4 mg/L for GR-2) and less dissolved silica. With these exceptions, there are no obvious major differences in composition between the GR-2 and GR-4formulations. Thus, the solution factor or factors which are the cause(s) of these differences in technetium removal from solution behavior seem to be subtle.

The link between these results and the causes can best be explored by additional investigation of the mechanisms of the reduction, precipitation, and sorption reactions for technetium(VII) with basalt. Some of these mechanisms are being investigated in parallel research being conducted under NRC/RESEARCH project FIN #B0462. In some findings from that research (MEYER 1983, MEYER 1984a), it was suggested that the reduction of technetium probably is a heterogeneous reaction occurring at or on the surface of some phase(s) of the basalt, rather than a homogeneous reaction occurring within the groundwater.

Such a heterogeneous reaction would probably first require a surface sorption step and then electron transfer (reduction) from the ferrous atoms in the basalt to the adsorbed Tc(VII) species. If this is the correct mechanism, then a number of experimental observations could be rationalized. Because negative ions are not strongly adsorbed by minerals, the concentration of adsorbed Tc(VII) species on the surface of the basalt is not likely to be high. For complete reduction to Tc(IV), the presumed reduced technetium valence, a three electron transfer would be required. If the basalt is covered by a thin passivating (non-conducting) layer, the electron transfer could be hindered. The formation of a passivating layer could be readily influenced by small amounts of oxygen and subtle changes in groundwater composition. Furthermore, aggressive solutions, inc., solution compositions out of steady state with the baselt phases and thus itkely to promote dissolution of basalt phases, such as 0.1 M NaCL, could attack the passivating layer and expose fresh surfaces or phases and thus enhance the ferrous ion activity. In this conceptual model for Tc(VII) removal from solution by basalt, the degree of removal is linked to the nature of the basalt surface and the alteration of this surface during the anoxic redox condition experiment.

3.5 EVALUATION OF PUBLISHED TECHNETIUM SORPTION AND SOLUBILITY INFORMATION

The current conclusions from our experimental evaluation of the published information describing either the sorption behavior or apparent concentration limit for technetium relevant to the candidate repository site in the Columbia River basalts are briefly summarized in this section.

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If an oxic redox condition is utilized in the site performance assessment analysis, then all investigators seem to be in agreement on the technetium sorption and solubility value to be employed in the analysis. No significant technetium(VII) sorption (Rs = 0 L/kg) would be expected and no solubility limit would be encountered. Thus, technetium released from the waste package into the groundwater would likely be modeled as migrating with the contaminated groundwater front, i.e., the retardation factor would be 1. Little additional laboratory evaluation work for the oxic redox condition seems warranted for basalt/groundwater systems.

If, on the other hand, the site performance assessment <u>analysis elects to</u> <u>invoke</u> a reducing redox condition, we feel that the available information on technetium may not be sufficient at this time to make any meaningful analysis of the technetium retardation to be expected. The published data for technetium obtained in the presence of hydrazine (SCR 1982) probably can not be considered defensible or conservative and likely can not be used in performance assessment calculations (KELMERS 1984b). Our results under anoxic redox conditions at 27°C, described in this report, suggest that some retardation of technetium(VII) migration by sorption and/or solubility limit effects may exist due to reduction of the technetium to an unknown lower valence, but the present data seem too limited for defensible performance assessment calculations. The results of our anoxic redox condition experiments were sensitive to the synthetic groundwater composition; the cause of this sensitivity is not not possible basalt surface properties are dominant. Understanding this geochemical

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system may be important for the development of a defensible and conservative performance assessment analysis if technetium retardation by the basalt site is assumed or becomes necessary to meet regulatory requirements.

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4. URANIUM

4.1 PUBLISHED SOLUBILITY AND SORPTION INFORMATION

A summary of the published information describing uranium solubility limits or sorption distribution coefficient values relevant to the candidate repository site in the Columbia River basalts was given in the preceding report (KELMERS 1984c). The basalt site sorption and solubility information has also been separately reviewed and assessed (BLENCOE 1984, KELMERS 1984d). While uranium is not considered to be one of the key radionuclides, i.e., those which appear to pose the greatest hazard to man from a repository in basalt (BARNEY 1980), knowledge of uranium behavior seems important since it will be the major component of the spent fuel Under an oxic redox condition (air present), uranium exists waste form. state in the +6 valence and the species present in groundwater solutions may be cationic, neutral, or anionic depending upon the pH and presence or absence of complexing ions such as carbonate or fluoride. Uranium(VI) sorption ratios of 13 to 56 L/kg were reported (SALTER 1981b) for various basalt flows at 23°C, and a solubility limit of 10^{-4} mol/L was apparently calculated (SCR 1982). Under a reducing redox condition (hydrazine added to the groundwater), a "conservative best estimate" sorption ratio of 40 L/kg was given (SCR 1982). Published uranium information which was obtained by the addition of hydrazine to the synthetic groundwater is now believed to be of questionable relevance to the in situ repository redox condition (KELMERS 1984b). A solubility limit of 2 x 10⁻¹⁰ mol/L was calculated for the reference groundwater GR-4 (EARLY 1982).

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4.2 EXPERIMENTAL METHODS AND MATERIALS

The work with uranium this report period involved determination of sorption isotherms at $60\,^{\circ}$ C under an oxic redox condition with McCoy Canyon basalt and synthetic groundwater GR-2. The batch contact experimental methodo-logy followed for our oxic redox condition experiments with uranium(VI) and characterization of the McCoy Canyon basalt sample and the synthetic groundwater formulation GR-2 has been previously described (KELMERS 1984c).

4.3 RESULTS

The results of the oxic redox condition sorption tests with uranium(VI) from 10^{-7} to 10^{-4} mol/L initial concentration in synthetic groundwater GR-2 at 60°C are shown in Table 4.1; included for comparison are the results previously reported for 27°C (KELMERS 1984c). Sorption ratios ranged from about 1.8 to 2.4 L/kg at initial uranium concentrations of 10^{-7} to 10^{-5} mol/L. These 60°C results should be considered as preliminary, since considerable loss of uranium from solution was observed in parallel blank tests (no basalt present) at the higher uranium concentrations. The uranium loss from solution at 60°C ranged from about 8 to 16%, with initial uranium(VI) concentrations of 10^{-7} to 10^{-5} mol/L. A white precipitate was observed in the blank test for an initial concentration of 10^{-4} mol/L; the nature of this precipitate is unknown at this time. Because of the presence of basalt, we could not determine whether a similar precipitate was formed in the parallel test with basalt. Thus, the high Rs value (17 \pm 1 L/kg) obtained with basalt at an initial uranium concentration of 10^{-4} mol/L may be due in part to precipitation as well as sorption.

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	Initial uranium (mol/L)	14-	d contact	50-d contact	
Contact temperature (°C)		рН	Rs ^b (L/kg)	рĦ	Rs ^b (L/kg)
27	10-7	9.0	1.6 ± 0.2	8.9	1.7 ± 0.3
	10-6	9.0	2.0 ± 0.3	8.9	1.7 ± 0.2
	10-5	9.0	1.3 ± 0.1	8.9	1.2 ± 0.1
	10 ⁻⁴	9.0	1.8 ± 0.1	8.9	1.4 ± 0.1
60	10-7	9.0	1.8 ± 0.2	9.0	2.2 ± 0.8
	10-6	9.1	2.3 ± 0.4	8.9	2.6 ± 0.4
	10 ⁻⁵	9.1	2.4 ± 0.2	9.0	2.6 ± 0.4
	10-4	9.0	17.0 ± 1.0	8.9	35.0 ± 2.0

Table 4-1. Uranium sorption onto McCoy Canyon basalt from synthetic groundwater GR-2 under an oxic redox condition^a

^aContact conditions: 0.4 g McCoy Canyon basalt, -70/+35 mesh size, and 4 ml GR-2 contacted for 14 and 50 d, solution recovered by centrifugation for 30 min at 5000 rcf.

^bMean ± one standard deviation for triplicate samples.

The 27 and 60°C data is presented as sorption isotherms in Fig. 4.1. There is very little difference among the sets of results, except for the higher apparent concentration of uranium on the basalt at 60°C at the highest uranium concentration. As discussed above, this is presumed to be due to formation of a uranium-containing precipitate. The uranium sorption ratios increased only very slightly on extending the contact time from 14 to 50 d. Apparently, near steady state was reached for these tests in 14 d or less.

4.4 DISCUSSION AND CONCLUSIONS:

Our average Rs value of 2.0 L/kg for uranium at 60°C under an oxic redox condition at the lowest uranium concentration (least likely to be affected by uranium precipitation) is essentially the same as the value of 1.6 \pm 0.3 L/kg reported for the same test conditions and Flow E basalt, the same as McCoy Canyon (SALTER 1981b). The "conservative best estimate" sorption ratio value of 6 L/kg given in Table 6.20 of the Site Characterization Report (SCR 1982) for basalt under an oxic condition is higher than our value. Table 6.18 of the Site Characterization Report also gives a much higher uranium sorption ratio of 103 \pm 12 L/kg for basalt at 60°C. Our results do not seem to be in good agreement with these higher published sorption values and suggest that use of the values in the Site Characterization Report in performance assessment calculations could be questionable.

No experimentally measured uranium solubility limit data were reported which are directly comparable with our highest uranium concentration, but a value of 7.75 x 10^{-6} mol/L was given for the concentration of uranium in the solution after the sorption contact at the highest uranium concentration tested (SALTER 1981b). This value compares favorably with the maximum solution concentration of 8.0 x 10^{-6} mol/L uranium obtained in our experiments. However, we observed a slightly lower solution concentration (5.5 x 10^{-6} mol/L) in a parallel blank experiment without basalt. Both our sorption isotherms and the results of sorption experiments reported by the BWIP project seem to indicate a lower apparent concentration limit for uranium(VI) under an oxic redox condition than the value of 10^{-4} mol/L given in the Site Characterization Report (SCR 1982).



5. STRONTIUM

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5.1 PUBLISHED SOLUBILITY AND SORPTION INFORMATION

Strontium release to the environment is not considered to be solubility controlled for the candidate repository in the Columbia River basalts (SALTER 1981a); i.e., if retardation is desirable or necessary in order to meet performance standards, it would have to be achieved primarily by sorption. Although strontium-90 has not been identified as one of the more hazardous radionuclides (BARNEY 1980), it has been extensively investigated in sorption experiments (BARNEY 1981, SALTER 1981b). The Site Characterization Report gives a "conservative best estimate" sorption ratio of 170 L/kg for basalt under an oxic redox condition (SCR 1982). For Flow E basalt, the same as McCoy Canyon, a value of 174 \pm 16 L/kg was reported with GR-2 under an oxic condition (SALTER 1981b).

We have not given strontium a high priority in our experimental work but have explored its sorption behavior with basalt as time permits. These experiments were generally done when the 14-d and 50-d contact periods for the higher priority nuclides were underway.

5.2. MATERIALS AND METHODS

Standard oxic redox condition batch contact techniques were used for these experiments, as described in previous reports (KELMERS 1984a, KELMERS 1984b, KELMERS 1984c). Characterization of the McCoy Canyon basalt sample and synthetic groundwater GR-2 used was also given in those reports.

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5.3. RESULTS AND DISCUSSION

The data for strontium sorption onto McCoy Canyon basalt from synthetic groundwater GR-2 at 27°C are shown in Table 5.1. These sorption ratio values are compared in that table to data from Salter (1981b) for essentially the same experimental conditions with Flow E basalt, the same as McCoy Canyon. Our data show slightly higher values of Rs, but the agreement may be considered good; an average of 225 L/kg vs 182 L/kg.

The published information (SALTER 1981b, SCR 1982) indicates that strontium sorption is not much affected by groundwater composition, basalt flow, or temperature. It would not be expected to be affected by changes in redox condition since only the +2 valence can exist in these groundwater systems. Because strontium does not form stable complexes with the inorganic components of groundwater, it is reasonable that groundwater reference? effects on sorption would be minimal. Our limited results are in general agreement with the published information. Sorption ratios as high as 100 to 200 L/kg will result in substantial strontium retardation; thus, it may be reasonable to assume that the basalt site could exhibit favorable strontium retention characteristics. One possible exception could be the formation of stable strontium-organic complexes, if organics were present in site groundwaters. The groundwater in the repository may be saturated with methane and radiolysis of the methane could lead to a variety of organic compounds (GRAY 1984). Formation of such complexes could lead to lowered sorption by basalt; further work would be required to explore this possibility.

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Initial strontium (mol/L)	_{Rs} b (L/kg)	Rs ^C (L/kg)	
10-12	231 ± 22	178	
10-10	224 ± 11	186	
10-8	221 ± 12	182	
10-6	217 ± 3	186	

Table 5.1 Sorption of strontium onto McCoy Canyon basalt from synthetic groundwater GR-2 under an oxic redox condition^a

aContact conditions: 0.4 g McCoy Canyon basalt, -70/+325 mesh size, contacted with 4 mL ⁸⁹Sr-traced groundwater GR-2 for 14 and 50 d; solution recovered by centrifugation at 5000 rcf.

^bMean ± 1 standard deviation for triplicate samples.

Ccalculated from Table A-7 in SALTER 1981b.

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Radionuclide sorption ratio (Rs) values measured by batch contact methodology have been used to calculate radionuclide retardation factors (Rf) in performance assessment analyses to model radionuclide transport through the basalt site far field (SALTER 1981a, SCR 1982). Such an approach to the development of retardation factors is limited in that the kinetics of sorption or desorption reactions, as well as effects due to radionuclide multiple speciation or colloid formation, are not easily evaluated. If sorption/desorption disequilibrium exists (usually due to slow desorption kinetics), then use of sorption ratio values to calculate retardation factors may be conservative but will not yield accurate Rf values. On the other hand, if multiple radionuclide species exist or colloids are present between solution species in solution which have slow re-equilibration rates, then the retardation factor calculated from a sorption ratio value may be non-conservative for that fraction of the radionuclide which is present in a species (more form (less strongly adsorbed) than the weighted average value for all the species present. In such situations, direct measurement of the retardation factor by column chromatographic methodology is the best experimental method of exploring the effect of multiple speciation or colloid formation on radionuclide retardation. Multiple speciation may be likely to occur in repository groundwater systems for elements which can exist in more than one solution species, either ionic or non-ionic, or can be present both as solution species and as colloids. Plutonium frequently exhibits such behavior, as do fission products such as iodine. The mobility of significant fractions of some radionuclides in low-level waste sites is well known, for example see Robertson, et al. (1984).

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Neptunium-237 is considered to be the third most hazardous radionuclide for a repository in the Columbia River basalts (BARNEY 1980). We have previously shown under both oxic and reducing (hydrazine added) redox consingly in the Columbia River basalts (BARNEY 1980). We have ditions that Np(V) is the predominant valence present in synchetic $N\rho(V) \neq V\alpha|_{ence}$ groundwater/basalt systems (KEIMERS 1984c). The chemistry of neptunium(V) in dilute carbonate systems, such as these repository synthetic groundwaters is not well known, but there is some evidence to suggest that stable anionic carbonate complexes such as Np0₂CO₃⁻, Np0₂(CO₃)₂³⁻, and Np0₂(CO₃)₃⁵⁻ may exist in addition to Np0₂⁺ (MAYA 1983). Also, since Np(V) and uranium(VI) are known to interact and form cation-cation pairs under some conditions (GUILLAUME 1979, MADIC 1979), it will be important to explore the behavior of neptunium in solutions which also contain uranium in order to evaluate the effect of cation interaction on the retardation factor.

Because neptunium is a key radionuclide (one likely to be a major contributor to radioactivity release to the environment) and Np(V) may exist as more than one species in these synthetic groundwater formulations, we have initiated column chromatographic experiments to directly measure the Np(V) retardation factor under an oxic redox condition at column temperatures from 25 to 80°C. The experimental set up and the preparation of the McCoy Canyon basalt samples used were previously reported (KELMERS 1984c). For these experiments, high specific activity $^{239}Np(V)$ was used in synthetic groundwater GR-4.

The Rf and Rs values were calculated from the column elution data as follows. From experimental results consisting of radionuclide activity (corrected for any background contributions) of each sample along with

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the cumulated elution volume, an elution curve was constructed by plotting "Fraction of Applied Activity (A/At) vs Volume Eluted," and a breakthrough curve by plotting "Cumulated Fraction of Activity Applied (C/At) vs Volume Eluted." The A represents the activity of each sample collected, C represents a sum of activities of the samples collected, and At represents the total activity applied to the column. For the 239Np(V) elution profiles, the total activities eluted instead of the total activity applied were used to avoid uncertain activity corrections for each sample resulting from radionuclide decay of the short half-life (2.4 days) of the 239Np isotope (Figs. 6.1 through 6.4). A mass balance of ²³⁹Np can be done, but the propagated errors could lend a high degree of uncertainty to the results. As indicated by the elution curves, the elution of 239Np(V) was not completed after 66.4 ml of groundwater were passed through the columns, except for the experiment at 25°C. Therefore, the substitution of the total activity eluted for the total activity applied results in an underestimation (i.e., a conservative estimate) of Rf value by shifting the breakthrough curve to the left, i.e., a lower estimation of elution volume at 50% breakthrough point.

From the breakthrough curves of ^{239}Np at the selected column temperatures, the eluted volumes (V2 in Figures) were obtained before the eluted ^{239}Np activity reached 50% of total activity. In the same manner, the eluted volumes (V1) for $^{3}H(HTO)$ were obtained from each experiment. After V Rg=1 correcting both V1 and V2 for dead void volume (Vo, 2.5 ml for the present set-up) of the column fitting and tubing, the Rf values were determined by need to bhave # of parentheses the ratio of corrected V2 to V1; (V2-Vq/(V1-Vo)) Since the experimental column void volume (V1-Vo) was close to the calculated value (0.73 ml),

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the calculated value was used. However, the Vo and Vl for each new column was measured by ³H (as HTO) elution prior to other radionuclide elutions. Why? If you have the numbers, why not use them.

The Rs was calculated using the experimental Rf value and other constants particular to this experiment in the equation,

$$Rs = (Rf-1) P/BD$$
,

where P = porosity (0.412) and BD = bulk density (1.56 g/cm³). The calculations (Table 6.1) indicated considerable differences of Rf and Rf values at various temperatures, with both increasing with temperature.

Temperature (°C)	Volume eluted, V2 ² (mL)	Retardation factor, Rf ³ (dimensionless)	Sorption ratio, Rs (L/kg)
25	7.7 .<	10.5	2.5
45	15.7 6	- 21.5	5.4
60	17.7 .62	24.2	6.1
80	33.4 .67	45.8	11.8

Table 6.1. Neptunium(V) Retardation and Sorption Ratio at Several Column Temperatures¹

¹Column size: 3 mm ID by 25 mm L; flow rate 0.96 mL/min; particle size of McCoy Canyon basalt, -45/+2 µm; particle density, 2.65 g/cm.

²Volume eluted before activity reached 50% of the total eluted activity, corrected for void volume (2.5 ml) of the column fitting and tubing; ²³⁹Np in synthetic groundwater GR-4.

³Determined from volume eluted for Np divided by column void volume (0.73 ml).

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The increasing temperature leads not only to the increasing elution volumes but also to a shifting of peak position and peak broadening. The asymmetrical nature of the Np elution curves could be caused by dispersion (diffusion transport), differences in adsorption/desorption kinetics, or chemical reactions involved between Np and a basalt phase(s). The results obtained from ³H(HTO) and ^{95m}TcO₄⁻ experiments (reported in KELMERS 1984c) could, however, rule out possible involvement of effects of dispersion.

The calculated sorption ratios at 25 and 60°C are close to those obtained for McCoy Canyon basalt in oxic redox condition batch contact experiments with neptunium(V) in synthetic groundwater GR-2 (KELMERS 1984b, KELMERS 1984c) at these temperatures (2.5 vs 1.7 L/kg at 25°C, and 6.1 vs 5.8 L/kg at 60°C). This close agreement between Rs values obtained by different experimental methods is encouraging and suggests that the Rs values may be acceptable for modeling purposes in simplified performance assessment calculations, i.e., methods which employ a single Rs value rather than a sorption isotherm to describe radionuclide sorption behavior. None of the Np elution curves (Figs. 6.1 through 6.4) were as symmetric as those obtained previously with technetium(VII) (KELMERS 1984c), and the skewing or asymmetry increased at higher temperatures, especially at 60 and 80°C. Complete elution of all the neptunium activity applied to the column probably was not achieved in any of the experiments. Such behavior is new desorption kinetics or chemisorption. T/ Then why do you reaction rates should mercase WT/ Then why do you see characteristic of slow desorption kinetics or chemisorption.

Rs values for neptunium in groundwater GR-1 for Flow E basalt (the same as McCoy Canyon) at an oxic redox condition at 23°C of 4.1 \pm 0.9 L/kg and 8.3 \pm 0.5 L/kg at 60°C have been reported (SALTER 1981b). These values

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are significantly higher than those we have obtained with McCoy Canyon basalt in either batch contact or chromatographic experiments. In the Site Characterization Report (SCR 1982), a sorption ratio of 30 ± 13 L/kg was given for Umtanum basalt at 23°C and 31.2 \pm 4.7 L/kg at 60°C. The reported absence of a temperature effect on neptunium sorption is in disagreement with both our batch contact and chromatographic experiment results. However, our work was with McCoy Canyon basalt while the Site Characterization Report describes results with Umtanum basalt. We have previously suggested that neptunium sorption may exhibit basalt flow specific behavior (KELMERS 1984c). If this supposition is correct, then the differences between our results and the published results could be significant. Our batch contact or column chromatographic experiments do not seem to be yielding results which are in agreement with or support the "conservative best estimate" values for neptunium sorption given in the Site Characterization Report. Use of those higher values in site performance calculation could lead to questionable or non-conservative neptunium retardation estimates.

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Figure 2. Elution and breakthrough curves of 239Np(V) at 45°C of column temperature.

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Figure 3. Elution and breakthrough curves of 239Np(V) at 60^oC of column temperature.

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Figure 4. Elution and breakthrough curves of $^{239}Np(V)$ at 80°C of column temperature.

7. GEOCHEMICAL MODELING

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Activities this quarter have concentrated on the aquisition and debugging of the EQ3/EQ6 software package (WOLERY 1979 and 1983). The code has been obtained and is currently undergoing modifications to allow it to be run on the ORNL computers. When the code is operational, test cases supplied with the program, as well as sample test cases of our own, will be run to verify the conversion of the code.

It is anticipated that future geochemical modeling activities will emphasize the use of the EQ3/EQ6 software package. Other codes currently available (e.g. PHREEQE, WATEQ, GEOCHEM, and MINTEQ) will be used on an "as needed" basis only. The reasons for emphasizing the EQ3/EQ6 software package include: (1) all the DOE sites are apparently using (or are planning to use) the EQ3/EQ6 software package to at least some extent, and (2) the EQ3/EQ6 package has the most capabilities important to repository applications at this time and additional capabilities should be available within a year.

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8. ACKNOWLEDGEMENTS

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